Final Rapport

ACTIONS BILATERALES

COOPERATION S&T AVEC LE VIETNAM

A JOINT VIETNAMESE – BELGIAN PROJECT

CONTRAT DE RECHERCHE N° BL/13/V11

(Duration : 1st November 2006 au 31st October 2008)

Title of the Project

Rebirth of wasted agro-matters: New silica and carbon based nanomaterials prepared from rice husk as catalysts for the conversion of vegetable oil sludge to green fuels (biodiesel) and as adsorbent for the concentration of alcohols

Recyclage des déchets issus de l'agriculture : Fabrication de Nano-Matériaux silicés et carbonnés à partir des cosses de riz utilisés comme catalyseurs pour le raffinage des huiles végétales en biodiesel et comme adsorbants pour la concentration d'alcool

Prof. Dr. Bao-Lian Su

Member of the Royal Academy of Belgium,
Francqui Chaire
Fellow of the Royal Society of Chemistry, UK

Director of the Research Center for Nanomaterials Chemistry (CNANO),
Director of the Laboratory of Inorganic Materials Chemistry (CMI),

University of Namur
61 rue de Bruxelles, B-5000 Namur, Belgium

Preface

In this **Final Report**, we have given at first in **Introduction**, a summary of Tasks realized during the project, objective of the project, partners of the project, description of Tasks to be realized and the organization of the project.

The second part, **Report**, as each semiannual report, will be divided into three parts. Firstly, information on scientific mission and recruitments of researcher and technician will be given by period. Secondly, the realizations following different tasks will be then described, giving information on the completeness of different tasks and how different tasks have been completed and started and the reasons why some tasks have been delayed and removed from the project and time schedule has been modified to accommodate to new organization. This has been given also by period. Finally, detailed scientific results related to each task will be presented in **Scientific Report**. For the facility of lecture, this part has been given by period.

All the Tasks and modified Tasks have been completed. All the objectives of the project have been reached.

We attached two annexes concerning **Repartition of Tasks** (**Annex 1**) and **Time Schedule** (**Annex 2**) for a better understanding of this report. **Annex 3** gives all the information on the poster presented and papers published.

Summary

First period: November 2006-April 2007

The project was officially started by a kicking off meeting which was held in Hanoi Vietnam on 15 April 2007 during the visit of Prof. Bao-Lian Su to Vietnam. During the kicking off meeting, all the tasks have been reviewed. Belgian partner, to realize all the tasks, engaged Dr. Xiao-Yu Yang, an expert in the synthesis of nanomaterials and Mr. Thomas Ligot as technician.

Ordered nanoporous material involving microporous materials (ZSM-5) and mesoporous materials (MCM-41, Al-MCM-41, and SBA-3) has been successfully synthesized using extracted silicon by RHs as silicon source. Furthermore, heteroatoms such as Al and Ti species have been easily introduced into the mesoporous and microporous walls of MCM-41 and ZSM-5 by simple mixture of extracted silicon with aluminum or titanium source in initial reaction gel. This part of results from this period demonstrated that rice husks can be a good precursor for the production of high value added materials.

The first analysis using the first series of nanoporous zeolites and mesoporous materials as catalysts showed very promising results that materials using rice husks as precursors are more active than commercial catalysts in the cracking of n-Hexane and TIPB. This part of results from this period demonstrated that rice husks can be a good precursor for the production of high value added materials.

The rude ethanol was obtained by distillation with a concentration of 96.5%. A microreactor to screen the best adsorbents has been constructed. A zeolite adsorbent produced from Kaolin of Vitenam has been used to test the microreactor.

Second period: May 2007-October 2007

During this period, Dr. Xiao-Yu Yang, Mr. Thomas Ligot (three months) and Mrs. Hadj Sadok have been engaged for a best realization of the project.

This period is of great success with a huge amount of materials and results have been obtained. A very efficient and innovative silica extraction process from rice husks has been developed to give simulataneously silica and a very nice nanoporous carbon network. This process has never previously been reported. It is shown that by adjusting the base concentration, the porosity and surface area of nanoporous carbon materials can be tailored. A large series of zeolite and mesoporous materials (such as Nano-mesoporous ZSM-5, Al-MCM-41, Si-SBA-15, HY, HY/MCM-441 and ZSM-5/MCM-41) have been obtained, characterized and evaluated by VP1.

The evaluation results by VP1 have been very helpful to select the best catalysts. After first analysis, we have concentrated this period on the synthesis, characterization of mesoporous ZSM-5 catalysts. More information on these catalysts will be given in next period report. The cracking products have been evaluated and analyzed by VP1 using the microreactor they constructed using n-hexane, TIPB and waste oil sludge as reagents. A comparison has been made with a standard catalyst (ECAT) and also with thermal cracking. It is shown that our materials are more performant that ECAT and thermal cracking. VP1 partner realized a great work on the valuation of catalysts and also the quality of cracking products.

After construction of microreactor for the concentration of ethanol by adsorption process and evaluation of this microreactor by using Zeolie A as adsorbent, VP2 concentrated their work on the construction of pilot. Due to the time limit (2 years project), VP2 modified their objective on the construction of pilot which needs more time. Differn Tasks have been accordingly modified to accommodate to the new objective. We selected Zeolite A as the adsorbent of test for the concentration of ethanol. This choice was based on the pore size of Zeolite A. This zeolite can be synthesized using Kaolin of Vietnam as detailed in the project. After designing, the construction of Pilot for the concentration of ethanol by adsorption process has been started and different devices have been constructed.

All the Tasks defined initially in the project and modified after kicking off the project have been successfully accomplished. In spite of some modifications in Tasks, the objective of this period has been reached. A very good collaboration has been established between partners.

Third period: November 2007-April 2008

This period is very rich in scientific exchange and also in results. A large amount of results have been obtained.

The first **Annual Meeting** has been held in Namur from 31st October to 6th November 2007 to exchange the information and for the discussion of next steps.

During this period, Mr. Do Xuan Dong made a scientific stay in Namur following the program initially defined.

BP engaged Dr. Xiao-Yu Yang and Mrs. Hadj Sadok for a better realisation of the project.

A new series of micro-mesoporous zeoite ZSM-5 catalysts by variation of hydrothermal treatment times have been synthesized and characterized by a series of techniques (IR, XRD, SEM, TEM) (**BP**) and have been evaluated in the waste oil sludge cracking reaction and compared with thermal cracking. All the results have been also compared with a pure ZSM-5 catalyst synthesized from silica extracted from rice husks. The results showed that the catalyst with ZSM-5 zeolite structure with the highest crystallinity and a mesoporosity gives the highest conversion, the highest amount of desired products (Gasoline and LPG), more propylene and butenes and less coke. The products distribution in gas products and in liquid products has been analyzed. Pyrolysis gives more paraffinic hydrocarbons and catalytic cracking gives more aromatic hydrocarbons (**VP1**).

As described in **Semiannual Report**, VP2 modified the objective and put the construction of pilot as the primary goal. Instead to waiting for the synthesis of different zeolites by BP as adsorbents and then to selecting the best adsorbent, it is decided to use zeolite A as adsorbent due to the pore size of this zeolite is quite similar to that of ethanol. In fact due to the time limit (two years project), it is not possible to finish the selection of a best adsorbent with different steps in two years term (synthesis, characterize, adsorption testing and pelletization). At the end of the project, it is necessary to deliver a technology for the concentration of ethanol, becoming urgent due to the society need. The modification the objective and the use of zeolite A as adsorbent are fully justified. As a consequence, different Tasks of VP2 have been modified.

A new protocol to synthesize zeolite A using silica extracted from rice husks has been developed. The zeolite A obtained has been characterized by using a large series of techniques such as XRD, IR, ^{27}Al solid state MAS NMR. The behavior of zeolite in ethanol concentration by adsorption process and the quality of ethanol obtained have been evaluated.

Fourth period: May 2008-OOctober 2008

Second Annual Meeting has been held in Namur September 2008 to analysis the research state of the project, to modify some tasks following the situation and to prepare the closing of the project. A **General Meeting** has been organized by Belspo on 16 June 2008 in Brussels. BP presented the project progress. This meeting gathered Vietnamese partners and Belgian partners involved in different Belgo-Vietnamese cooperation projects. Mr. Tran Quong Vinh and Mrs. Le Thi Kim Lan made their scientific stay from 26 August to 12 September in Namur to prepare and characterize new materials.

BP, VP1 and VP2 presented the results obtained from this Belgo-Vietnamese bilateral Cooperation project by two poster presentations in The 6th International Mesostructured Materials Symposium has been held in Namur from 8th to 12th September 2008.

The **Closing Meeting of the project** has been organized in Hanoi, Viet Nam at the beginning of 2010 and September 2011 in Namur, Belgium, separately for Vietnamese partners and for Belgian partners. The **Closing Meeting** in Namur, Belgium was organized from 11-14 September 2011 with the participation of Viet Names partners, Prof. Le Thi Hoai Nam from Institute of Chemistry and Dr. Van Dinh Son Tho from University of technology Hanoi.

BP synthesized HY and HY/MCM-41 catalysts using silica extracted from rice husks and characterized these new materials.

BP One-Pot Synthesized Catalytically Stable and Active Nanoreactors by the encapsulation of Size-Controlled Nanoparticles within a Hierarchically Macroporous Core@Ordered Mesoporous Shell System. The results are quite interesting and published ina TOP journal "**Advanced Materials**", a great success for the project.

VP1 evaluated HY and HY/MCM-41 catalysts synthesized during this period in the waste oil sludge catalytic cracking and compared with thermal cracking. This study shows that the presence of a mesoporosity is favorable to crack heavier fraction.

From this project on the basis of the catalytic cracking reaction of waste oil sludge over a large series of catalysts synthesized**, the best catalyst is a material with larger acidity (ZSM-5) and the presence of a mesoporosity**.

The Pilot after a long time construction is completely built and used for the first concentration of ethanol by adsorption process using zeolite A adsorbent. The Pilot contains two main columns with zeolite A adsorbents, a tank for the storage of rude ethanol, the pump for the injection of ethanol,

In Conclusion, all the Tasks and modified Tasks for this period from point of view of time schedule have been completed. All the objectives of this period have been reached.

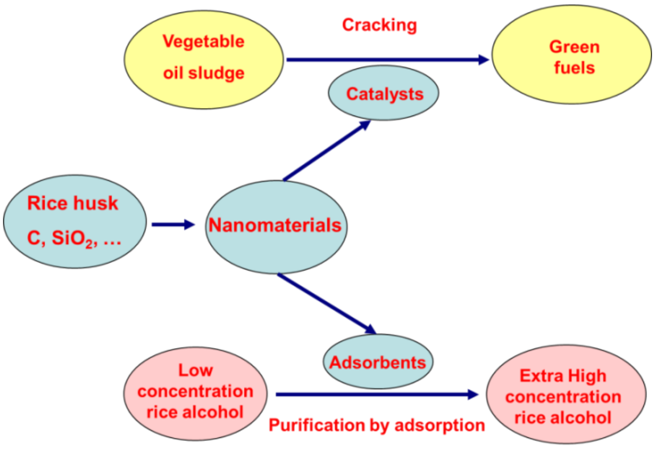
Content

1. Introduction

1.1. Objectives of the project

The purpose of this joint study is the recycle of wasted agro-matters as precursors to generate new nanomaterials and biofuels from rice husk and vegetable oil sludge. The prepared nanomaterials can be used as catalysts and adsorbents for the green diesel production from vegetable oil sludge and the concentration of alcohols from primary products from fermentation. The present project can be the beginning of the construction of a network of excellence Belgo-Vietnamese in the field of nanomaterials, catalysis and purification.

Scientific strategy of the project is described in the following figure.



The project will have the following objectives:

1. Extraction of silica and carbon from the wasted agro-products such as rice husk by physico-chemical techniques;
2. Utilisation of the carbon and silica extracted from rice husk as starting chemical sources and precursors for the conception of new silica and carbon based nanomaterials;
3. Synthesis of nanomaterials directly from rice husk as silica and carbon precursors;
4. Modification and functionalization of these new nanostructures;
5. Application of these modified and functionalized nanostructures as catalysts for the conversion of another waste of agro-matters, vegetable oil sludge to green fuels (biodiesel) by thermal, pyrolysis and catalytic cracking reactions.
6. Application of these modified and functionalized as selective adsorbents for the concentration of alcohols.

1.2. Partners of the Project

Belgium: Prof. Bao-Lian Su
Laboratoire de Chimie des Matériaux Inorganiques,
Facultés Universitaires Notre Dame de la Paix (University of Namur),
61 rue de Bruxelles, B-5000 Namur
Tel.: + 32 81 72 45 31
Fax: + 32 81 72 54 14
E-mail: bao-lian.su@fundp.ac.be

hereafter referred to as the Belgian Partner (**BP**),

Vietnam: Dr. Vu Anh Tuan,
Dr. Le Thi Hoai Nam
Department of Surface Chemistry and Catalysts, Institute of Chemistry,
Vietnamese Academic of Science and Technology
18 Hoang Quoc Viet Street, Hanoi Vietnam
Tel: + 84.7912184, Handphone : + 84 95.33.76.268,
Fax: + 84.8361283
Email: tuanva@ich.ncst.ac.vn and namlh@ich.ncst.ac.vn

hereafter referred to as the Vietnamese Partner 1 (**VP1**),

Dr. Van Dinh Son Tho
Hanoi University of Technology
Faculty of Chemical Technology
Petrochemical and Catalysis Materials Laboratory
No1 DaiCoViet Street, Hanoi, Vietnam
Email: thovds@yahoo.com

hereafter referred to as the Vietnamese Partner 2 (**VP2**)

1.3. Organization of the project (Workpackages)

The project is organized in three Workpckages (Scheme 1):

Workpackage 1. Preparation of silica based and carbon based nanostructured materials from rice husks

The wasted agro-products such as rice husk very rich in carbon and silica will be used as starting materials for the conception of new silica and carbon based nanomaterials.

This is the main tasks of Belgian partner (**BP**) with some subtasks contributed from Vietnamese partners. The Workpackage 1 will be coordinated by Belgian partner.

Tasks:

1.1 Furniture of rice husk by Viet Namese partner,
1.2 Bibliographic research,
1.3 Chemical analysis of rice husks obtained from different regions of Vietnam. Chemical or physical extraction of silica from rice husk. This work will be performed during the whole period of the project,
1.4 Using extracted silica as starting silica source to synthesize silica based nanostructures such as pure siliceous mesoporous materials,
1.5 Using extracted silica as starting silica source and other synthetic inorganic sources
to synthesize silicoaluminate, metallosilicate mesoporous materials,
1.6 Chemical or physical extraction of carbon from rice husk. This work will be performed during whole period of the project.

1.7 Using extracted carbon as starting carbon source to synthesize carbon based nanostructures such as porous carbon materials and carbon nanotubes,
1.8 Using directly rice husk as carbon source to synthesize porous carbon materials and carbon nanotubes,
1.9 Using directly rice husk as silica source and other synthetic inorganic source to synthesize silicoaluminate, metallosilicate mesoporous materials,
1.10 Using directly rice husk as silica and carbon sourcse to synthesis Si carbide materials,
1.11 Characterization of these new nanomaterials synthesized from rice husk,
1.12 Preparation of the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.4 and 3.5**),
1.13 Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.7 and 3.9**),
1.14 Characterization of these modified nanomaterials by a series of physico-chemical techniques,
1.15 Remodification and Functionalization of our as prepared porous materials and our modified porous nanomaterials on the basis of the test results supplied by Vietnamese partners (**VP1** and **VP2**) (**See tasks 2.10 and 3.12**) and characterization of these re-modified and functionalized porous nanomaterials by a series of physico-chemical techniques,
1.16 After testing by **VP1** and **VP2** (**See Tasks 2.13 and 3.15**), production in large quantity of the best catalyst and adsorbent by **BP** and the use of these materials by **VP1** and **VP2** for the long period testing in Viet Nam**.** The characterization of these porous nanomaterials produced in large quantity by a series of physico-chemical techniques.

The researcher, a full time engaged Doctor in chemistry will be responsible for the good realization of all the tasks and will take in charge on the tasks 1.1, 1.2, 1.4, 1.5, 1.7, 1.8, 1.9, 1.10, 1.12, 1.13, 1.15, and 1.16. A half time technician (18 months) will be engaged for the tasks of 1.3, 1.6, 1.11 and 1.14. These last four tasks will be performed during whole period of the project.

Workpackage 2. Application of these new nanostructures as catalysts for the conversion of another waste of agro-matters, vegetable oil sludge to green fuels (biodiesel) by thermal, pyrolysis and catalytic cracking reactions.

This is the main tasks of the Vietnamese partner **VP1** with contribution from **VP2** and also **BP.** The Workpackage 2 will be coordinated by Viet Namese partner 1.

Tasks:

2.1 Biobliographic research,
2.2 Determination of main characteristics of vegetable oil sludge as boiling point, heavy metal contents, iodine index …etc,
2.3 Construction and evaluation of the catalytic testing system (Microreactor),
2.4 First analysis with **BP** for the selection of the first series of catalysts (**See Task 1.12**),
2.5 Production of biodiesel by pyrolysis and catalytic cracking, using catalysts from Belgium partner (**BP**-CMI laboratory) as well as zeolites catalysts from

Vietnamese partners. First screening of the catalysts in microreactor and the characterization of used catalysts by a series of physico-chemical techniques by **BP**,

2.6 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc

2.7 Establishment of the criteria for the selection of the best catalysts with the participation of **BP** (**See Task 1.13**),

2.8 Catalytic Testing of the modified porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.13**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**,

2.9 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc

2.10 Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour withy the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**),

2.11 Catalytic Testing of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**Task 1.15**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**,

2.12 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc,

2.13 Selection of the best catalyst for the long period catalytic testing with the participation of **BP**,

2.14 Catalytic testing with large quantity of catalysts and characterization of used catalysts by a series of physico-chemical techniques by **BP**,

2.15 Evaluation of the quality of biodiesel products by using difference techniques : Cetane number, viscocity index, Acid number.. etc

Workpackage 3. Application of these new nanomaterials as selective adsorbents for the concentration of alcohols.

This is main tasks of Vietnamese partner **VP2** with contribution of **VP1** and **BP**. The Workpackage 3 will be coordinated by Viet Namese partner 2.

Tasks:

3.1 Production of alcohols from fermentation of rice, sugarcane and cassava (Vietnamese agro-products) by distillation.

3.2 Construction and evaluation of the purification system (Microreactor),

3.3 Establish the technology of absolute alcohols production for use as “clean fuel” with capacity of 100litters/day.

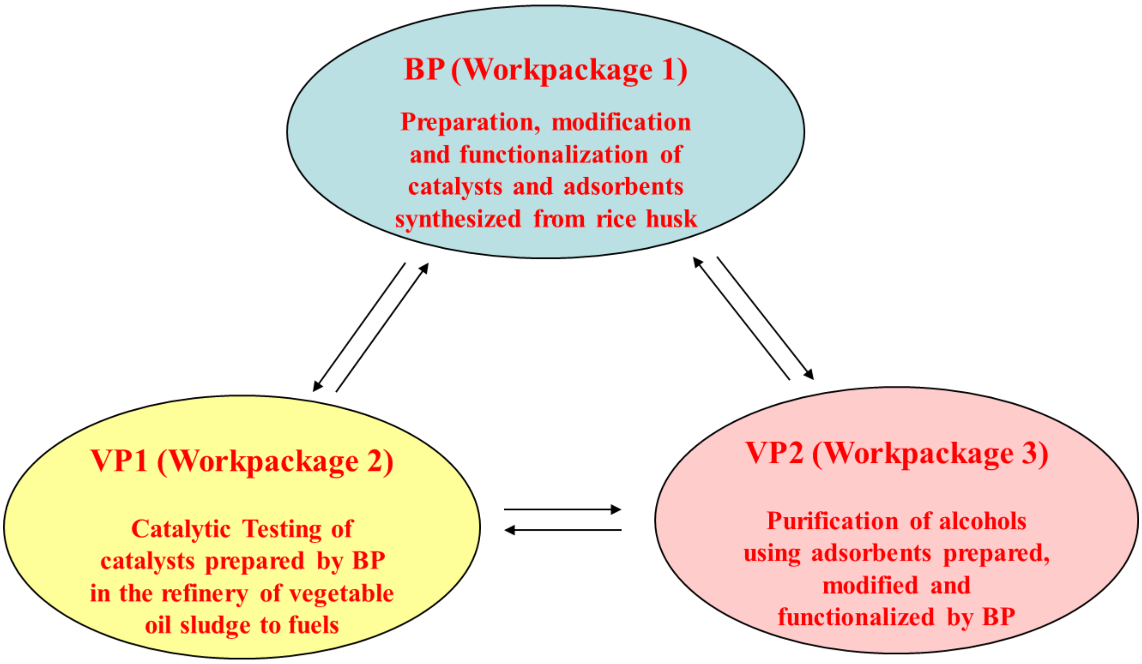
3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period,

3.5 First analysis with **BP** for the selection of the first series of adsorbents (**See Task 1.12**),

3.6 Concentration of alcohols (concentration>99.5%) by using selective adsorbents (from **BP**– CMI labolatory) as well as zeolites prepared from Kaolin of Vietnam. First screening of the adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques,

3.7 Evaluation of the quality of alcohols produced with adsorbents supplied by **BP** by using difference techniques,

3.8 Establishment of the criteria for the selection of the best adsorbents with the participation of **BP** (**See Task 1.13**),
3.9 The information obtained from 3.6 and 3.7 will be supplied to Belgian partner to modify porous adsorbents,
3.10 Catalytic Testing of the modified porous adsorbents supplied by Belgian partner (**BP**) and characterization of used adsorbents by a series of physico-chemical techniques,
3.11 Evaluation of the quality of alcoholic products by using different techniques,
3.12 Establishment of the correlation between the characteristics of adsorbents and the purification behaviour in order to further modify or functionalize the modified porous nanoadsorbents by **BP** (**See Task 1.15**),
3.13 Alcohol concentration test of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.15**) and characterization of used adsorbents by a series of physico-chemical techniques,
3.14 Evaluation of the quality of alcohol products by using different techniques,
3.15 Selection of the best adsorbents for the long period catalytic testing on the besis of the information obtained from 3.13 and 3.14 with the participation of **BP**,
3.16 Purification testing in a pilot with large quantity of catalysts and characterization of used adsorbents by a series of physico-chemical techniques,
3.17 Evaluation of the quality of alcohol products by using different techniques.



Scheme 1: Coordination and organization of the project.

This Final Report will be divided into three parts, first part deals with the research activity report (scientific missions and researchers recruitment). The realizations following different tasks, giving information on the completeness of different tasks and how different tasks have been completed and started and on the reasons why some tasks have been delayed and removed and on time schedule modification to accommodate to new organization will be then described. The third part concerns detailed scientific results related to each task.

2. Reports

2.1. Research Activity Reports

2.1.1. Meetings

First period: November 2006-April 2007

Kicking off meeting of the project

Due to the reception of signed contract at the end of November of 2006, the project was effectively started by 1st January 2007.

The Kicking-Off meeting was held during the scientific visit of Prof. Bao-Lian Su in Hanoi, Vietnam from 14 to 18 April 2007 (see **Annexe 3, Scientific Mission Report**).

Second period: May 2007-October 2007

No meeting organized in this period.

Third period: November 2007-April 2008

First Annual Meeting

Visit of Prof. Le Thi Hoai NAM and Prof. Van Dinh Son THO from 31st October to 6th November 2007 for a one week stay for this first **Annual Meeting**.

Namur, from 31st October to 6th November 2007,

Vietnamese Participants: VP1: Prof. Le Thi Hoai NAM and VP2: Prof. Van Dinh Son THO

Belgian participants: Prof. Bao-Lian Su, Dr. Xiao-Yu Yang and Mrs. Hadj Sodok

Objectives: 1) Discussion on the results obtained during the first year (two first periods),
2) Modification of different tasks,
3) Exchange of the information
4) Discussion on the researcher exchange
5) Plan the work for the second year

Fourth period: May 2008-October 2008

Second annual meeting, General meeting at Belspo and Closing Meeting in Namur

A **General Meeting** has been organized by Belspo on 16 June 2008 in Brussels. BP presented the project progress. This meeting gathered Vietnamese partners and Belgian partners involved in different Belgo-Vietnamese cooperation projects.

Second Annual Meeting has been held in Namur September 2008 to analysis the research state of the project, to modify some tasks following the situation and to prepare the closing of the project.

The **Closing Meeting of the project** has been organized in Hanoi, Viet Nam at the beginning of 2010 and September 2011 in Namur, Belgium, separately for Vietnamese partners and for Belgian partners. The **Closing Meeting** in Namur, Belgium was organized from 11-14 September 2011 with the participation of Viet Names partners, Prof. Le Thi Hoai Nam from Institute of Chemistry and Dr. Van Dinh Son Tho from University of technology Hanoi.

2.1.2. Scientific mission and stays

First period: November 2006-April 2007

Prof. Bao-Lian Su peformed a scientific mission in Viet Nam to organize the Kicking off meeting and to start officially the project. During the mission, Prof. Bao-Lian Su visited the Institute of Chemistry, Viet Namese Academy of Sciences and Technologies and Hanoi University of Technology, two partners of the project. He delivered also two lectures on the preparation of the nanomaterials. His visit to the Refinery Factory of vegetable oil sludge was also organized and a discussion with the director of the Factory was held.

Second period: May 2007-October 2007

No scientific stay was organized in this period.

Third period: November 2007-April 2008

Mr. Do Xuan DONG made a scientific stay from 16th to 26th March 2008 for the synthesis and characterization of a series of nanoporous materials using silica from extracted rice husks as precursor.

Fourth period: May 2008-November 2008

Mr. Tran Quong Vinh and Mrs. Le Thi Kim Lan made their scientific stay from 26 August to 12 September in Namur to prepare and characterize new materials.

The 6th International Mesostructured Materials Symposium has been held in Namur from 8th to 12th September 2008 and organized by BP with the participation of Vietnamese partners (VP1 and VP2). BP, VP1 and VP2 presented the results obtained from this Belgo-Vietnamese bilateral Cooperation project by two poster presentations.

2.1.3. Recruitments

As the Contract allowed the Belgian Partner to recruit one researcher with Doctorate degree and one Technician for a better realization of the project.

First period: November 2006-April 2007

Mr. Xiao-Yu Yang who was waiting for his PhD thesis defense was engaged for the realization of project **from 1st April 2007**.

Mr. Yang is an expert in the synthesis of porous nanomaterials. His engagement for this project can ensure an excellent realization of the project.

Mr. Thomas Ligot was engaged as Technician to assist to Mr. Yang was engaged for the project for at first three months (a trial period) **from 1st May 2007**.

Second period: May 2007-October 2007

Mr. Xiao-Yu Yang continued to work for the project. **1st May-31 October 2007**.

Mr. Yang is an expert in the synthesis of porous nanomaterials. His work in the first period was quite impressive.

Mr. Thomas Ligot was engaged as Technician to assist to Mr. Yang for the project **from 1st May to 31st July 2007**. After a three month trial period, the contract of technician for Mr. Thomas Ligot was stopped.

Miss Zoulika Hadj Sadok after the announcement of job vacancy and after a series of tests and, looked like a best candidate among different candidates, was engaged from **1st September 2007**.

Third period: November 2007-April 2008

Mr. Xiao-Yu Yang continued to work for the project. **1st November 2007 to 30th April 2008**.

Mr. Yang is an expert in the synthesis of porous nanomaterials. His work in the second period was quite impressive.

Miss Zoulika Hadj Sadok continued to work as Technician to assist to Mr. Yang for the project **from 1st November 2007to 30th April 2008**.

Fourth Period: May 2008-October 2008

Mr. Xiao-Yu Yang continued to work for the project. **1st May to 30th September 2008**. Unfortunately Dr. Yang left from the project since he was engaged by the FNRS from 1st October 2008 for a research fellow position. But he continues to work for the project.

2.2. Realizations of different tasks

2.2.1. WorkPackage 1

First period: November 2006-April 2007

1.1: Furniture of rice husk by Vietnamese partner: **Completed.**

Viet Namese partners mailed around 500 grams rice husks of different origins and during the visit of Prof. Bao-Lian Su to Viet Nam in April 2007, Viet Namese partners passed some new samples of husks of different origins.

1.2 Bibliographic research: **Completed**.

Few papers on the utilization of rice husks as silica and carbon sources foe the preparation of zeolites, mesoporous materials and other advanced materials were found in the literature.

1.3 Chemical analysis of rice husks obtained from different regions of Vietnam. Chemical or physical extraction of silica from rice husk. This work will be performed during the whole period of the project: **Partly completed and to be continued**.

This analysis is indispensable for the use of rice husks as precursors for the synthesis of porous nanomaterials as catalysts and adsorbents.

From the first series of rice husks supplied by Viet Namese partners, the elemental analysis showed that the main components are SiO_2 (19.12 wt%) and C (43.20%). Other oxides are present in insignificant amount, but can affect the synthesis of porous nanomaterials.

Table 1. Chemical composition of rice husks (wt%)

C	SiO_2	MgO	P_2O_5	K_2O	Na_2O	SO_3	Fe_2O_3	Al_2O_3	CaO
43.20	19.12	0.422	0.380	0.337	0.211	0.187	0.001	0.0002	0.211

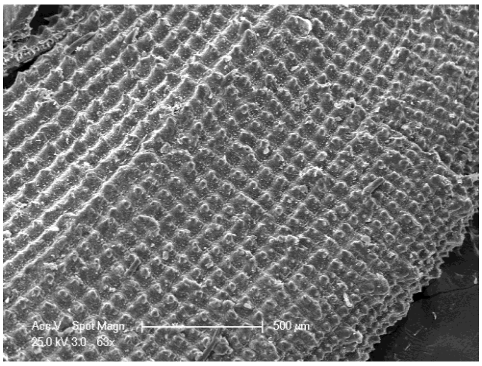


Fig.1, SEM Picture of rice Husks

We developed a new and very efficient protocole to extract silica (**see and 2.3.1. and 2.3.2.**). It can be seen that higher NaOH concentration favors the extraction of silica from rice husks.

1.4 Using extracted silica as starting silica source to synthesize silica based nanostructures such as pure siliceous mesoporous materials: Partly **Completed and To be continued**.

Ordered siliceous mesoporous materials (MCM-41 and SBA-3) has been successfully synthesized using extracted silicon by RHs as silicon source.

1.5 Using extracted silica as starting silica source and other synthetic inorganic sources to synthesize silicoaluminate, metallosilicate mesoporous materials: **Partly completed and to be continued**.

Ordered nanoporous material involving microporous materials (ZSM-5) and mesoporous materials (Al-MCM-41) has been successfully synthesized using extracted silicon by RHs as silicon source. Heteroatoms such as Al and Ti species have been easily introduced into the mesoporous and microporous walls of MCM-41 and ZSM-5 by simple mixture of extracted silicon with aluminum or titanium source in initial reaction gel.

1.11 Characterization of these new nanomaterials synthesized from rice husk: **Partly Completed and to be Continued**.

All the materials have been largely characterized by a large series of techniques. X-ray diffraction patterns (XRD) for solid phase information, Transmission electron microscopy (TEM) for structural information, the N_2 adsorption-desorption for textual information, the inductively-coupled plasma analysis for chemical compositions have been used.

1.12 Preparation of the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.4 and 3.5**): **Partly Completed and To be Continued**.

All the nanomaterials prepared can be used directly as catalysts for the processing of vegetable oil sludge to biodiesel. More details will be given in the next report.

Second period: May 2007-October 2007

1.3 Chemical analysis of rice husks obtained from different regions of Vietnam. Chemical or physical extraction of silica from rice husk. This work will be performed during the whole period of the project**: Completed**.

This task was partly completed during the first period. The analysis of rice husks from four different origins showed that the chemical compositions are quite similar and we do not need to adjust the silica and carbon extraction procedures and we do not need the modification of the synthesis protocols. We found also that although the origin of rice husks is different, the chemical composition varies insignificantly. Since we obtained a quantity large enough for whole period of the project, we do not need to continue to analyze other sources of rice husks. It is not necessary to analyze each time the rice husks although the origin is different. That is why this task was completed much earlier than planned.

1.4 Using extracted silica as starting silica source to synthesize silica based nanostructures such as pure siliceous mesoporous materials**: Completed**.

We continue the work realized during the first period. We developed a quite reproducible protocol for the extraction of silica source from rice husks and for the synthesis of pure siliceous mesoporous materials used extracted silica. This task was quite successful and completely accomplished.

1.5 Using extracted silica as starting silica source and other synthetic inorganic sources to synthesize silicoaluminate, metallosilicate mesoporous materials**: Completed**.

We continue the work realized during the first period. A series of new nanoporous materials, such as Nano-mesoporous ZSM-5, Al-MCM-41, Si-SBA-15, HY, HY/MCM-441 and ZSM-5/MCM-41 have been synthesized. These Catalysts have been tested in the n-Hexane and TIPB (triisopropylbenzène) cracking and also in waste oil sludge cracking (**see Tasks 1.7, 1.8, 1.12, 1.13 and 2.7**). **This Task was completely accomplished**.

1.6 Chemical or physical extraction of carbon from rice husk: **Completed**.

The **Task 1.6** was combined with **Tasks 1.7 and 1.8**. This task was planned to be carried out during whole period of the project. **This task is then completely accomplished**.

1.7 Using extracted carbon as starting carbon source to synthesize carbon based nanostructures such as porous carbon materials and carbon nanotubes: **Continued and modified.**

1.8 Using directly rice husk as carbon source to synthesize porous carbon materials and carbon nanotubes**: Continued and modified.**

A very efficient protocol was developed to extract silica from rice husks (**Task 1.6**) to generate directly from rice husks the highly porous carbon materials (**Tasks 1.7 and 1.8**). It was found that by extraction of silica from rice hiusks, different porosities can be generated, giving a nanoporous carbon material. We can extract silica and generate directly a nanoporous carbon material, two goals by one extraction.

The synthesis of carbon based nanostructures (**Tasks 1.6, 1.7 and 1.8**) was fully **Completed**, while the synthesis of carbon nanotubes (**Task 1.7**) using carbon source extracted from rice husks or using directly rice husks as precursor (**Task 1.8**) was removed from project since carbon nanotubes can not be used and are not interesting to be used as catalysts or adsorbents for vegetable oil sludge cracking and alcohol concentrations which are two main goals of the project. Due to the time limit, we would like to concentrate on our main objectives. That's why the synthesis of carbon nanotubes using rice husks was abandoned. Furthermore, after a large series of experiments, we found that during the extraction of silica, we can directly prepare nanoporous carbon materials from rice husks.

1.9 Using directly rice husk as silica source and other synthetic inorganic source to synthesize silicoaluminate, metallosilicate mesoporous materials**: Started and Removed**.

On the basis of a large series of experiments, using rice husks as silica precursor was not successful. It is much more efficient if we use silica extracted from rice husks as silica precursor. Due to the time limit, this task was moved from the project to concentrate our efforts on the preparation of zeolites and mesoporous materials using silica extracted from rice husks.

1.10 Using directly rice husk as silica and carbon source to synthesis Si carbide materials: **Removed from the project**.

The synthesis of Si carbide materials using carbon source extracted from rice husks or using directly rice husks as precursor was removed from project since Si carbide materials can not be used and are not interesting to be used as catalysts or adsorbents for vegetable oil sludge cracking and alcohol concentrations which are two main goals of the project. Due to the time limit, we would like to concentrate on our main objectives. That's why the synthesis of Si carbide materials using rice husks was removed from the project.

1.11 Characterization of these new nanomaterials synthesized from rice husk**: Started and to be Continued**.

A large series of techniques have been used to characterize all the porous materiials synthesized. For more details, please consult **Scientific Report 2.3.1**.

1.12 Preparation of the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners **(VP1 and VP2) (See Tasks 1.5, 1.7, 1.8, 2.4, 2.5, 2.7, 2.8, 2.10 and 3.5): Started and to be Continued.**

1.13 Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners **(VP1 and VP2) (See Tasks 2.7, 2.8, 2.10 and 3.9): Started and to be continued**.

We prefer to combine these two Tasks since these two Tasks are closely linked.

We continue the work (**Task 1.12**) realized during the first period. The first series of catalysts and adsorbents have been prepared (**Tasks 1.5, 1.7, 1.8**) and tested in Viet Nam. During the first period, due to the fact that the construction of the microreactor for catalytic testing was not completely finished, VP1 used Hexane and TIPB as molecular probes for the test instead of waste oil sludge. The results have been reported in the first semiannual report. For more details on the testing results, please consult **Scientific Report 2.3.2** of first **Semiannual Report**. During the second period, VP1 tested a large series of materials using waste oil sludge. The results are presented in **Tasks 2.4, 2.5, 2.7, 2.8, 2.10**. These results showed that microporous ZSM-5 zeolite catalysts with a mesoporosity are much more efficient. That is why we started to synthesize microporous ZSM-5 catalysts with mesoporosity. First results on the synthesis were reported here (**See Tasks 2.7, 2.8, 2.10**).

The obtained results on the synthesis and catalytic testing of these nanomaterials have been published in two SCI Journals: ***Fuel*** and ***J. Experimental. Nanosci***. in 2011, the proof of the success of the two periods.

Third period: November 2007-April 2008

1.11 Characterization of these new nanomaterials synthesized from rice husk: **Practically completed and to be continued.**

In this period, a series of new materials following the information from VP1 after the evaluation of a large series of samples, have been prepared and characterized. There are still some characterizations necessary for the next period.

1.12 Preparation of the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners (**VP1** and **VP2**) (**See Task 2.4**): **Completed**.
1.13 Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (**VP1** and **VP2**) (**See Task 2.7**): **Practically completed and to be continued.**
1.14 Characterization of these modified nanomaterials by a series of physico-chemical techniques: **Practically completed and to be continued**
1.15 Remodification and Functionalization of our as prepared porous materials and our modified porous nanomaterials on the basis of the test results supplied by Vietnamese partners (**VP1** and **VP2**) (**See tasks 2.10 and 3.12**) and characterization of these re-modified and functionalized porous nanomaterials by a series of physico-chemical techniques: **Started and to be continued**.

It is better to discuss together these Tasks. A new series of catalysts have been prepared (Faujasite Y with mesoporosity) (**Tasks 1.12 and 1.13**). The synthesis was based on the information provided by VP1 concerning the catalytic performances of materials synthesized in the previous reports. It was shown that catalysts containing a zeolite structure with the presence of mesoporosity will be the best catalysts. The new samples have been synthesized and characterized (**Task 1.14**). We realized a detailed study on the crystallization of zeolite as a function of hydrothermal treatment to select the best catalyst. On the basis of the evaluation by VP1 of this new series of catalysts, we started to modify the protocol to synthesize Faujasite Y zeolite with mesoporosity (**Tasks 1.15**).

<u>Fourth period: May 2008-October 2008</u>

Due to the fact that a very large amount of rice husks is needed to extract silica and then to synthesize in large quantity of the best catalyst (**Task 1.16**), it is not possible to send such huge quantity from Viet Nam to Belgium and due to also the fact that in the project, it is planned to construct the large scale extraction equipment and large quantity synthesis equipment, the **Task 1.16** is removed from the project and modified. BP concentrated on the synthesis of novel materials.

1.11 Characterization of these new nanomaterials synthesized from rice husk: **Completed**.

During all the period of the project, all the synthesized materials have been characterized using a large number of techniques.

1.13 Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.7 and 3.9**); **Completed**.
1.14 Characterization of these modified nanomaterials by a series of physico-chemical techniques: **Completed**
1.15 Remodification and Functionalization of our as prepared porous materials and our modified porous nanomaterials on the basis of the test results supplied by Vietnamese partners (**VP1** and **VP2**) (**See tasks 2.10 and 3.12**) and characterization of these re-

modified and functionalized porous nanomaterials by a series of physico-chemical techniques: **Completed**

On the basis of the results reported in the **Second Semiauual Report**, we synthesized HY and HY/MCM-41 catalysts using silica extracted from rice husks and characterized these new materials (**Tasks 1.11, 1.13, 1.14 and 1.15**). All these materials have been evaluated in the waste oil sludge cracking (**Tasks 2.10, 2.11, 2.12, 2.13, 2.14 and 2.15**). The synthesis of HY catalysts has been justified by the fact that HY catalyst is largely used for the fluidizing catalytic cracking reaction in industry and is well recognized as the best catalyst for the hydrocarbon cracking. However, our results showed that due to the hydrocarbon fraction of waste oil sludge, this kind of catalyst is not the best catalyst due to it low acidity although a mesoporosity was introduced in the final HY zeolite to give HY/MCM-41 catalyst. The functionalization and modification by the introduction of mesoporosity can help the cracking of higher fraction, but can not make a total cracking due to the low acidity.

On the basis of the results obtained during all the period of project, our marerial ZSM-5 with a mesoporosity is the best catalyst for the waste oil sludge catalytic cracking due to its high acidity and the presence of mesoporosity.

1.16: After testing by **VP1** and **VP2** (**See Tasks 2.13 and 3.15**), production in large quantity of the best catalyst and adsorbent by **BP** and use of these materials by **VP1** and **VP2** for testing long period in Viet Nam. The characterization of these porous nanomaterials produced in large quantity by a series of physico-chemical techniques: **Modified and completed**

Due to the reasons described at the beginning of this section, we modified this task and concentrated on the synthesis of novel materials. A catalytically stable core/shell nanoreactor with the encapsulation of uni-sized metal oxide active component has been prepared. This novel structured nanocatalyst is for the first time reported. The catalytic reaction showed that this novel structured catalyst is very stable and active for the oxidation of aromatics.

All these results have been published in the TOP journal “**Advanced Materials (Impact Factor > 13)**”.

2.2.2. Work Package 2,

First Period: November 2006-April 2007

2.1: Bibliographic research: **Completed**. (BP is not involved in this task).

2.2: Determination of main characteristics of vegetable oil sludge as boiling point, heavy metal contents, iodine index …etc: **Completed**. (BP is not involved in this task).

The melting point, Acidic number, Base number, Iodium number, Ester number, the content of free fatty acid and that of triglyxerit have been determined. Small amount of contaminants have also be detected. These informations are essential to determine the cracking reaction conditions.

2.3: Construction and evaluation of the catalytic testing system (Microreactor): **Partly Completed and to be continued**.

Two different microreactors, one at for vegetable oil sludge cracking reaction was being constructed.

For the sake of the facility, we discussed together Tasks 2.4 and 2.5.

2.4: First analysis with **BP** for the selection of the first series of catalysts (**See Task 1.12**): **Completed.**

2.5: Production of biodiesel by pyrolysis and catalytic cracking, using catalysts from Belgium partner (**BP**-CMI laboratory) as well as zeolites catalysts from Vietnamese partners. First screening of the catalysts in microreactor by **VP1 and VP2** and the characterization of used catalysts by a series of physico-chemical techniques by **BP: Partly Completed and to be continued.**

A series of nanoporous zeolites and Al-MCM-41 synthesized and described in WP1 have been tested using constructed microreactors.

Due to the fact that microreactors for vegetable oil sludge cracking is still under construction. The tests have been realized using n-Hexane and TIPB (Tri-isopropylbenzene) as reaction probes. Compared to commercial zeolitic catalyst, our catalysts are more active in n-hexane and TIPB cracking reactions. (**For more details, please consult point 2.3.2. in Scientific reports section**).

Second Period: April 2007- October 2007

2.3. Construction and evaluation of the catalytic testing system (Microreactor): **Completed.**

The microreactor was successfully constructed and can evaluate our materials using waste oil sludge.

2.4. First analysis with **BP** for the selection of the first series of catalysts (**See Tasks 1.5, 1.7, 1.8, 1.12**): **Completed**.

2.5. Production of biodiesel by pyrolysis and catalytic cracking, using catalysts from Belgium partner (**BP**-CMI laboratory) as well as zeolites catalysts from Vietnamese partners. First screening of the catalysts in microreactor and the characterization of used catalysts by a series of physico-chemical techniques by **BP**: **Completed**.

It is better understandable to combine these two Tasks. A large series of materials have been evaluated (**See Tasks 1.5, 1.7, 1.8 and 1.12**). The first screening showed that microporous ZSM-5 zeolite catalysts with a mesoporosity will be much more efficient catalysts, giving the guidelines for the modification of materials (**See Tasks 1.13**, **2.7, 2.8 and 2.10**). For more details, see **Scientific Report 2.3.2**.

2.6. Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc: **Completed**.

2.7. Establishment of the criteria for the selection of the best catalysts with the participation of **BP** (**See Task 1.13**): **Partly completed and to be continued**

2.8. Catalytic Testing of the modified porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.13**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**: **Started and to be continued**

2.10. Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour with the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Tasks 1.15**): **Started and to be Continued**.

For the sake of the clarity, it is better to combine these three Tasks.

A large series of nanoporous materials (zeolites and mesoporous materials) have been evaluated by microreactor using n-Hexane, TIPB and waste oil sludge as reagents. ZSM-5 zeolite catalyst with the presence of mesoporosity and pure ZSM-5 catalyst, both prepared from rice husks showed higher conversion than thermal cracking process (see **Scientific Report 2.3.2, Workpackage 2**) and also higher than ECAT, a standard cracking catalyst. To establish the criteria for the selection of the best catalyst and the correlation between the characteristics of catalysts and catalytic performances of our materials, more work will be done and will be reported in the **Semiannual Report** of third period. All these three Tasks are started and should be continued during next period.

2.9. Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc. **Partly Completed and to be Continued**.

The quality of liquid products from the cracking of waste oil sludge was evaluated after each test.

<u>Third period: November 2007-April 2008</u>

2.7 Establishment of the criteria for the selection of the best catalysts with the participation of **BP** (**See Task 1.13**): **Completed**.

After the evaluation of a very large series of materials synthesized, the criteria for the selection of the best catalyst has been established: an acid zeolite with the highest crystallinity and a mesoporosity.

2.8 Catalytic Testing of the modified porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.13**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**: **Completed**.

After the modification of the synthesis protocol, a new series of catalysts have been synthesized, characterized and evaluated.

2.9 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc: **Completed**.

The products obtained from the waste oil sludge catalytic cracking over this new series of catalysts have been analyzed in detail.

2.10 Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour with the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**): **Partly completed and to be continued.**

A correlation between the characteristics of catalysts and the catalytic behavior has been established. We decided to synthesize Y zeolite with mesoporosity.

2.11 Catalytic Testing of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**Task 1.15**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**: **Partly Completed and to be continued**.

We will continue to evaluate the series of Y zeolite with mesoporosity.

2.12 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscosity index, Acid number.. etc: **Partly completed and to be continued**.

<u>Fourth period: May 2008-October 2008</u>

For the same reason, the **Task 2.14** has been removed from the project.
2.10 Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour with the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**): **Completed**
2.11 Catalytic Testing of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**Task 1.15**) and characterization of used catalysts by a series of physico-chemical techniques by **BP: Completed**
2.12 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc: **Completed**
2.13: Selection of the best catalyst for the long period catalytic testing with the participation of **BP**: **Completed**
2.14: Catalytic testing with large quantity of catalysts by **VP1**, the characterization of used catalysts by a series of physico-chemical techniques by **BP**: **Removed from the project.**

2.15: Evaluation of the quality of biodiesel products by using difference techniques : Cetane number, viscocity index, Acid number.. etc: **Completed**

VP1 evaluated HY and HY/MCM-41 catalysts synthesized during this period in the waste oil sludge catalytic cracking and compared with thermal cracking. A detailed analysis of catalytic cracking products, waste oil sludge and thermal cracking has been made. The evaluation results are quite surprising (**Tasks 2.11, 2.12 and 2.15**).

This study shows that the presence of a mesoporosity is favorable to crack heavier fraction. This is owing to the easy penetration of large fraction of hydrocarbons into the catalyst framework. Whilst due to the lower acidity, HCO can not be completely cracked to give more Gasoline and LPG. That is why in the final products, there is still a significant fraction of LCO. This fraction of LCO is at least partly from HCO. Over HY, due to the lack of mesoporosity, larger molecules of hydrocarbons can not penetrate into the framework of catalyst. No cracking of fraction of HCO over this catalyst.

In waste oil sludge, the most important fraction is located at between 270-330 °C with a significant fraction located at between 510-540 °C. After cracking over HY/MCM-41 both fractions of 33-330 and 510-540 °C are largely reduced. More fractions between 90-360 °C, indicating the efficient cracking reaction over HY/MCM-41. Whilst over HY, no change between 270-330 °C. This detailed analysis (**Tasks 2.12 and 2.15**) confirms the observation. Over HY, more total dry gases is obtained compared that over HY/MCM-41.

The total dry gases obtained from the waste oil cracking reaction over HY/MCM-41 and HY and by thermal cracking demonstrated that the thermal cracking gives more ethylene, ethane and methane and also C_6+ and propylene products. Less total dry geses are btained over HY/MCM-41 than over HY. Over HY, more also C_6+ , propylene, n and iso-butenes and ethylene. Over HY/MCM-41 more C_6+ and propylene, n-butane and iso-pentane products

The best catalyst is a material with larger acidity (ZSM-5) and the presence of a mesoporosity (**Tasks 2.10, 2.11 and 2.13**). This conclusion is totally in agreement with previous results.

2.2.3. Work Package 3,

First period: November 2006-April 2007

3.1: Production of alcohols from fermentation of rice, sugarcane and cassava (Vietnamese agro-products) by distillation: **Completed**

3.2: Construction and evaluation of the purification system (Microreactor): **Partly Completed and to be continued.**

3.3: Establishment of the technology of absolute alcohols production for use as "clean fuel" with capacity of 100litters/day: **Partly Completed and to be Continued**

3.4: Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period: **Partly Completed and to be Continued**

3.5: First analysis with **BP** for the selection of the first series of adsorbents (**See Task 1.12**): Partly **Completed and to be continued**;

3.6: Concentration of alcohols (concentration > 99.5%) by using selective adsorbents (from **BP**– CMI labolatory) as well as zeolites prepared from Kaolin of Vietnam. First screening of the adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques: **Partly Completed and to be Continued**;

Second period: May 2007-October 2007

3.2 Construction and evaluation of the purification system (Microreactor): **Completed**.

The microreactor for the concentration of ethanol by adsorption process was successfully constructed and tested.

3.3 Establish the technology of absolute alcohols production for use as "clean fuel" with capacity of 100litters/day: **Completed**.

This has been completed since the technology for the centration of ethanol by adsorption process has been chosen.

3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period: **Started and to be continued**.

Different devices used for the construction of pilot for the concentration of ethanol by adsorption process have been assembled.

3.5 First analysis with **BP** for the selection of the first series of adsorbents (**See Task 1.12**),
3.6 Concentration of alcohols (concentration>99.5%) by using selective adsorbents (from **BP**–CMI labolatory) as well as zeolites prepared from Kaolin of Vietnam. First screening of the adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques,
3.7 Evaluation of the quality of alcohols produced with adsorbents supplied by **BP** by using difference techniques,

3.8 Establishment of the criteria for the selection of the best adsorbents with the participation of **BP** (**See Task 1.13**),

3.9 The information obtained from 3.6 and 3.7 will be supplied to Belgian partner to modify porous adsorbents,

3.10 Adsorption Testing of the modified porous adsorbents supplied by Belgian partner (**BP**) and characterization of used adsorbents by a series of physico-chemical techniques,

In the first **Semiannual Report**, a microreactor was constructed by VP2. To evaluate this micrireactor, VP2 used zeolite A as adsorbent since no materials were ready from BP due to the late setting-up of the project and the late engagement of researchers. Furthermore, it is a long term study to develop a good adsorbent for ethanol concentration by adsorption since the powder can not be used in the concentration process. Powdery products should be made in form of pellet. The choice of binder, size of pellet, form of pellet, all these need a detailed study. It could be more practical to use Zeolite A adsorbent synthesized from Kaolin Vietname to solve the urgent problem in Vietnam. That is why VP2 will focus the evaluation of zeolite A adsorbent for ethanol concentration. The **Tasks 3.5, 3.6, 3.7, 3.10 and 3.12 will be thus modified**.

3.5 First analysis with **BP** using Zeolite A adsorbent: **Completed**.

3.6 Concentration of alcohols (concentration>99.5%) by using zeolites prepared from Kaolin of Vietnam. First test of the adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques: **Completed**

3.7 Evaluation of the quality of alcohols produced with zeolite A adsorbents: Completed

3.8 Synthesis of zeolite A using silica extracted from rice husks with the participation of **BP** (**See Task 1.13**): **Started and to bo continued**

3.9 Characterization of zeolkite A adsorbents: **Started and to bo continued**

3.10 Adsorption Testing of the modified zeolite A adsorbents and characterization of used adsorbents by a series of physico-chemical techniques: **Completed**

VP2 continued to supply information on the performance of zeolite A adsorbent although Tasks 3.5-3.7 and 3.10 have been modified. This information allows to select the best adsorbent for VP2 partner.

3.11 Evaluation of the quality of alcoholic products by using different techniques: **Started and to be continued**.

After each test of zeolite A adsorbent, the analysis of quality of ehanol obtained has been realized.

<u>Third period: November 2007-April 2008</u>

3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period: **To be continued**.

Two adsorption columns have been built and different electrical devices for the control of pilot have been assembled.

3.8 Synthesis of zeolite A using silica extracted from rice husks with the participation of **BP** (**See Task 1.13**): **Completed**

A new protocol has been invented to synthesize zeolite A using silica extracted from rice husks and Kaolin of Vietnam.

3.9 Characterization of zeolkite A adsorbents: **Completed**

The synthesis is successful. Zeolite A obtained has been characterized by a series of techniques such as XRD, IR, and solid state MAS NMR.

3.11 Evaluation of the quality of alcoholic products by using different techniques: **Completed**.

The quality of ethanol obtained with zeolite A adsorbent has been analyzed.

3.12 Establishment of the correlation between the characteristics of adsorbents and the purification behaviour in order to further modify or functionalize the modified porous nanoadsorbents : **Partly completed and to be continued.**

The adsorption behavior has been analysed and can be very helpful to adjust the ethanol concentration by adsorption process. It is found that it is indispensable to regenerate zeolite A adsorbent after 40 minutes operation due to the adsorption of large amount of water by zeolite.

3.13 Alcohol concentration test of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.15**) and characterization of used adsorbents by a series of physico-chemical techniques: **Removed from the project**

This Task has no sens after the modification of the objective for the Workpackage 3.

3.14 Evaluation of the quality of alcohol products by using different techniques: **Partly completed and to be continued**.

3.15 Selection of the best adsorbents for the long period catalytic testing on the basis of the information obtained from 3.13 and 3.14 with the participation of **BP**: **Removed from the project**.

Since the adsorbent has been selected on the basis of pore size of zeolite and molecular size of ethanol, this task is not necessary now.

Fourth period: May 2008-October 2008

For the same reason as described at the beginning of the **Sections 2.2.1 and 2.2.2**, the **Task 3.16** has been removed from the project.

3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period: **Completed**

3.12 Establishment of the correlation between the characteristics of adsorbents and the purification behaviour in order to further modify or functionalize the modified porous nanoadsorbents: **Completed**

3.14 Evaluation of the quality of alcohol products by using different techniques: **Completed**

3.16: Purification testing in a pilot with large quantity of catalysts and characterization of used adsorbents by a series of physico-chemical techniques: **Removed from the project.**

3.17: Evaluation of the quality of alcohol products by using different techniques: **Completed**

The Pilot has been completely built and used for the first testing of ethanol concentration by adsorption process. The Pilot composed of two large columns for adsorption of ethanol with zeolite A adsorbent (**Task 3.4**). A correlation between the characteristicsq od zeolite A adsorbent and its performances in ethanol adsorption has been established (**Task 3.12**). The quality of ethanol obtained at different conditions has been evaluated (**Tasks 3.15 and 3.17**). In spite of huge difficulty, the Pilot has been finally successfully constructed and used, the main objective of VP2 after modification of their Tasks.

2.2.4. Conclusion

All the tasks defined initially and modified during the realization of project from WPs 1, 2 and 3 have been completed.

2.3. Scientific Report

2.3.1. WorkPackage 1

First period: November 2006-April 2007

(Tasks: 1.3, 1.4, 1.5, 1.11 and 1.12): Synthesis of Nanoporous Silica-based Materials Using Extracted Silica from Rice Husks

ABSTRACT: Ordered nanoporous material involving microporous materials (ZSM-5) and mesoporous materials (MCM-41, Al-MCM-41, and SBA-3) has been successfully synthesized using extracted silicon by RHs as silicon source, which are characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption-desorption isotherms, differential thermal analysis (DTA), and thermogravimetric analysis (TG), as well as ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. Furthermore, heteroatoms such as Al and Ti species have been easily introduced into the mesoporous and microporous walls of MCM-41 and ZSM-5 by simple mixture of extracted silicon with aluminum or titanium source in initial reaction gel.

Introduction

Nanoporous materials as an important class of nanostructured materials possess high specific surface area, large pore volume, uniform pore size, and rich surface chemistry. These materials present great promises and opportunities for a new generation of functional materials with improved and tailorabel properties for applications in adsorption, membranes, sensors, energy storage, catalysis, and biotechnology, etc. For example, zeolites are crystalline microporous aluminosilicates consisting of tetrahedral SiO_4 and AlO_4 as basic building units, and have many industrial applications in catalysis, adsorption, and separation. The silica content of rice husks (RHs) is around 19.1% (see Table 1), which could be possible used as silica source for the synthesis of zeolites and ordered mesoporous materials. We demonstrate here that when the extracted silica of the rice husks is used as silicon source, zeolites and ordered mesoporous silica materials are successfully synthesized in alkaline media.

Table 1. Chemical composition of rice husks (wt%)

C	SiO_2	MgO	P_2O_5	K_2O	Na_2O	SO_3	Fe_2O_3	Al_2O_3	CaO
43.20	19.12	0.422	0.380	0.337	0.211	0.187	0.001	0.0002	0.211

Experimental Section

Preparation of Materials

Dry raw RHs were supplied by Vietnam partner, which were sieved to eliminate residual rice and clay particles. (1) A 10g sample of RHs was taken in a flask with a condenser. After mixed 200mL HCl (3%), the mixture were heated at 100°C for 12hrs. the solid product was filtered, washed with water, and dried in air for 12 h. Calcination of the product was carried out at 550 °C for 5 h in flowing oxygen to remove the organic components. The final product was almost SiO_2 aerogels. (2) In a typical synthesis of ZSM-5 zeolite, the aluminosilicate gels were prepared by mixing TPAOH aqueous solution (25%), followed by addition of $Al_2(SO_4)_3 \cdot 18H_2O$ and the solution containing extracted silicon under stirring

(Al_2O_3/SiO_2/TPAOH/ H_2O molar ratios of 1.0/30/8/120/1500). After adjusted pH value (pH=14), the mixture was transferred into an autoclave for additional reaction at 140 °C for 5 days. The crystallized product was washed by water, filtered, dried, and ultrasonic redispersion in water. (3) In a typical synthesis mesoporous material MCM-41, CTAB were added into water, followed by addition of the solution containing extracted silicon. After stirring for 8 h, the mixture gel with molar ratio of SiO_2/CTAB/KOH/H_2O at 1/0.35/0.6/50 was aged at room temperature for 24 h. Then, the gel was transferred to a Teflon-lined stainless-steel autoclave for crystallization at 110 °C for 3 days. After crystallization, the solid product was filtered, washed with water, and dried in air for 12 h. Calcination of the product was carried out at 550 °C for 5 h in flowing oxygen to remove the organic templates such as CTAB. (4) In a typical synthesis mesoporous material SBA-3, CTAB were added into water, followed by addition of the solution containing extracted silicon. After stirring for 8 h, the mixture gel with molar ratio of SiO_2/CTAB/HCl/H_2O at 1/0.4/4.5/65 was aged at room temperature for 24 h. Then, the gel was transferred to a Teflon-lined stainless-steel autoclave for crystallization at 110 °C for 3 days. After crystallization, the solid product was filtered, washed with water, and dried in air for 12 h. Calcination of the product was carried out at 550 °C for 5 h in flowing oxygen to remove the organic templates such as CTAB.

Characterization

X-ray diffraction patterns (XRD) were obtained with a Panalytical X'Pert diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) experiments were performed on a Philips TECNAI-10 at with an acceleration voltage of 100 kV. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010M system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution for mesopores was calculated using Barrett-Joyner-Halenda (BJH) model. The ratios of Si/Al in solid samples were determined by the results of inductively-coupled plasma analysis (ICP, Perkin-Elmer 3300DV).

Results and discussion

At first, a study on the effect of NaOH concentration on the extraction of silica from rice husks has been realized. It can be seen that higher NaOH concentration favors the extraction of silica from rice husks.

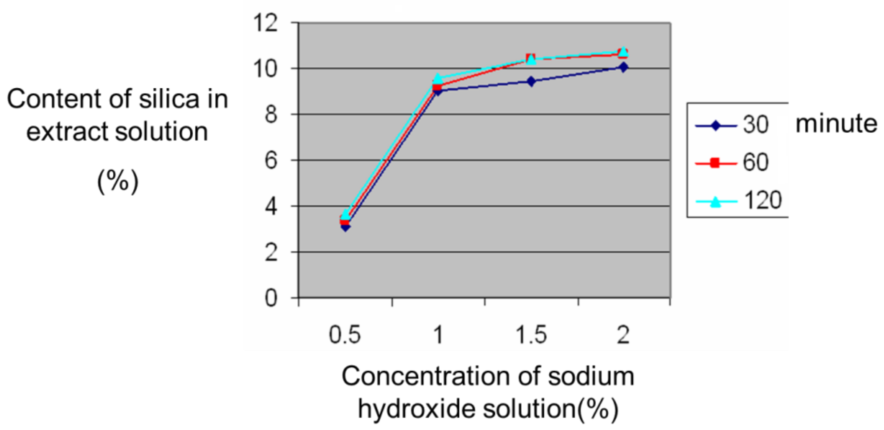


Fig. 2, Extraction of Silica from Rice Husks as a function of NaOH concentration in solution

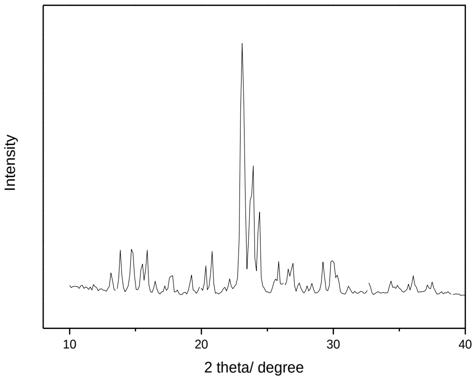


Figure 3. XRD patterns of ZSM-5

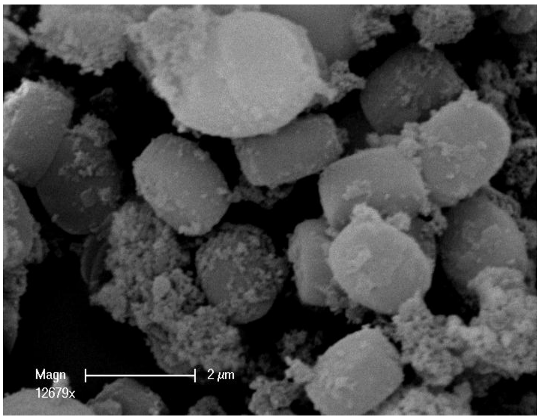


Figure 4. the scanning electron microscopy image of ZSM-5

Figure 3 shows X-ray diffraction (XRD) patterns of ZSM-5 crystals synthesized by extracted silicon. Notably, the XRD peaks of the sample are characteristic of ZSM-5 crystals. **Figure 4** shows scanning electron microscopy (SEM) image of the ZSM-5 samples. The sample has a uniform morphology with a particle size of 2-4 μm (**Fig. 5**). This suggests that the sample has good crystallinity using extracted silicon as silicon source. SEM image of calcined ZSM-5 exhibits ordered arrays of micropores with one-dimensional channels and further confirm that the sample has crystals with high crystallinity (**Fig. 4**).

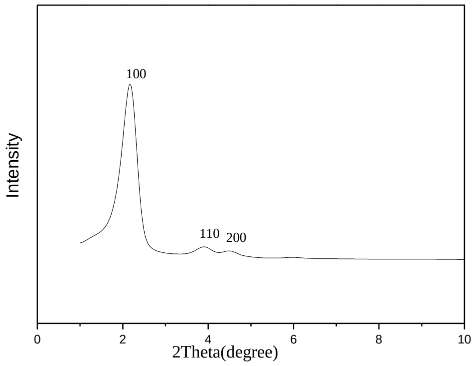


Figure 5. XRD patterns of as-synthesized MCM-41

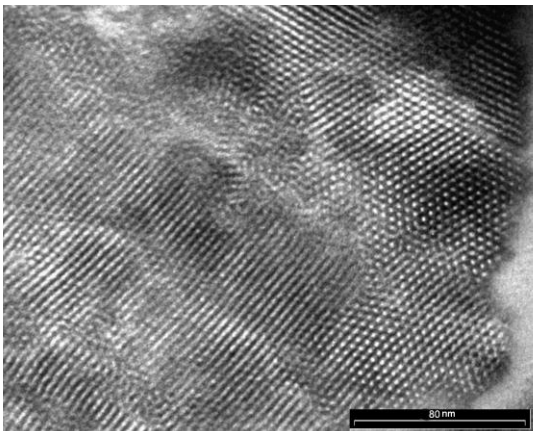


Figure 6. TEM image of MCM-41

Figure 5 shows XRD patterns for MCM-41 material synthesized by extracted silicon in alkaly media. Notably, as-synthesized MCM-41 (**Figure 5**) exhibits clearly well-resolved peaks that can be indexed as the (100), (110), and (200) diffractions associated with the *p6mm* hexagonal symmetry with a lattice constant a = 44 Å. TEM image of calcined MCM-41 (**Figure 6**) exhibits ordered hexagonal arrays of mesopores with one-dimensional channels and further confirm that the sample has a 2-D hexagonal (*P6mm)* mesostructure. The N_2 adsorption isotherms of calcined MCM-41 (**Figure 7**) exhibit a typical adsorption curve of type IV. The steps can be identified in the adsorption curve at a relative pressure $0.3<p/p_o<0.4$ for MCM-41, which is due to the characteristic of mesopores.

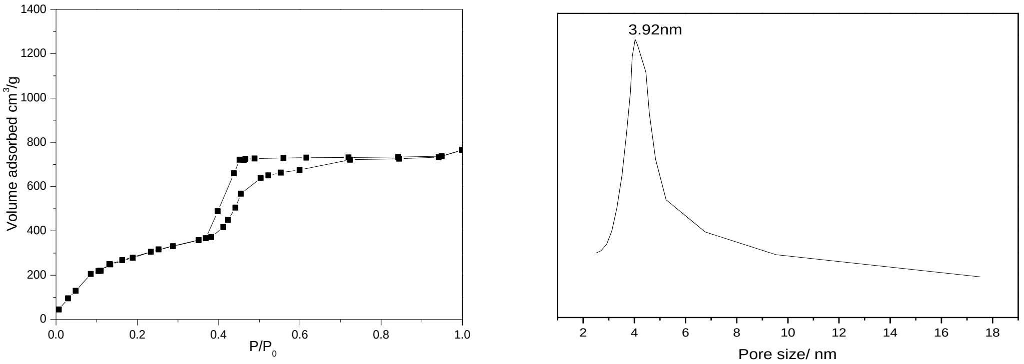


Figure 8. N_2 isotherms (left) and the corresponding pore size distribution (right) of calcined MCM-41. The corresponding pore size distribution curve (right) is obtained from the adsorption branch of the isotherm using the BJH method.

Additionally, under alkaline media (pH=11), heterogeneous atoms of Al and Ti substituted materials, with the goal of introducing catalytically active sites, have been easily introduced into the mesoporous walls of MCM-41 by simple mixture of extracted silicon with aluminum or titanium source in initial reaction gel. For example, ^{27}Al MAS NMR spectrum of the as-synthesized Al-MCM-41 shows a strong signal centered at near 53 ppm (**Figure 8**), indicating that Al species have been successfully incorporated into the mesoporous walls with 4-coordinated number, which suggests that Al-MCM-41 may be used as acidic catalysts and ion-exchangers.

Furthermore, **Figure 9** shows XRD patterns for SBA-3 material synthesized by extracted silicon in acid media. Notably, as-synthesized SBA-3 (**Figure 10**) exhibits clearly well-resolved peaks that can be indexed as the (100), (110), and (200) diffractions associated with the *p6mm* hexagonal symmetry with a lattice constant a = 3.86Å. TEM image of calcined

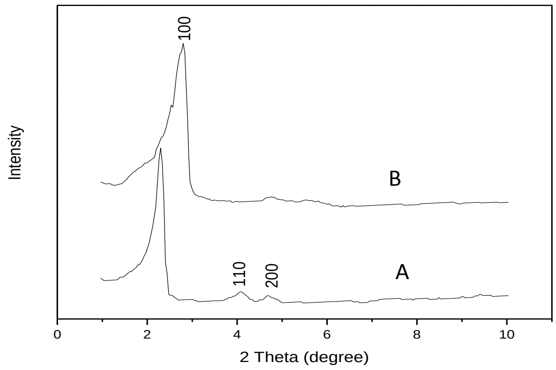


Figure 9. XRD patterns of as-synthesized SBA-3 (A), calcined SBA-3 (B),

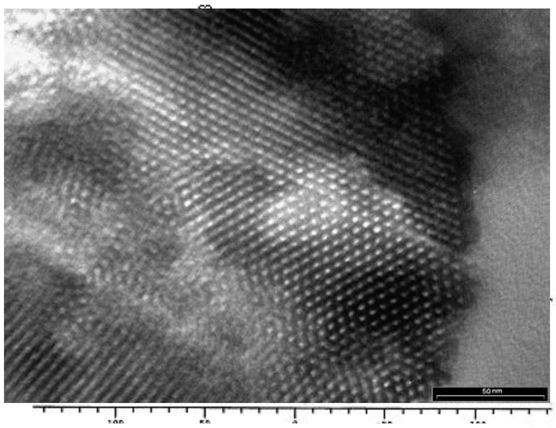


Figure 10. the TEM image of SBA-3

SBA-3 (**Figure 10**) exhibits ordered hexagonal arrays of mesopores with one-dimensional channels and further confirm that the sample has a 2-D hexagonal (*P6mm)* mesostructure.

Second period: May 2007-November 2007

Introduction

Proper utilization of agro-industrial by-products is very important for the national economy. It would not only help in solving the disposal problem, but would also help in reducing the shortages with respect to several materials. A large quantity of rice husk is available as waste from rice- milling industries. Dry husk contains 70–85% organic matter (lignin, cellulose, sugars) and the inorganic remainder consists of silica.

Porous carbons are carbons which generally have a high surface area and complex pore structure resulting from physical or chemical activation processes. The structure of an activated carbon is composed of pores classified into three groups, namely micropores, mesopores and macropores. Conventional porous carbons are tri-disperse, having all three types of pores present within their structure. Adsorbed molecules penetrate through the wider pores and into the micropore structure.

Preliminary studies have shown that rice husk was also suitable for the production of porous carbon. The objective of this work was to prepare porous carbon and nanoporous materials using carbon and silica extracted from the rice husks.

Experimental Section.

Preparation of Nanomaterials

Dry raw RHs were supplied by Vietnam partner, which were sieved to eliminate residual rice and clay particles.

(1) A 10g sample of RHs was taken in a thick walled cylindrical adiabatic container closed with a adiabatic lid. RHs were subjected to pyrolysis at 500°C for 1 h in an inert atmosphere of Nitrogen. Nitrogen flow was maintained at 0.1 litre/min and the heating rate employed was 2^oC/min. After mixed 12g KOH, the solid product was again taken in the cylindrical adiabatic container. Calcination of the product was carried out at 800°C for 2 h in an inert atmosphere of Nitrogen to extract the silicon in RHs. Nitrogen flow was maintained at 0.1 litre/min and the heating rate employed was 2^oC/min. After the final solid product was dipped in water and washed with water, and filtered, the porous carbon was obtained and the solution containing extracted silicon was also obtained.

(2) In a typical synthesis of ZSM-5 zeolite, the aluminosilicate gels were prepared by mixing TPAOH aqueous solution (25%), followed by addition of $Al_2(SO_4)_3 \cdot 18H_2O$ and the solution containing extracted silicon under stirring (Al_2O_3/SiO_2/TPAOH/ H_2O molar ratios of 1.0/30/8/120/1500). After adjusted pH value (pH=14), the mixture was transferred into an autoclave for additional reaction at 140 °C for 5 days. The crystallized product was washed by water, filtered, dried, and ultrasonic redispersion in water. (3) In a typical synthesis mesoporous material MCM-41, CTAB were added into water, followed by addition of the solution containing extracted silicon. After stirring for 8 h, the mixture gel with molar ratio of SiO_2/CTAB/KOH/H_2O at 1/0.35/0.6/50 was aged at room temperature for 24 h. Then, the

gel was transferred to a Teflon-lined stainless-steel autoclave for crystallization at 110 °C for 3 days. After crystallization, the solid product was filtered, washed with water, and dried in air for 12 h. Calcination of the product was carried out at 550 °C for 5 h in flowing oxygen to remove the organic templates such as CTAB.

Characterization

X-ray diffraction patterns (XRD) were obtained with a Panalytical X'Pert diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) experiments were performed on a Philips TECNAI-10 at with an acceleration voltage of 100 kV. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010M system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution for mesopores was calculated using Barrett-Joyner-Halenda (BJH) model. The ratios of Si/Al in solid samples were determined by the results of inductively-coupled plasma analysis (ICP, Perkin-Elmer 3300DV).

Results and discussion

1.6: Chemical or physical extraction of carbon from rice husk.

1.7: Using extracted carbon as starting carbon source to synthesize carbon based nanostructures such as porous carbon materials and carbon nanotubes

1.8: Using directly rice husk as carbon source to synthesize porous carbon materials and carbon nanotubes,

1.11: Characterization of these new nanomaterials synthesized from rice husk**;**

We found that when silica is extracted from rice husks, a very nice nanoporous carbon material can be obtained. We do not need to extract carbon from rice husks and the using this carbon as precursor.

A very efficient protocol was developed to extract silica from rice husks. This protocol can lead directly to the synthesis of nanoporous carbon. There have some successfully primary result, for example, the BET surface areas of the porous carbon prepared from rice husk impregnated with KOH are around 2500 m^2g^{-1}; the pore size of porous carbons can be adjusted and controlled by amount of KOH.

Figure 11 depicts the representative scheme of preparation steps. Using KOH, we can extract all the silica from rice husks, then giving a nanoporous carbon network (**Figure 12**). One step allows the accomplishment of two goals: extraction of silica and preparation of porous carbon materials.

Figure 13 showed the low angle zone of XRD pattern of material obtained with a KOH/Carbon (weight ratio). One broad reflection peak indicated that the material obtained has a homogeneous pore size distribution. N_2 adsorption-desorption isotherms and pore sizes distribution obtained by BJH method are presented in Figure 4. Isotherms are characteristics of Type IV following the classification of IUPAC, indicative of the mesoporous material. The pore size centers at 4 nm. It is clear that by a simple base extraction, we can generate a mesoporous carbon material.

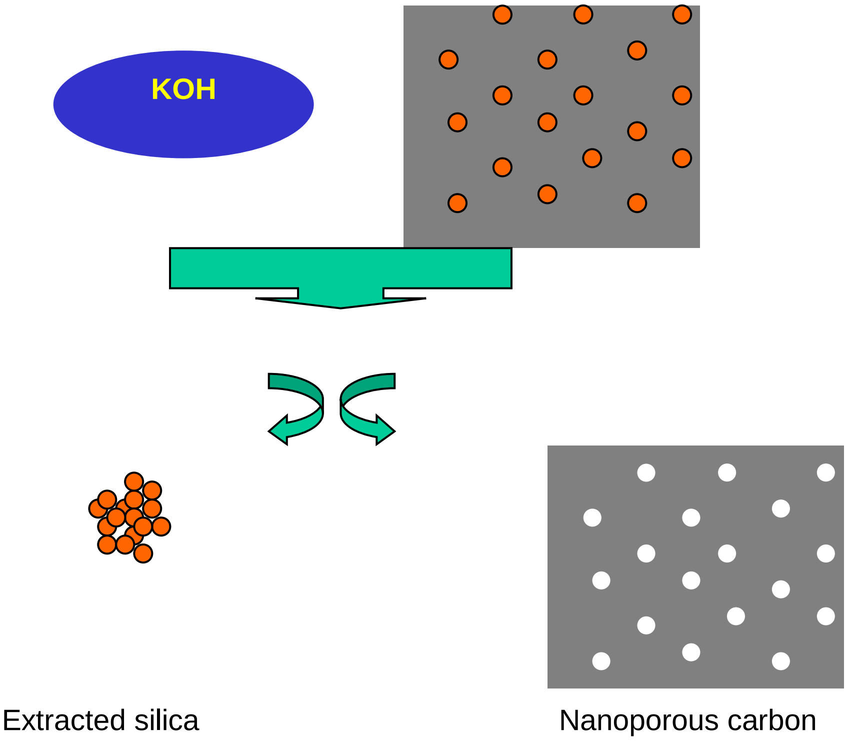


Figure 11, Scheme presenting the extraction protocole of silica from rice huasks

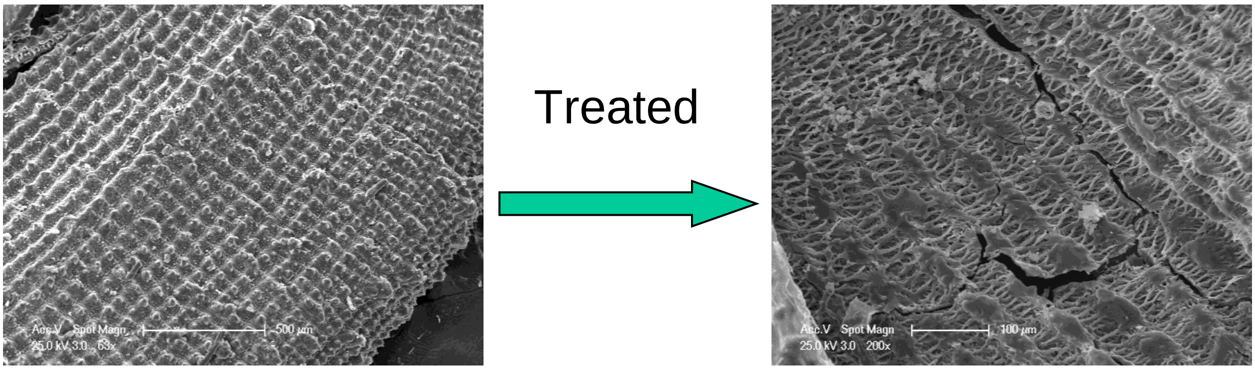


Figure 12, SEM images of nanoporous materials obtained by extraction of silica from rice husks before (left) and after (right) extraction of silica by KOH

Table 2 gives textural properties of samples obtained using different extraction conditions. It is worth noting that higher KOH concentrations give larger pore size, indicating the corrosion effect of higher KOH concentrations is stronger. The highest surface area is obtained with the sample using intermediate KOH concentrations.

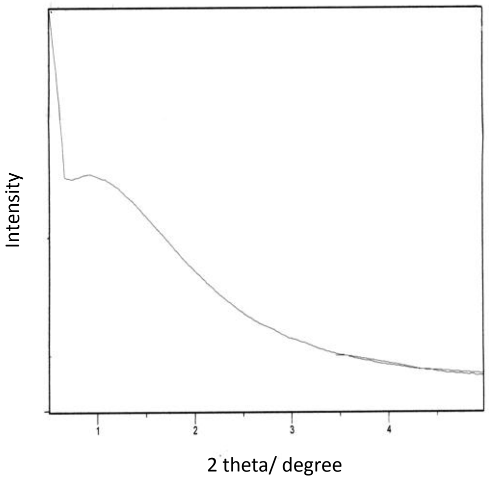


Figure 13. XRD patterns of nanoporous carbon prepared using KOH/Carbon=4 (weight ratio).

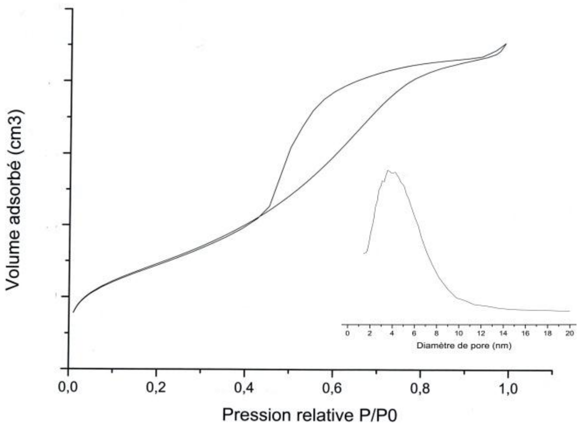


Figure 14. N_2 isotherms and the corresponding pore size distribution (inset) of nanoporous carbon prepared using KOH/Carbon=4 (weight ratio). The corresponding pore size distribution curve (right) is obtained from the adsorption branch of the isotherm using the BJH method.

Table 2. Textural properties prepared using various weight ratio of KOH and Carbon of RHs.

Weight Ratio	**Surface area (m^2/g)**	**Pore size (nm)**
mKOH/mC=2/1	**1980**	**1.8**
mKOH/mC=3/1	**2500**	**2.3**
mKOH/mC=4/1	**2210**	**4.3**

1.9: Using directly rice husk as silica source and other synthetic inorganic source to synthesize silicoaluminate, metallosilicate mesoporous materials

A large series of experiments have been realiszed by using rice husks as silica source, the synthesis was not very successful due to the low amount of silica in rice husks. The best way to use rice husks to synthesize nanomaterials is to extract silica and then to synthesize the materials. However, as **Tasks 1.6, 1.7 and 1.8** indicated, nanoporous carbons can be prepared directly from rice husks by extraction of silica. This method can allow the synthesis of both nanoporous carbon materials and also to get silica source.

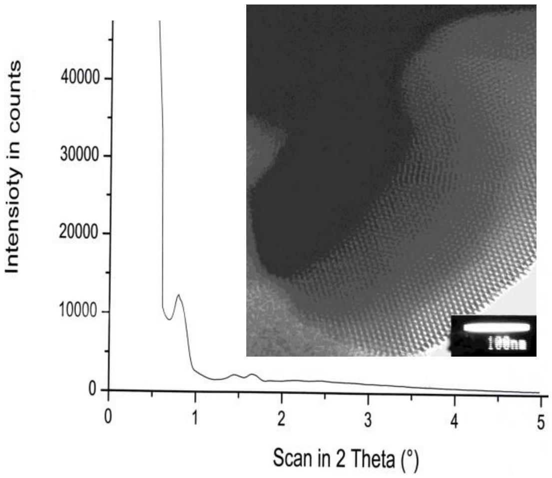


Figure 15, TEM image and low angle zone of XRD pattern of the sample prepared using silica extracted from rice husks

Figure 15 showed the TEM picture and low angle zone of XRD pattern of the sample prepared using silica extracted from rice husks. As reported in the first Semiannual report, using silicas extracted from rice husks and using conventional preparation protocole, we can synthesize highly ordered mesoporous silicas, silicoaluminate and metallosilicate mesoporus materials. Our synthesis method is quite successful.

1.10: Using directly rice husk as silica and carbon source to synthesis Si carbide materials;

This task has been removed from the project due to the fact as described in Report 2.2.1.

1.12: Continuation to Prepare the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners (VP1 and VP2) (See Tasks 2.4, 2.12, 2.13, 2.15, 2.16, 2.18 and 3.5);

1.13: Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (VP1 and VP2) (See Tasks 2.4, 2.5, 2.7, 2.8, 2.10 and 3.9);

For the sake of clarity, we discuss **Tasks 1.11 and 1.12** together. These two taskes are in connection with **Tasks 2.4, 2.5, 2.7, 2.8 and 2.10 of WorkPackage 2.**

We have synthesized a large series of materials such as Nano-mesoporous ZSM-5, Al-MCM-41, Si-SBA-15, HY, HY/MCM-441 and ZSM-5/MCM-41. All these materials have been evaluated.

On the basis of first evaluation, we found that catalysts present multiporosities in one body give better catalytic performances (see **Tasks 2.4, 2.5, 2.7, 2.8, 2.10 of WorkPackage 2**). We decided to modify our synthesis protocol to synthesize ZSM-5 zeolite with a mesoporosity to get microporous-mesoporous ZSM-5 zeolite catalyst.

The first synthesis is quite successful. Here are some first results. Their catalytic performance is quite good (see **Task 2.4 and 2.5**).

Figure 16 shows the XRD patterns of ZSM-5 zeolite (a) and ZSM-5 zeolite with mesoporosity synthesized from rice husks (b). It is evident that our protocole conducts to the synthesis of ZSM-5 structure. It is more interesting that our ZSM-5 zeolite presents a large reflection at very low angle and two other low intensity reflections. These three diffraction lines correspond exactly to a hexagonal arrangement of mesochannels, indicating that our material contains microporosity of zeolite and also highly ordered mesoporosity. The N2 adsorption-desorption isotherms displayed in **Figure 17** indicate that our material is really mesoporous with the presence of even larger porosity (N_2 uptake at high relative pressures). By HK calculation we can see a pore size of around 0.5 nm, corresponding to the pore size of ZSM-5 zeolite and two other pore sizes at 4 and 30 nm, respectively.

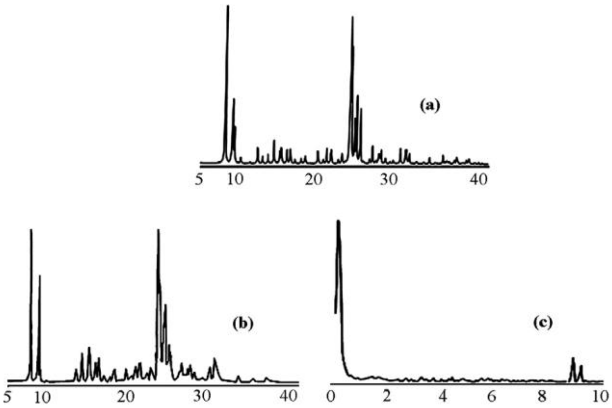


Figure 16, XRD patterns of ZSM-5 standard sample at large angle zone (5–40° 2θ) (a), ZSM-5 with mesoporosity at large angle zone (5–40° 2θ) (b) and at small angle zone (0–10° 2θ) (c).

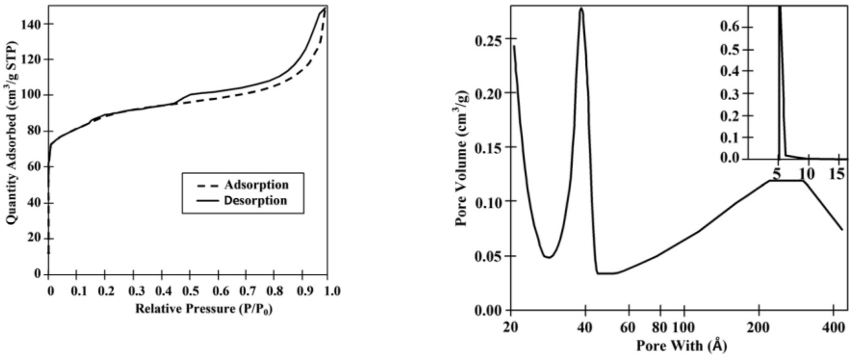


Figure 17, N_2 adsorption-desorption isotherms (left) of ZSM-5 with mesoporosity and pore size distribution (right)

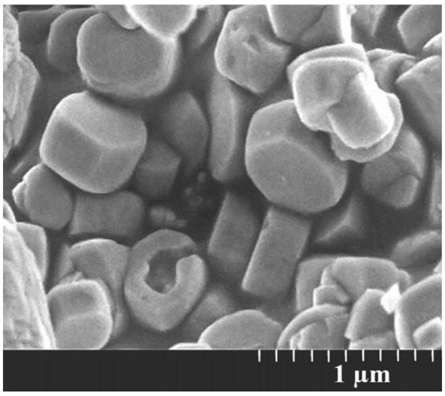


Figure 18, SEM image of ZSM-5 zeolite with mesoporosity

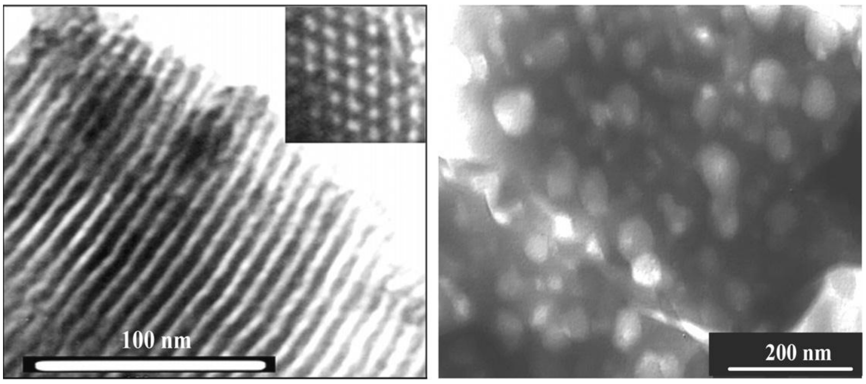


Figure 19, TEM images of ZEM-5 sample with small ordered mesoporosity (left) and large disordered mesoporosty (right)

Figure 19 demonstrated TEM images of our first material, presenting a highly ordered mesoporosity of 4 nm and a larger mesoporosity of 30-40 nm. All these results confirm N_2 adsorption-desorption and XRD observations.

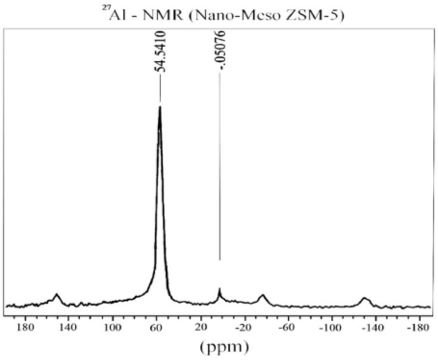


Figure 20, ^{27}Al solid state MASNMR spectrum of ZSM-5 zeolite with mesoporosity

Figure 20 displayed ^{27}Al solid state MASNMR spectrum of ZSM-5 zeolite with mesoporosity synthesized from silica extracted from rice husks. The signal at -54 ppm corresponds to the aluminium atoms located at tetrahedral position of zeolite. Only few octahedral extraframework Al atoms are observed.

<u>Third Period: November 2007-April 2008</u>

1.11 Characterization of these new nanomaterials synthesized from rice husk,
1.12 Preparation of the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners (VP1 and VP2) (See Task 2.4),
1.13 Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (VP1 and VP2) (See Task 2.7),
1.14 Characterization of these modified nanomaterials by a series of physico-chemical techniques,
1.15 Remodification and Functionalization of our as prepared porous materials and our modified porous nanomaterials on the basis of the test results supplied by Vietnamese partners (VP1 and VP2) (See tasks 2.10 and 3.12) and characterization of these re-

modified and functionalized porous nanomaterials by a series of physico-chemical techniques,

Following the information from VP1 after the evaluation of a large series of samples, we at first focused on the synthesis of Zeolite ZSM-5 with different mesoporosities by modification of crystallization time and then we will evaluate these new materials in waste oil sludge cracking. A new synthesis protocol has been established (**Figure 21**). To accelerate the crystallization rate, in the synthesis gel, an amount of ZSM-5 zeolite seeds was added. The detailed synthesis conditions used have been described in **Table 2**. A series of Micro-mesoporous ZSM-5 materials have been synthesized (**Tasks 1.11, 1.12; 1.13 and 1.14**). Information on the catalytic evaluation in the waste oil cracking reaction (**VP1, Tasks 2**.) will allow us to select the best hydrothermal treatment time (**Tasks 1.15,**) and to modify our synthesis protocol to get the best catalysts (**Task 1.15**). All the synthesized materials have been characterized by a series of techniques such as XRD, IR spectroscopy, SEM and TEM (**Tasks 1.11 and 1.14**)

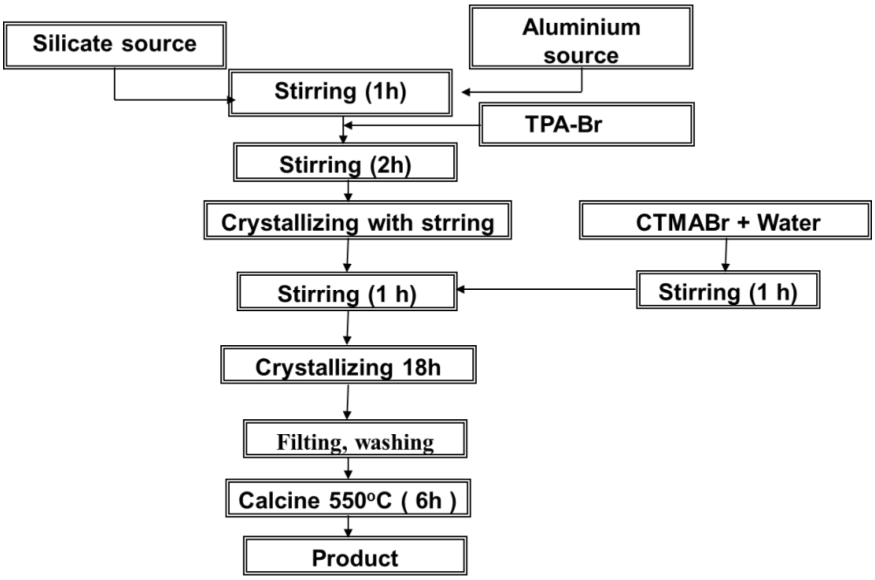
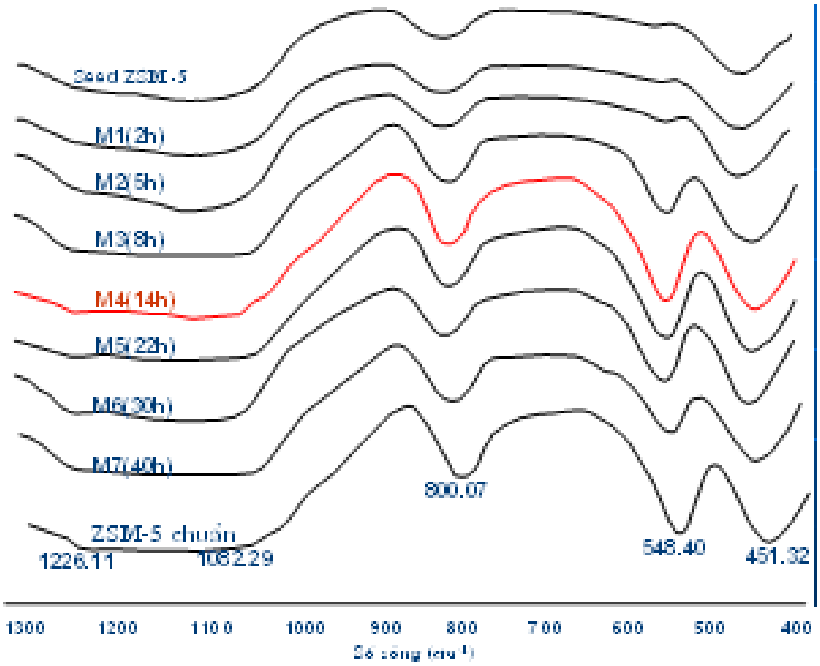


Figure 21, Schematic representation of the synthesis protocol to micro-mesoporous ZSM-5 zeolite using silica extracted from rice husks

Table 2, Synthesis parameters to micro-mesoporous ZSM-5 zeolite catalysts

Sample	Crystalline condition		
	Temperature (^{0}C)	Time (h)	
		Seed	Meso
Seed	135	10	0
M1	135	10	2
M2	135	10	5
M3	135	10	8
M4	135	10	14
M5	135	10	22
M6	135	10	30
M7	135	10	40

Figure 22 depicts IR spectra of materials obtained at different crystallization times. Infra-red spectroscopy is quite suitable for Structural characterization. The peak at 550 cm^{-1} corresponding to the 5 membered-ring of ZSM-5 zeolite increases its intensity with crystallization time, indicating the increased formation of ZSM-5 zeolite phase. The ratio of intensity of two peaks at 550 cm^{-1} and 450 cm^{-1} is usually used to evaluate the crystallinity of zeolite. In a pure ZSM-5 zeolite with 100% crystallinity, the ratio corresponds to 0.8. We found that after 14 hours hydrothermal treatment, this raio reaches 0.8, suggesting that M4 material has a crystallinity around 100%. If the hydrothermal treatment time increased further, this ratio starts to decrease, indicative of the decrease in crystallinity of zeolite formed.



Sample	I_{550}/I_{450}	Crystalline (%)
M1	0.03	3.75
M2	0.07	8.25
M3	0.52	65
M4	0.8	100
M5	0.77	92.5
M6	0.71	88.75
M7	0.54	67.5

Figure 22, IR Spectra of materials obtained at different hydrothermal treatment times.

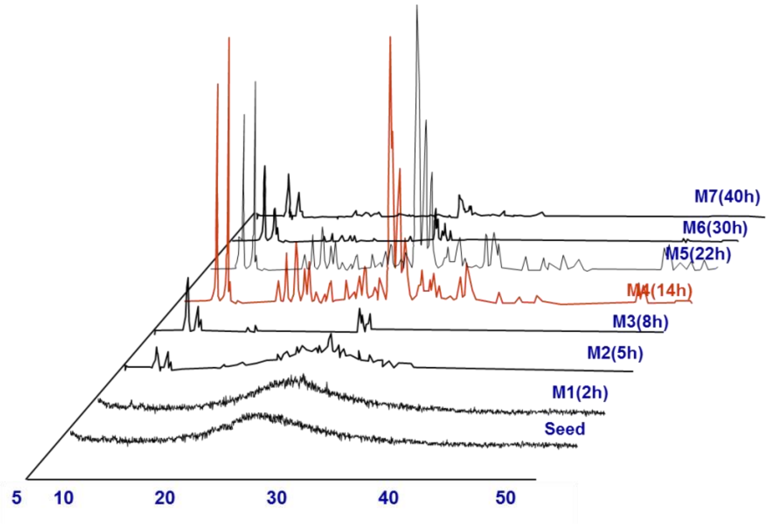


Figure 23, Wide angle range XRD pattern of materials synthesized at different hydrothermal treatment times

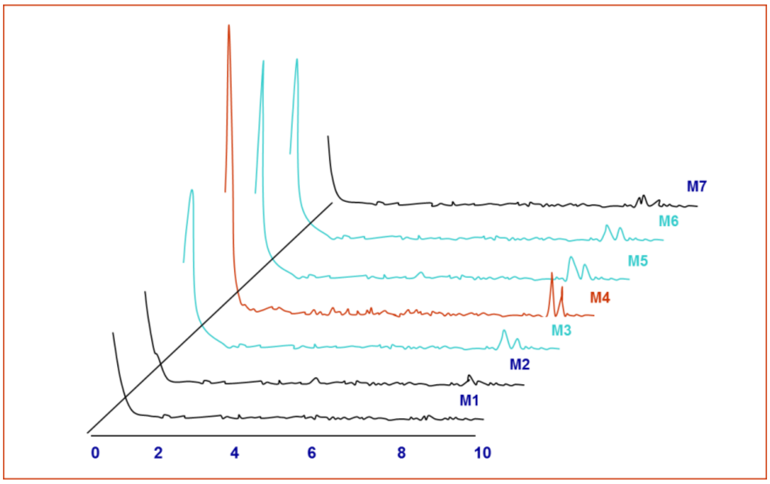


Figure 24, Small angle range XRD pattern of materials synthesized at different hydrothermal treatment times

Wide angle range XRD patterns of materials obtained at different hydrothermal treatment times are given in **Figure 23**. With increasing hydrothermal treatment time, the crystallinity increases at first and then after 15 hours crystallization starts to decrease, in good agreement with IR observation, suggestion that longer crystallization time reduces the crystallinity. This is probably due to the destruction of zeolite struction with longer crystallization time since zeolites are metastable framework. Low angle range XRD showed that after 5 hours crystallization, a sharp peak at very low angle and two low intensity reflections appears at 2° 2θ, significative of a very ordered mesoporous structure with a hexagonal arrangement of mesochannels. The most intense reflection decreases its intensity with hydrothermal treatment times.

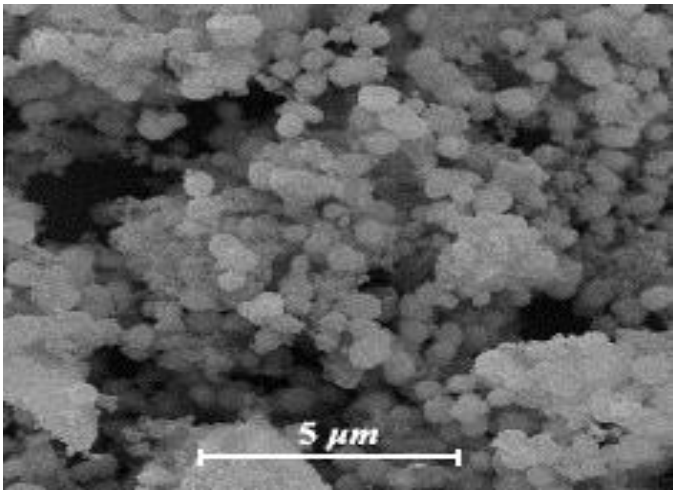


Figure 25, SEM amage of pure ZSM-5 zeolite sample synthesized using silica extracted from rice husks

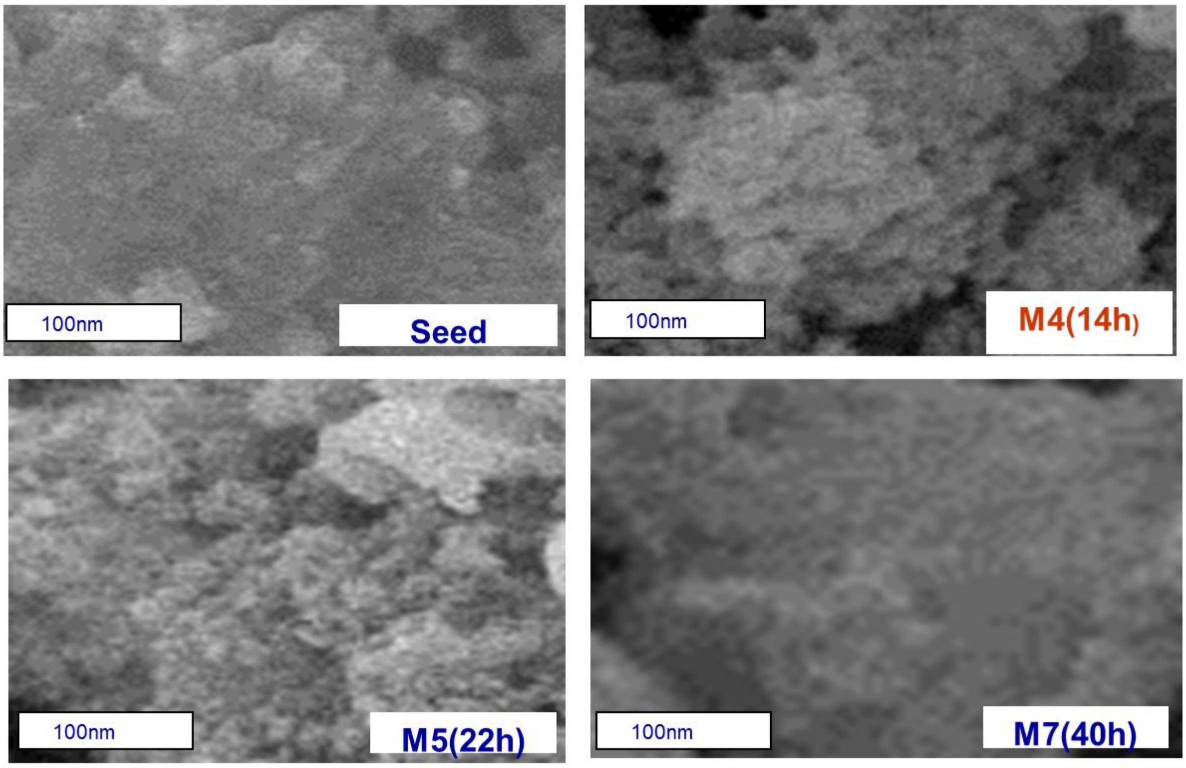


Figure 26, SEM images of materials obtained at different hydrothermal treatment times

SEM images of pure ZSM-5 zeolite (**Figure 25**) and materials synthesized at different hydrothermal treatment times (**Figure 26**) are displayed in **Figures 25 and 26**, respectively. Pure ZSM-5 gives a spherical morphology with a particle size of 0.5-1 μm. This kind of morphology is often observed. The protocol conducting to the synthesis of micro-mesoporous ZSM-5 gives ZSM-5 zeolite particle even much smaller. The particle size remained constant with increasing hydrothermal treatment time. The TEM picture confirmed the presence of mesoporosity.

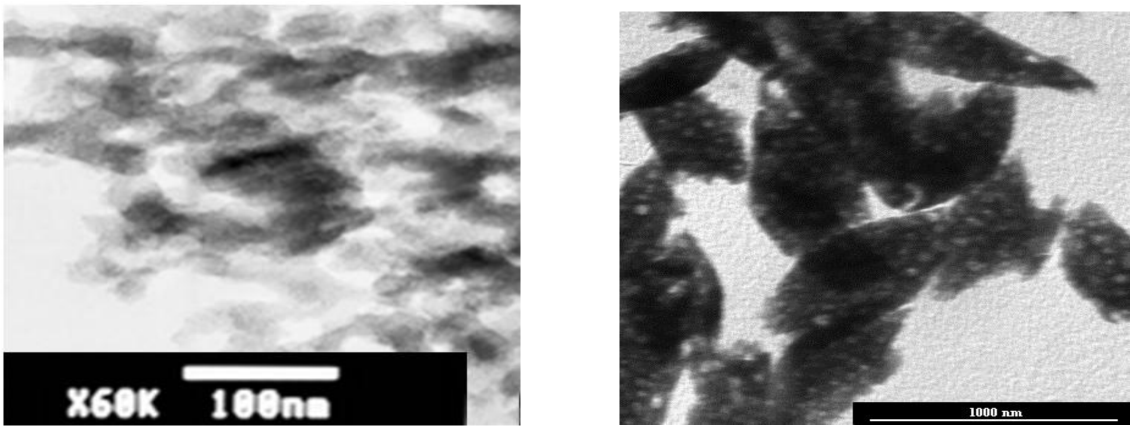


Figure 27, TEM image of micro-mesoporous ZSM-5 zeolite material

Following information supplied by VP1 (See **Semiannual Report** of second period) after catalytic evaluation of a large series of catalysts synthesized in the second period, here we concentrated on the synthesis of a series of micro-mesoporous ZSM-5 zeolite materials since the cracking conversion showed that the catalyst ZSM-5 with the presence of a mesoporosity gives the best catalytic performances. All these catalysts have been characterized and will be tested by VP1.

Fourth period: May 2008-October 2008

On the basis of the results obtained during second and third period (Workpackages 1 and 2), we decided to concentrate on the synthesis, characterization and evaluation of catalytic behavior of Faujasite Y type zeolite with a mesoporosity. In fact Faujasite Y zeolite is very well known acid catalyst and largely used in Fluidizing Catalytic Cracking (FCC) process of petroleum. The FCC catalyst is composed of dealuminated Faujasite Y zeolite with a mesoporosity and a silicoaluminate amorphous binder with a macroprosity. However, our first evaluation on their n-hexane, TIPB and waste oil sludge catalytic cracking behavior was not very conclusive. That is why it is necessary to evaluate in a detail their behavior and then to decide to select the best catalyst for waste oil sludge cracking.

The results obtained during the third and forth periods have been presented jointly by BP, VP1 and VP2 in 6th International Mesostructured Materials Symposium which has been held in Namur from 8th to 12th September organized by BP.

By the way, the Task 1.16 is removed and modified. To offer a best catalytic activity, BP synthesized a new type of material with a core/shell structure with the presence of a highly ordered mesoporous shell and a meso-macroprous core. This kind of structure is quite interesting for large molecules treatment. After introduction of metal oxide active components, the catalyst showd its high catalytic activity and high stability in oxidation of aromatics to give products with highly added value. This work is quite successful since the obtained results have been published in highly impact journal “***Advanced Materials***”.

2.3.1.a Synthesis and characterization of Faujasite Y zeolite with a mesoporosity

1.11 Characterization of these new nanomaterials synthesized from rice husk: **Completed**.

1.13 Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.7 and 3.9**); **Completed**.

1.14 Characterization of these modified nanomaterials by a series of physico-chemical techniques: **Completed.**

1.15 Remodification and Functionalization of our as prepared porous materials and our modified porous nanomaterials on the basis of the test results supplied by Vietnamese partners (**VP1** and **VP2**) (**See tasks 2.10 and 3.12**) and characterization of these re-modified and functionalized porous nanomaterials by a series of physico-chemical techniques: **Completed.**

1.16: After testing by **VP1** and **VP2** (**See Tasks 2.13 and 3.15**), production in large quantity of the best catalyst and adsorbent by **BP** and use of these materials by **VP1** and **VP2** for testing long period in Viet Nam. The characterization of these porous nanomaterials produced in large quantity by a series of physico-chemical techniques: **Modified and completed.**

In the **First Semiannual Report**, we reported the catalytic activity evaluation results of a series of zeolite catalysts obtained by using silica extracted from rice husks. It was shown that ZSM-5 zeolite catalyst with a mesoporosity demonstrated the best activity while both Faujasite Y zeolite with a mesoporosity and Faujasite Y zeolite catalyst displayed a lower cracking activity of waste oil sludge. However, Faujasite Y zeolite catalyst is the most famous catalyst for catalytic cracking of petroleum. A series of Faujasite Y zeolite catalysts have been synthesized and characterized (**Tasks 1.11 and 1.14**) to check its catalytic activity in waste oil sludge cracking (**Tasks 1.12, 1.13 and 1.15**).

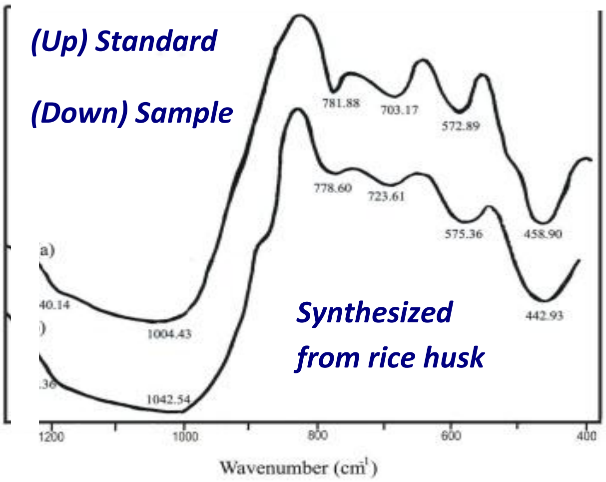


Figure 28. Infra-Red spectroscopy of a standard Faujasite Y zeolite sample (up) and Faujasite Y zeolite with a mesoporosity synthesized using silica extracted from rice husks (down)

From **Figure 28**, it can be seen that the Faujasite Y zeolite with a mesoporosity synthesized using silica precursor extracted from rice husks has a very similar Infra-Red spectrum to that of standard Faujasite Y zeolite in the zone of 400-1200 cm^{-1}, framework vibration range. SEM image in **Figure 29** shows the typical morphology of Faujasite Y zeolite.

The ^{27}Al MAS NMR spectrum of Faujasite Y zeolite and that of ZSM-5 zeolite are assembled in **Figure 30**. Practically all the Al atoms both in Y and ZSM-5 zeolites are located at the tetrahedral sites of zeolite framework. TEM photograph of Faujasite Y zeolite with a mesoporosity confirms very clearly the presence of mesoporosity with variable pore sizes.

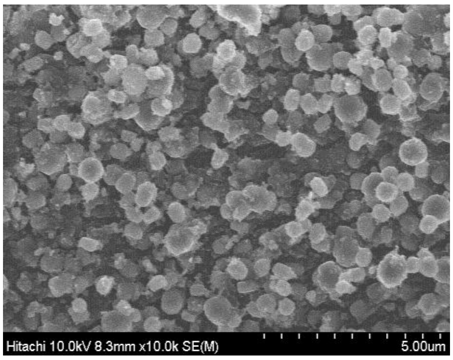


Figure 29, SEM image of Faujasite Y zeolite with a mesoporosity synthesized using silica extracted from rice husks

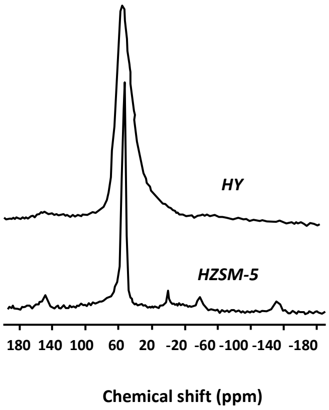


Figure 30, ^{27}MAS NMR spectra of Y and ZSM-5 zeolites synthesized using silica extracted from rice husks

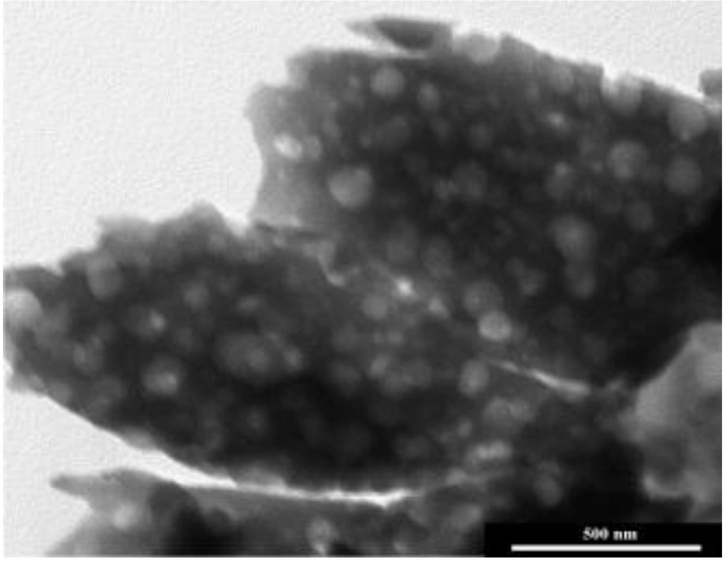


Figure 31, TEM image of Faujasite Y zeolite with a mesoporosity synthesized from silica extracted from rice husks

The presence of mesoporosity in addition to microporosity will certainly enhance the mass transport of reagents, in particular in waste oil sludge cracking reaction. The evalauation of catalytic properties of tehse materials will be made in Workpackage 2.

2.3.1.b One-Pot Synthesis of Catalytically Stable and Active Nanoreactors: Encapsulation of Size-Controlled Nanoparticles within a Hierarchically Macroporous Core@Ordered Mesoporous Shell System (Task 1.16)

It is observed on the basis of above work that zeolite catalysts with a hierarchical porosity present a better activity in the catalytic cracking of waste oil sludge. Due to the large molecular size of waste oil sludge, the large pore size in catalyst is necessary to allow a better diffusion of molecules inside of materials. BP continues their work in the synthesis of novel catalytic materials possible useful for specific catalytic reactions.

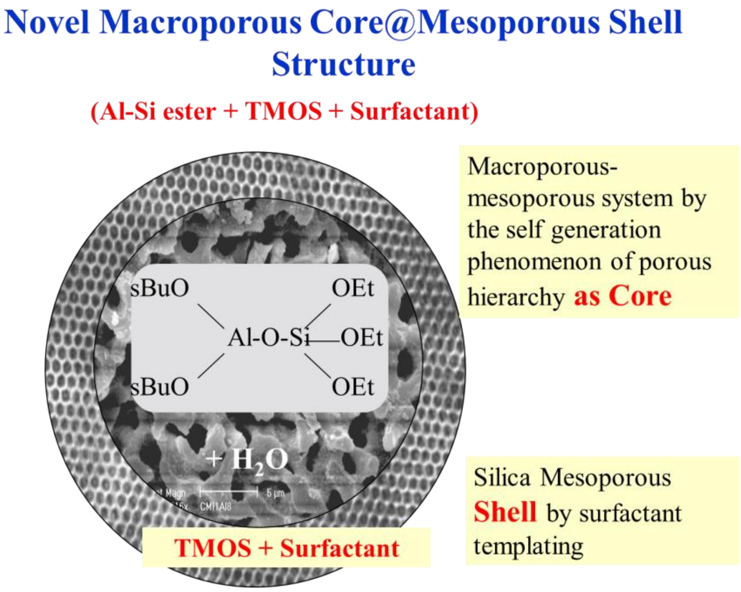


Figure 32, Synthesis strategy used for the fabrication of meso-macroporous core/highly ordered mesoporous shell structure

The synthesis expertise in the field of mesoporous materials obtained from this project has been used here. To create a hierarchical porosity, our idea is to generate a meso-macroporous core using the high hydrolysis and condensation rate of Si-Al ester and a highly ordered mesoporous shell using surfactant templating strategy (**Figure 32**).

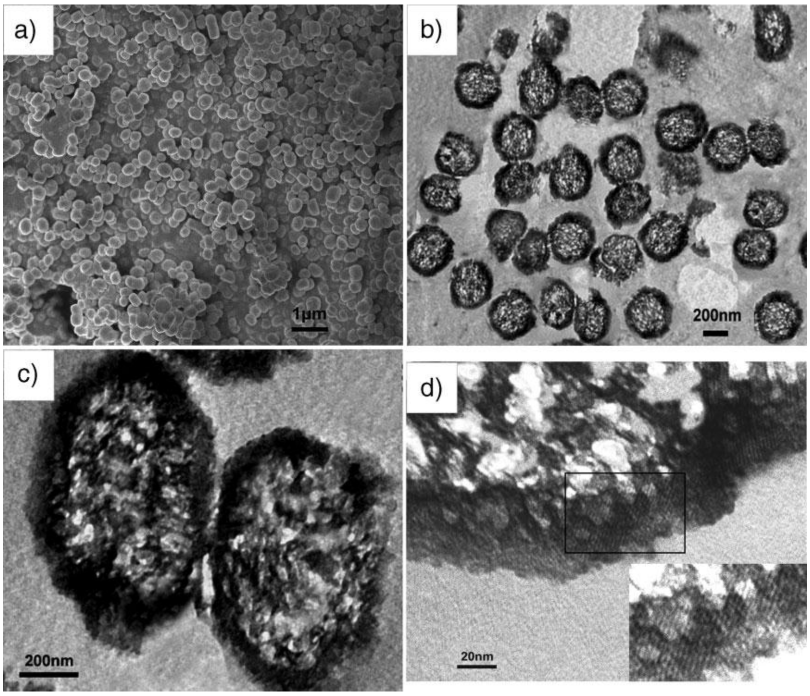


Figure 33, a) SEM image of as-synthesized and b–d) TEM images of calcined sample

Scanning electron microscopy (SEM) images of the as-synthesized sample show that the spheres are homogeneously sized, with a diameter of around 500nm (**Fig. 33a**). Transmission electron microscopy (TEM) studies confirm the uniform sizes of these sub-micrometer spheres (**Fig.33b**). Interestingly, foamlike hierarchically macroporous cages of sizes 50–80nm are observed inside these spheres (**Fig. 33b–d**). A higher-magnification image (**Fig. 33d and inset**) shows very good regularity in the denser shells of the spheres, which were formed by the ordered 2D hexagonal (P6mm) mesostructure covering the foamlike macroporous cores. The thickness of the shells is around 80 nm. More importantly, the TEM image shows that the macroporous cages are interconnected with uniformly ordered mesopores, which would be valuable for the fast diffusion of reactants and products in catalysis.

X-ray diffraction (XRD) pattern of the as-synthesized sample (**Fig. 34a**) exhibits clearly well-resolved peaks that can be indexed as the (100), (110), and (200) diffractions associated with the p6mm hexagonal symmetry with a lattice constant $a_0 = 4.32$ nm. After calcination in air at 500 ºC for 4 h, the three diffraction peaks of the sample become sharper due to the removal of surfactant molecules (**Fig. 34b**), showing highly thermal stability of the ordered hexagonal mesostructure in the shell.

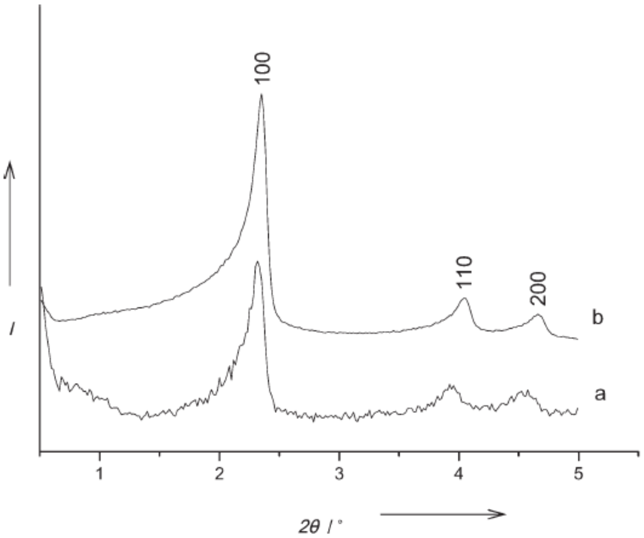


Figure 34, XRD patterns of a) as-synthesized and b) calcined sample

Figure 35 shows N_2 isotherms of calcined sample, and its pore size distribution. Notably, the sample calcined at 500°C for 4 h exhibits typical IV-type isotherm assigned to a 2-D hexagonal (*P6mm)* mesostructure. The N_2 adsorption isotherm gives a BET surface area of 892 m^2g^{-1} and pore volume of 0.68 cm^3g^{-1}. Interestingly, the sample isotherm exhibits two inflections (**Fig. 35**). The first one (a type H1 hysteresis loop at $0.30 < p/p_o < 0.70$) gives a pore size distribution in the range of 1-10 nm with one sharp maximum centered at around 2.4 nm and another less visible maximum at 5.7nm. These result from CTMAB-templated mesoporous shell with mesoporous size of 2.4 nm and worm-like mesopores in macroprous cores with a pore size of around 5.7 nm respectively. The second inflection (a hysteresis loop at $0.70 < p/p_o < 0.98$) indicates the presence of a significant amount of large pores, with a relatively large pore size distribution in the range of 40-100 nm (**Inset of Fig. 35**). These results further show the material presents both mesoporous and macroporous pore size distribution, which is in good agreement with TEM data. The existence of the mesopore of 2.4 nm is also in good agreement with XRD results.

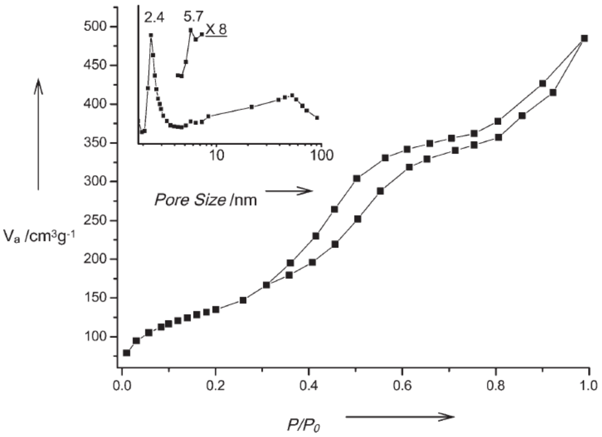


Figure 35, N_2 isotherm and the corresponding pore-size distribution (inset) of calcined sample.

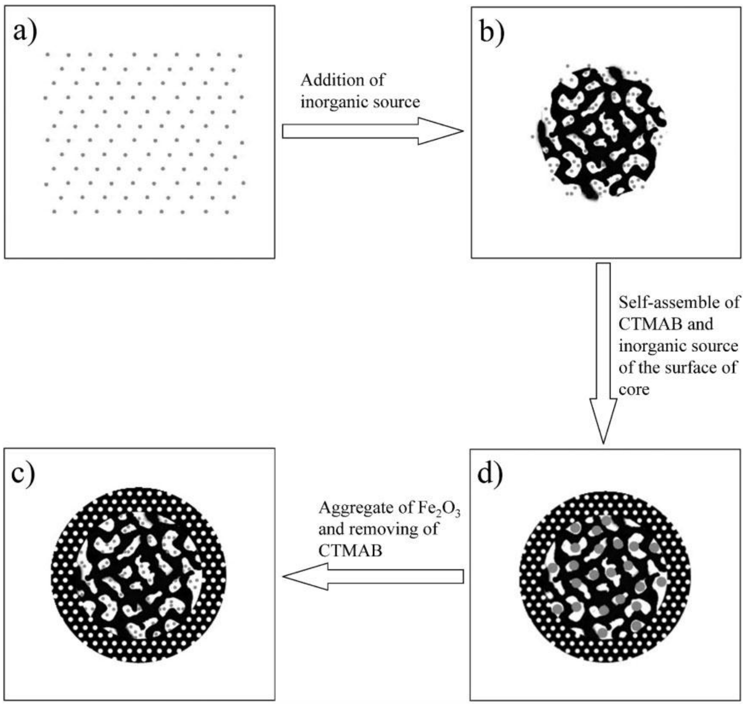


Figure 36, Proposed structure for the formation of macroporous core@mesoporous shell sample. a) The aqueous solution containing iron species, b) formation of foamlike macroporous core containing iron, c) formation of mesoporous shell in surface of macroporous core, and d) nanoreactor with Fe_2O_3 nanoparticles.

As an example of the introduction of the catalytically active sites into internal macroporous cores, the above synthesis strategy has been employed in the presence of an iron ions complex solution (**Fig. 36**). An aluminosilicate ester and TMOS, with a defined ratio, were added to an aqueous solution of $(NH_4)_3[Fe(CN)_6]$ (pH=11). The almuminosilicate ester and TMOS in the presence of CTMAB in the solution instantaneously created a foam-like macroporous core containing iron species and a denser, ordered mesoporous shell as discussed above.

The successful entrapment of Fe_2O_3 nanoparticles into the macroporous core was confirmed by TEM, XRD and HRTEM studies. As shown in **Figure 36**, the Fe_2O_3 nanoparticles exhibited a uniform size of 12 nm (**Fig. 36a**). Being larger than the entrance of mesoporous channels indicates that the nanoreactors can effectively prevent leaching of the active sites. The size of Fe_2O_3 nanoparticles of two samples synthesized with various concentrations of iron species was further determined by TEM images (**Fig. 36**). Interestingly, the particle size was tailored from 12 to 8 nm by varying the Fe/CTMAB molar ratio. More importantly, the ratio of size between two samples was in good agreement with the concentration of iron species. This indicates that the size of Fe_2O_3 nanoparticles could be efficiently tailored by controlling the concentration of iron species in the initial mixture of reactants. Meanwhile, the XRD peaks are characteristic of Fe_2O_3 crystals with high crystalline degree, which were mainly located in the center of the macroporous cages. High resolution observations of the Fe_2O_3 nanoparticles further display direct evidence of crystalline degree and sizes of the encapsulated Fe_2O_3 nanoparticles synthesized with various concentrations of iron species (**Fig. 36c and 36d**). The Fe_2O_3 nanoparticles synthesized with various concentrations of iron species show high crystalline degree, and the lattice fringes of 0.185 nm and 0.250 nm correspond to the (024) and (110) crystal plans of hematite structure of Fe_2O_3, respectively. Furthermore, these HRTEM images clearly exhibit that the sizes of Fe_2O_3 nanoparticles are gradually reduced with decreasing the concentration of iron species in the initial mixture of reactants. It is clear that main Fe_2O_3 particles are located in the cores. Fe_2O_3 particles in the mesochannels should be very small in size and relatively low in amount since our HRTEM did not clearly show the presence of Fe_2O_3 particles in mesochannels of the shell. The possible reason is its low quantity.

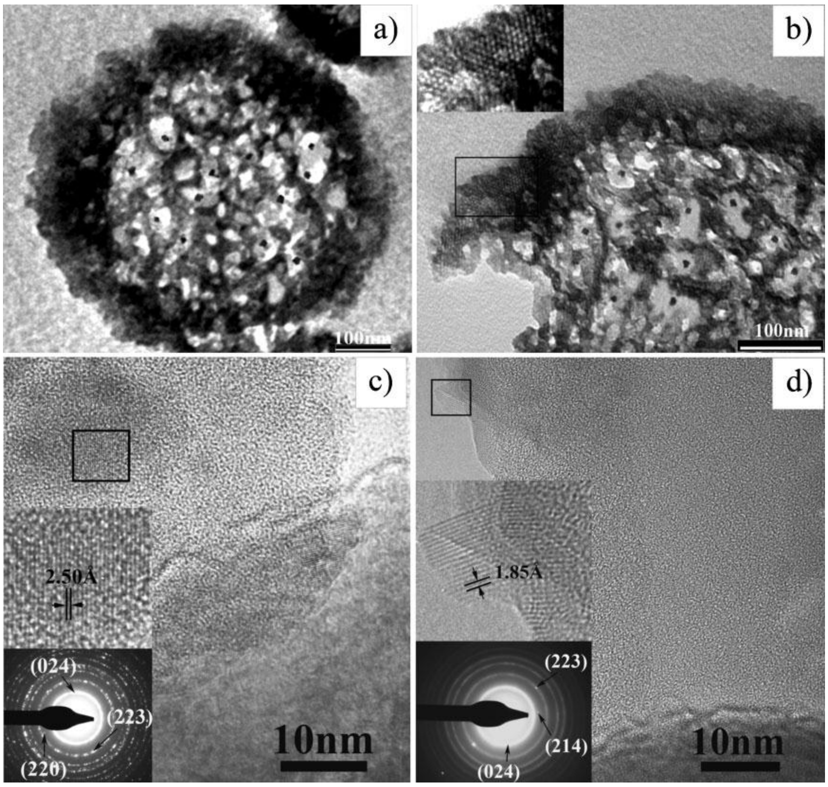
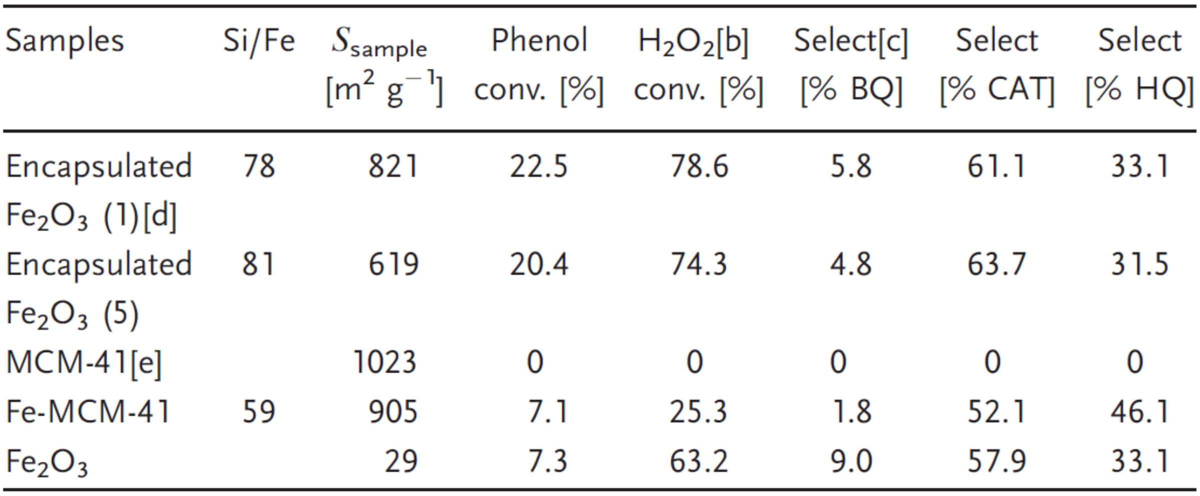


Figure 36, TEM and HRTEM images of calcined encapsulated Fe_2O_3 particles synthesized using various iron concentrations (a and c, Fe/CTAB = 10; b and d, Fe/CTAB = 5, molar ratio). The insets in the HRTEM images are the corresponding selected-area electron diffraction (SAED) patterns taken from many particles

Table 3, Chemical composition, surface area, and catalytic activity of meso-macroporous core and highly ordered mesoporous shell structure with encapsulated Fe_2O_3 nanoparticles in the core



Samples	Si/Fe	S_{sample} [m^2 g^{-1}]	Phenol conv. [%]	H_2O_2[b] conv. [%]	Select[c] [% BQ]	Select [% CAT]	Select [% HQ]
Encapsulated Fe_2O_3 (1)[d]	78	821	22.5	78.6	5.8	61.1	33.1
Encapsulated Fe_2O_3 (5)	81	619	20.4	74.3	4.8	63.7	31.5
MCM-41[e]		1023	0	0	0	0	0
Fe-MCM-41	59	905	7.1	25.3	1.8	52.1	46.1
Fe_2O_3		29	7.3	63.2	9.0	57.9	33.1

Catalytic activities for hydroxylation of phenol with H_2O_2 over the encapsulated Fe_2O_3 nanoparticles (12 nm) are presented in **Table 3**. For the comparison of catalytic activity, reference catalysts, MCM-41, Fe-MCM-41 and α-Fe_2O_3 were synthesized according to the published literature. Obviously, encapsulated Fe_2O_3 nanoparticles are very active for the catalytic conversion of phenol. It is also noteworthy that recycled, encapsulated Fe_2O_3 nanoparticles still show comparable activities to that of the initial encapsulated Fe_2O_3 nanoparticles. For example, after 5 cycles, the encapsulated Fe_2O_3 still exhibits 90% of the initial activity (**Table 3**). In contrast, Fe-MCM-41 and free Fe_2O_3 nanoparticles, used often as reference catalysts for similar reactions, show relatively low activity. The encapsulated Fe_2O_3 nanoparticles are stable, reusable, and active. The great efficiency of the encapsulated Fe_2O_3 nanoparticles can be attributed to this unique core-shell nanoreactor design. The nanosized particles were high dispersed and the macroporous structure of the core can minimize the aggregation of Fe_2O_3 nanoparticles whilst the mesoporous shell can prevent the active sites leaching and favor the diffusion of the reagents and products.

The high activity and stability and excellent recycling behavior of the encapsulated nanoparticles in the samples should directly be attributed to the unique core-shell synthesis of nanoporous materials with integral macro and mesoporosity. We believe that this method may open an exciting avenue for the preparation of hierarchically bimodal nanoporous materials with core-shell structures and for the design of nanoreactors with combined functionalities in the cores and the shells.

All the above results have been published in a top journal:"***Adv. Mater***." in 2009, showing the importance of these innovative results (**see Annexe-3**)

2.3.2. Work Package 2,

First period: November 2006-April 2007

(Tasks 3.1, 3.2, 3.4 and 33.5): Construction and evaluation of the catalytic testing system (Microreactor), First analysis with BP for the selection of the first series of catalysts (See Task 1.12) and Production of biodiesel by pyrolysis and catalytic cracking, using catalysts from Belgium partner

The main characteristics of vegetable oil sludge as melting point, heavy metal contents, iodine index …etc, have been determined. These informations are essential to determine the cracking reaction conditions.

- Acidic number: 76,27 mgKOH/g sample;
- Base number: 204,74 mgKOH/g sample;
- Iodium number: 39,76 gI_2/100g sample;
- Ester number: 128,47 mgKOH/g sample;
- Melting point: 40 °C;
- The content of free fatty acid 37%;
- The content of triglyxerit 61%;
- Small amount of contaminant.

Figure 37, Vegetable oil sludge at room temperature (Left) and at 40 °C (right)

A series of nanoporous zeolites and Al-MCM-41 synthesized and described in WP1 have been tested using constructed microreactors.

Due to the fact that microreactors for vegetable oil sludge cracking is still under construction. The tests have been realized using n-Hexane (**Figure 38** (left)) and TIPB (Tri-isopropylbenzene) (**Figure 38** (right)) as reaction probes. Compared to commercial zeolitic catalyst, our catalysts are more active in n-hexane and TIPB cracking reactions.

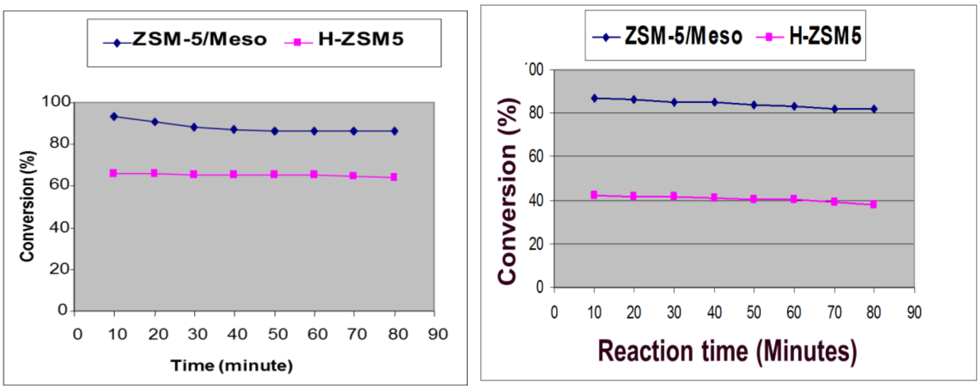


Figure 38, Cracking of n-Hexane (Left) and TIPB (Right) on home-made catalystZSM-5/Meso using rice husks as precursors and commercial H-ZSM-5 catalyst

Second period: May 2007-October 2007

2.3. Construction and evaluation of the catalytic testing system (Microreactor),

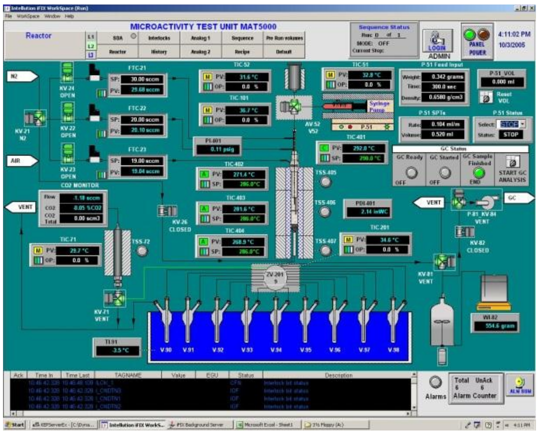


Figure 39, Scheme of Microreactor for Catalytic testing

Figure 39 demonstres the schematic representation of microreactor constructed by VP1 for the evaluation of catalysts prepared using rice husks.

2.4. First analysis with **BP** for the selection of the first series of catalysts (**See Task 1.12**),
2.5 Production of biodiesel by pyrolysis and catalytic cracking, using catalysts from Belgium partner (**BP**-CMI laboratory) as well as zeolites catalysts from Vietnamese partners. First screening of the catalysts in microreactor and the characterization of used catalysts by a series of physico-chemical techniques by **BP**,
2.7 Establishment of the criteria for the selection of the best catalysts with the participation of **BP** (**See Task 1.13**),
2.8 Catalytic Testing of the modified porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.13**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**,

2.10 Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour withy the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**),

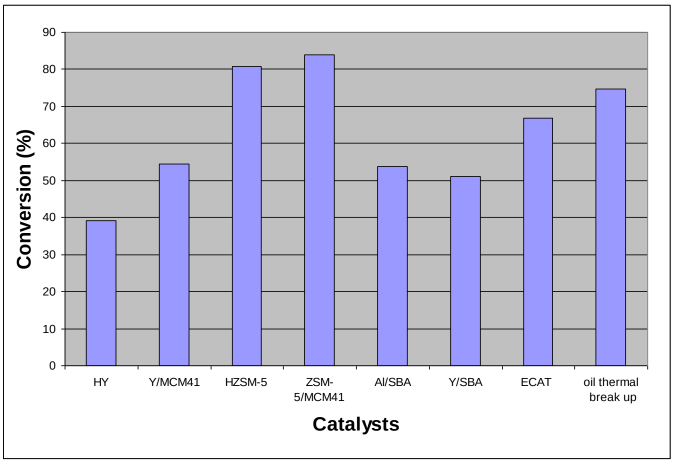


Figure 40, Conversion as a function of different catalysts prepared using rice husks

Figure 40 depicts the cracking conversion of waste oil sludge realized over a series of catalysts prepared using rice husks (**Tasks 2.4 and 2.5**). It is clear that over ZSM-5 zeolite catalyst and ZSM-5 with mesoporosity (ZSM-5/MCM-41) the cracking conversion is higher than that over ECAT, a standard cracking catalyst and also higher than that of thermal cracking. Howver the conversion obtained over HY zeolite catalyst, Faujasite Y zeolite catalyst with mesoporosity, mesoporous aluminosilicate (AlSBA) catalyst and Y zeolite catalyst with mesoporosity (Y/SBA) catalysts is lower than that over ECAT and also lower than that of thermal cracking. This part of work allows the establishment of criteria dor the selection of best catalysts for waste oil sludge cracking. It is clear that higher acidity and catalysts with micro and mesoporosity will be the best catalysts (**Task 2.7**).

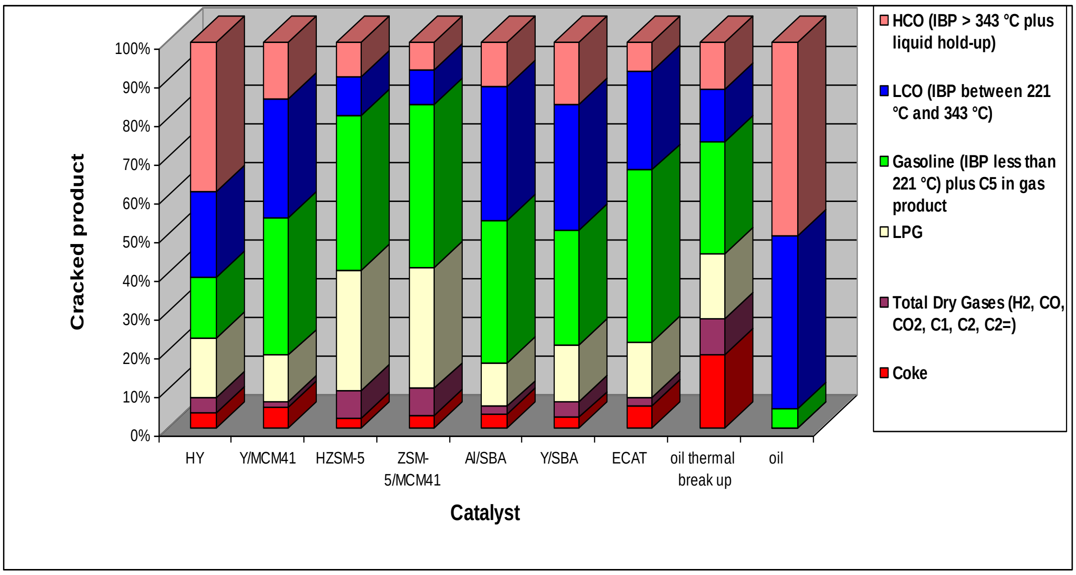


Figure 41, Products distribution of catalytic cracking of waste oil sludge over a series of catalysts prepared from rice husks and thermal cracking and a normal oil

It is evident that materials containing mesoporosity give more gasoline and LPG. In the case of AlSBA and Y/SBA a significant percentage of LCO is observed. Less coke is observed for catalytic cracking reaction over all the catalysts. More coke is formed from thermal cracking.

2.6 Evaluation of the quality of biodiesel products by using different techniques : Cetane number, viscocity index, Acid number.. etc

2.9 Evaluation of the quality of biodiesel products by using different techniques : Cetane number, viscocity index, Acid number.. etc

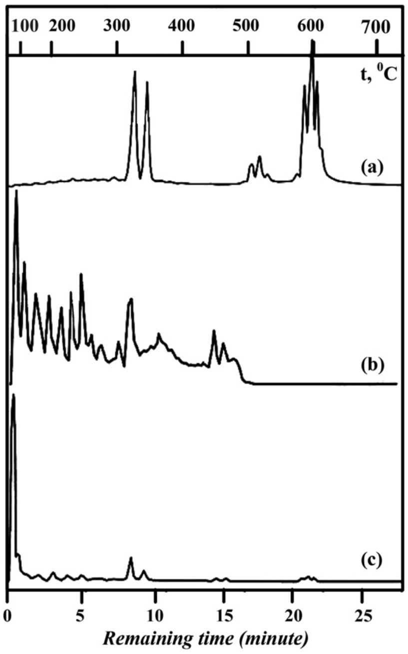


Figure 42. The distribution of liquid product with respect to the boiling point. Vegatable oil sludge (a), thermal cracking (b) and catalytic cracking using MCZSM- 5/MCM-41 (c).

The liquid product of the cracking reaction was analyzed by using SIMDIST GC Thermo Electro system. The composition of liquid fraction is measured via the distribution of boiling point (**Fig. 42**). The chromatogram of vegetable oil sludge shows that it has three areas of boiling point. All the boiling points that are above 343 _C correspond to the segments of HCO. After the catalytic cracking reaction and pyrolysis, the components are cracked chromatogram of the catalytic cracking reaction over MC-ZSM-5/MCM-41 shows the peaks near 75 °C and 343 °C; the intensity of peaks near 75 °C are higher than that of the peaks near 343 °C. This shows that the total yield of LPG and gasoline was higher than that of the total yield of HCO and LCO after the cracking reaction over this catalyst. This result is not clearly shown in the spectrum of thermal cracking (pyrolysis process). There are many peaks in range of 75–343 °C. This proves that the product selectivity of catalytic cracking reaction over MC-ZSM-5/MCM-41 is much better than that of the pyrolysis process.

Third period: November 2007-April 2008

2.7 Establishment of the criteria for the selection of the best catalysts with the participation of **BP** (**See Task 1.13**),

2.8 Catalytic Testing of the modified porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.13**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**, 2.9 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc

2.10 Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour withy the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**),

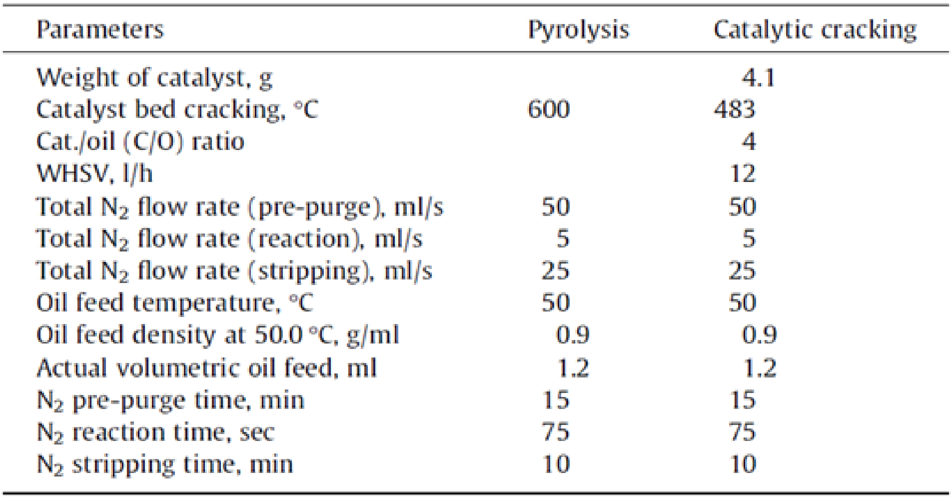
2.11 Catalytic Testing of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**Task 1.15**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**,

2.12 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc,

VP1 evaluated a series of catalysts synthesized by variation of hydrothermal treatment times presented in **2.3.1. WorkPackage 1** (**Task 2.8**). The main reaction parameters used for the waste oil sludge cracking using microreactor constructed in first period of project are described in **Table 4**. In **Table 4**, the condition for thermal cracking of waste oil sludge is also given for comparison.

Figure 43 depicts the conversion (%) of waste oil sludge over a series of micro-mesoporous ZSM-5 catalyst synthesized at different hydrothermal treatment times. It is clear that the most active catalyst is the sample synthesized at a hydrothermal treatment of 14 hours. As indicated above (**2.3.1. Workpackage 1**), the hydrothermal treatment of 14 hours gives a sample with the highest crystallinity and presents a highly ordered mesoporous structure. The conversion can ranks in the following order: M4 (14h) > M5 (22h) > M6 (30h) > M7 (40h) > M3 (8h) > M2 (5h) > M1 (2h). For the samples synthesized with a hydrothermal treatment of 5 and 2 hours, the crystallization time is too short to have a good crystallinity. Only after 8 h crystalization a relatively good crystallinity can be obtained. However, too long crystallization destroys the zeolite structure. The conversion of M4 (14h) sample is also much higher than that of pure ZSM-5 zeolite catalyst, showing again the benefit of the presence of mesoporosity. The criteria for the selection of the best catalysts could be the high crystallinity and high and well ordered mesoporosity (**Task 2.7**).

Table 4. Main reaction parameters used for the waste oil sludge cracking using microreactor



Parameters	Pyrolysis	Catalytic cracking
Weight of catalyst, g		4.1
Catalyst bed cracking, °C	600	483
Cat./oil (C/O) ratio		4
WHSV, l/h		12
Total N_2 flow rate (pre-purge), ml/s	50	50
Total N_2 flow rate (reaction), ml/s	5	5
Total N_2 flow rate (stripping), ml/s	25	25
Oil feed temperature, °C	50	50
Oil feed density at 50.0 °C, g/ml	0.9	0.9
Actual volumetric oil feed, ml	1.2	1.2
N_2 pre-purge time, min	15	15
N_2 reaction time, sec	75	75
N_2 stripping time, min	10	10

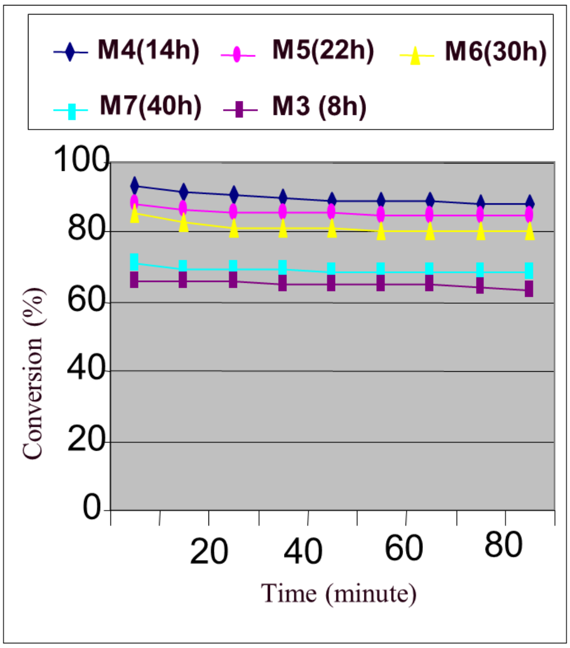


Figure 43, Conversion (%) of a series of micro-mesoporous ZSM-5 catalyst materials synthesized at different hydrothermal treatment times

Table 5, Correlation between crystallinity and conversion and products distribution

Samples	ZSM-5/MESO					H-ZSM-5
	M3(8h)	**M4(14h)**	**M5(22h)**	**M6(30h)**	**M7(40h)**	
Conversion (%)	**65.9**	**93.2**	**87.9**	**85.8**	**70.6**	**69.0**
Crystalline	**65**	**100**	**92.5**	**88.75**	**67.5**	**100**
Products						
CH_4 và C_2H_6	3.06	4.37	4.92	4.17	3.67	17.55
C_2H_4	9.90	12.33	13.45	11.82	12.24	17.35
C_3H_8	23.30	25.02	24.34	22.39	22.46	29.18
C_4H_{10}	18.56	12.30	13.34	15.92	17.08	7.33
C_3H_6	33.94	35.43	33.94	33.58	33.56	22.89
C_5H_{12}	2.56	1.77	1.33	1.86	1.95	0.54
C_4H_8	8.67	9.73	8.14	10.25	9.03	4.76
O/P	**1.11**	**1.36**	**1.30**	**1.25**	**1.22**	**0.81**

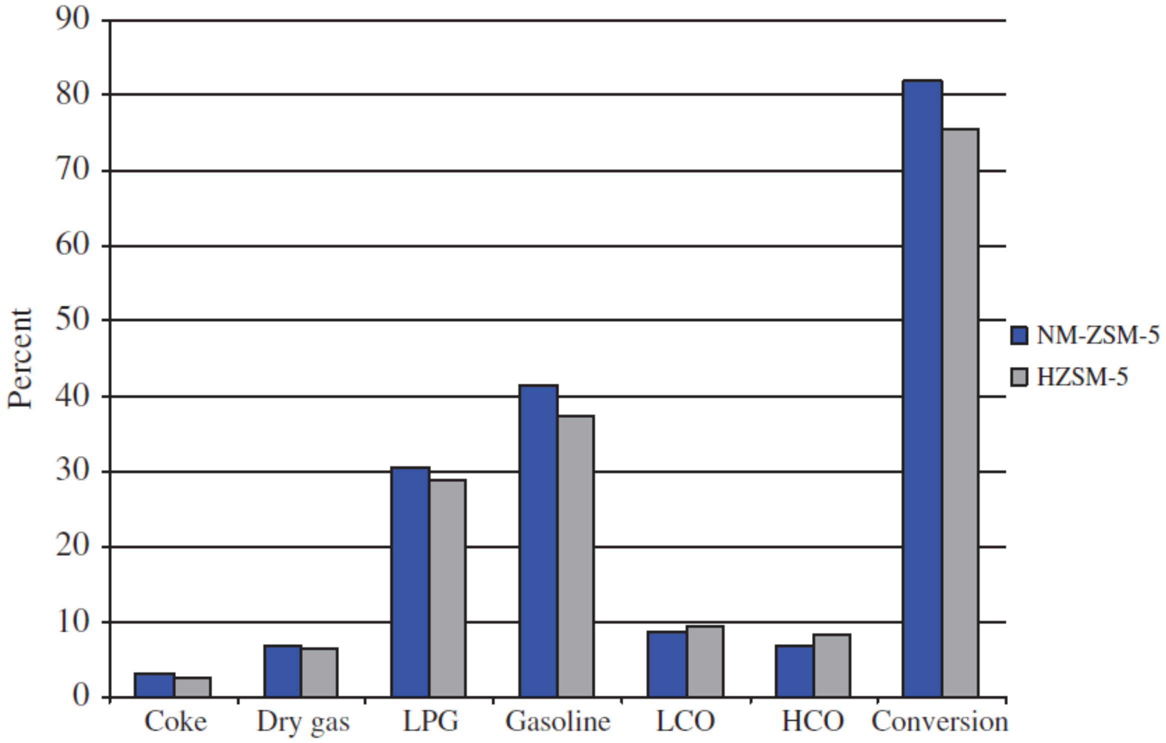
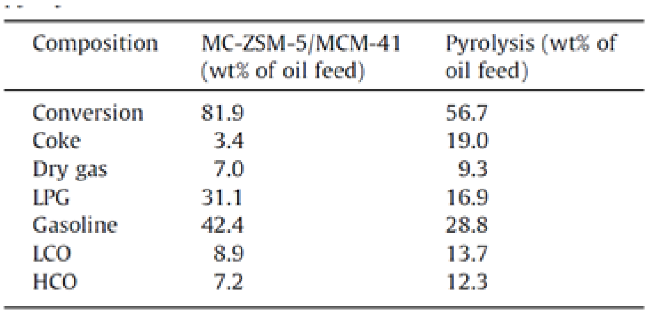


Figure 44, Comparison of products distribution obtained from the catalytic cracking of waste oil sludge over ZSM-5 and micro-mesoporous ZSM-5 catalysts

Table 5 and **Figure 44** give the correlation between crystallinity and conversion and products distribution (**Tasks 2.8, 2.10 and 2.11**) and quality of products obtained (**Tasks 2.9 and 2.12**). Pure ZSM-5 gives more methane, ethane and propane while micro-mesoporous ZSM-5 zeolite catalysts give more propylene, butane, butane and pentane, which are more desirable products, indicating the benefit of the presence of mesoporosity in the formation of these more valuable products. Among all the samples tested, M4 (NM-ZSM-5) gives the highest percentage of propylene and butene, the two most valuable and desirable products.

The comparison between catalytic cracking over M4 sample (Micro-mesoprous ZSM-5 zeolite catalyst with the highest crystallinity) and thermal cracking (pyrolysis) is gived in **Table 6** (**Tasks 2.7-2.12**). The catalytic cracking gives higher conversion, less coke formation, less dry gas, more LPG and Gasoline, more desirable products than pyrolysis, showing the advantages of catalytic cracking.

Table 6. Product distribution of vegetable oil sludge cracking reaction over M4 catalyst and pyrolysis



Composition	MC-ZSM-5/MCM-41 (wt% of oil feed)	Pyrolysis (wt% of oil feed)
Conversion	81.9	56.7
Coke	3.4	19.0
Dry gas	7.0	9.3
LPG	31.1	16.9
Gasoline	42.4	28.8
LCO	8.9	13.7
HCO	7.2	12.3

Table 7. Gas Products distribution

Composition	Formula	H-ZSM-5 (%)	NM-ZSM-5 (%)	Pyrolysis (%)
2-Methyl-2-butene	2M2C4=	0.56	0.97	1.56
Hydrogen	H2	0.11	0.13	0.00
Propane	C3	6.52	8.88	2.12
Propylene	C3=	8.61	7.06	7.30
i-Butane	*i*C4	**3.14**	**5.49**	**0.00**
Propadiene	Propadiene	0.00	0.00	0.00
n-Butane	*n*C4	1.90	2.94	0.24
1-Butene + *i*-butene	1C4 = +*i*C4=	4.85	3.86	1.92
trans-2-Butene	T2C4=	2.36	1.70	0.18
cis-2-Butene	C2C4=	1.59	1.20	0.14
1,3-Butadiene	1,3-Butadiene	0.00	0.00	1.11
3-Methyl-1-butene	3M1C4=	0.57	0.44	0.00
Ethylene	C2=	4.84	4.88	3.76
Ethane	C2	0.99	1.14	1.96
Methane	CH4	0.55	0.83	1.42

Table 7 show the products distribution of the gas obtained from the catalytic cracking over pure ZSM-5 catalyst synthesized using silica extracted from rice husks, micro-mesoporous ZSM-5 catalyst and thermal cracking, respectively (Tasks 2.9 and 2.11). Micro-mesoporous ZSM-5 and ZSM-5 catalysts give more propylene and butane and micro-mesoporous ZSM-5 catalyst gives even higher propylene and butane percentage

Table 8, Main products of pyrolysis of waste oil sludge

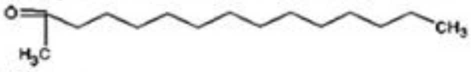
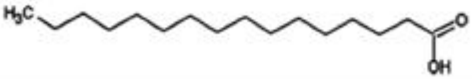
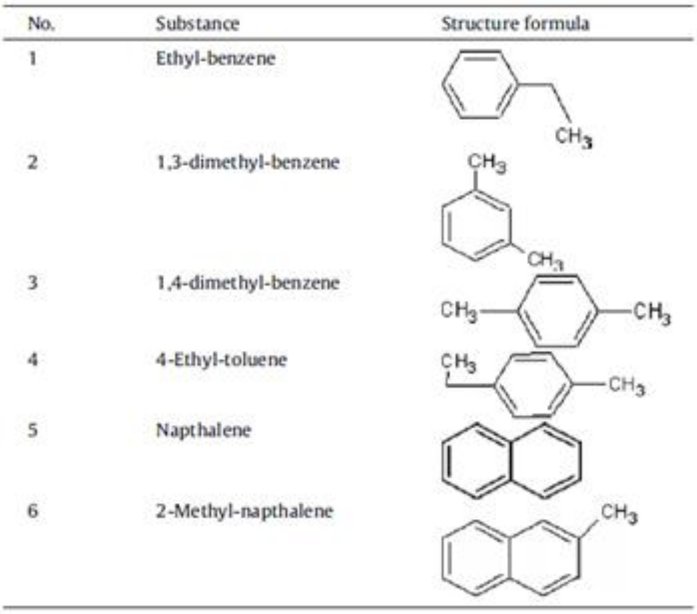
No.	Substance	Structure formula
1	1-Hexyl-2-methyl-cyclopropane	
2	Dodecanol	
3	1-Tetradecene	
4	Pentadecane	
5	1-Pentadecane	
6	2-Pentadecanone	
7	Hexadecanoic acid	

Table 9. Main products of catalytic cracking of waste oil sludge over micro-mesoporous ZSM-5 catalys



No.	Substance	Structure formula
1	Ethyl-benzene	
2	1,3-dimethyl-benzene	
3	1,4-dimethyl-benzene	
4	4-Ethyl-toluene	
5	Napthalene	
6	2-Methyl-napthalene	

Tables 8 and 9 describe some main products of the catalytic cracking of vegetable oil sludge over Micro-mesoporous ZSM-5 catalyst and the pyrolysis process. The results show that main products of pyrolysis are the derivatives of paraffinic hydrocarbon and that of the catalytic cracking are polycyclic aromatic hydrocarbons. The aromatic hydrocarbons are the desirous components because they lead to high octane number of gasoline. Moreover, they are the suitable initial feed for the petrochemistry.

Fourth period: May 2008-October 2008

2.10 Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour withy the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**): **Completed**
2.11 Catalytic Testing of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**Task 1.15**) and characterization of used catalysts by a series of physico-chemical techniques by **BP: Completed**
2.12 Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc: **Completed**
2.13: Selection of the best catalyst for the long period catalytic testing with the participation of **BP**: **Completed**
2.14: Catalytic testing with large quantity of catalysts by **VP1**, the characterization of used catalysts by a series of physico-chemical techniques by **BP**: **Removed from the project.**
2.15: Evaluation of the quality of biodiesel products by using difference techniques : Cetane number, viscocity index, Acid number.. etc: **Completed**

The waste oil sludge catalytic cracking has been carried out over HY and Y/MCM-41 (Faujasite Y zeolite with a mesoporosity) compared with NMZSM-5, ZSM-5/MCM-41 and HZSM-5 catalysts (**Figure 45**). Quite surprisingly, HY and HY/MCM-41 which are in general the best cracking catalysts of petroleum and largely used in FCC processes are much less active than NMZSM-5, ZSM-5/MCM-41 and HZSM-5 catalysts. It is very possible that ZSM-5 type of catalysts like NMZSM-5; HZSM-5 and ZSM-5/MCM-41 are more acid than HY and HY/MCM-41 and that waste oil sludge has heavier fraction of hydrocarbons, more difficult to be cracked. NMZSM-5 is more active than ZSM-5 catalyst is due to the presence of mesoporosity, favorable for the diffusion of larger molecules of waste oil sludge. In ZSM/MCM-41, due to the presence of MCM-41 which has a neglect able acidity, this catalyst has low activity compared to ZSM-5. The same phenomenon is observed for HY/MCM-41 which is less active than HY.

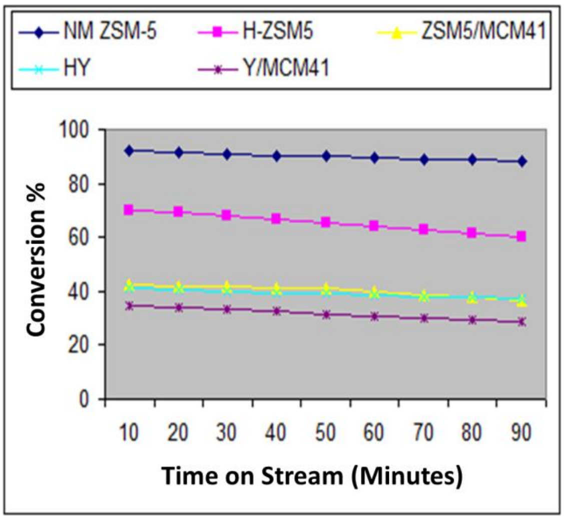


Figure 45, Waste oil sludge cracking over a series of catalysts: NMZSM-5, HZSM-5, ZSM-5/MCM-41, HY and HY/MCM-41

This part of results showed that the best catalyst for waste oil sludge synthesized in this project using silica extracted from rice husks is NMZSM-5 catalyst.

Figure 46 compares the products distribution of waste oil sludge cracking reaction realized over HY and HY/MCM-41. The fraction of waste oil sludge is also given. In waste oil sludge, there are around 50% of HCO (fraction of hydrocarbons with a boiling point > 343 °C), 45% of LCO (the fraction of hydrocarbons with a boiling point between 221 and 343 °C), less than 5% of Gasoline (fraction of hydrocarbons with a boiling point < 221 °C with more C5

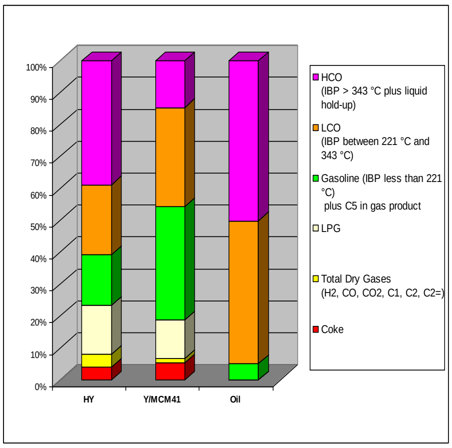


Figure 46, products distribution of waste oil sludge cracking reaction realized over HY and HY/MCM-41. For comparison, the products distribution in waste oil sludge is also given.

fraction). After cracking reaction, the percentage of HCO is largely reduced over HY/MCM-41 owing to the presence of mesoporosity to give a large fraction of Gasoline and a fraction of LPG while LCO fraction is only slightly reduced. The coke in the final product is only around 5% of the total products. Over HY, the fraction of HCO is only slightly reduced while the fraction of LCO is significantly reduced to give Gasoline and LPG. The LPG fraction in the products is slightly larger over HY than HY/MCM-41 with less coke formation.

This study shows that the presence of a mesoporosity is favorable to crack heavier fraction. This is owing to the easy penetration of large fraction of hydrocarbons into the catalyst framework. Whilst due to the lower acidity, HCO can not be completely cracked to give more Gasoline and LPG. That is why in the final products, there is still a significant fraction of LCO. This fraction of LCO is at least partly from HCO. Over HY, due to the lack of mesoporosity, larger molecules of hydrocarbons can not penetrate into the framework of catalyst. No cracking of fraction of HCO over this catalyst.

The best catalyst is a material with larger acidity (ZSM-5) and the presence of a mesoporosity (**Tasks 2.10, 2.11 and 2.13**). This conclusion is totally in agreement with previous **Semiannual reports 1, 2 and 3**.

Figure 47 gives a detailed analysis of products fraction in the point of view of boiling point. In waste oil sludge, the most important fraction is located at between 270-330 °C with a significant fraction located at between 510-540 °C. After cracking over HY/MCM-41 both fractions of 33-330 and 510-540 °C are largely reduced. More fractions between 90-360 °C, indicating the efficient cracking reaction over HY/MCM-41. Whilst over HY, no change

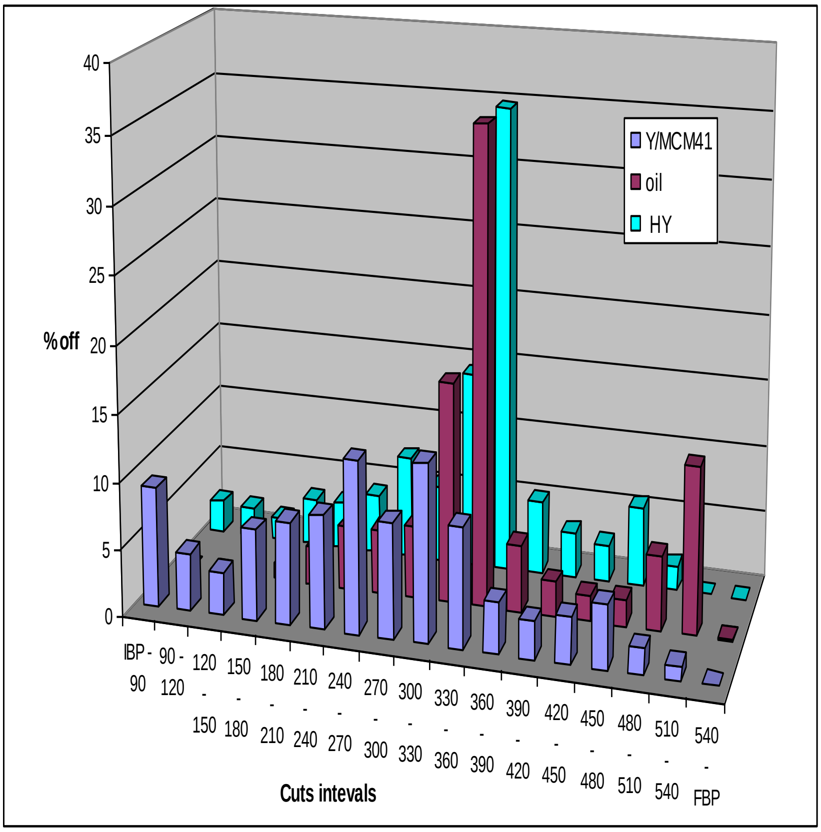


Figure 47, Product distribution given in the fraction of BP.

between 270-330 °C. This detailed analysis (**Tasks 2.12 and 2.15**) confirms the observation from **Figure 46**. Over HY, more total dry gases is obtained compared that over HY/MCM-41.

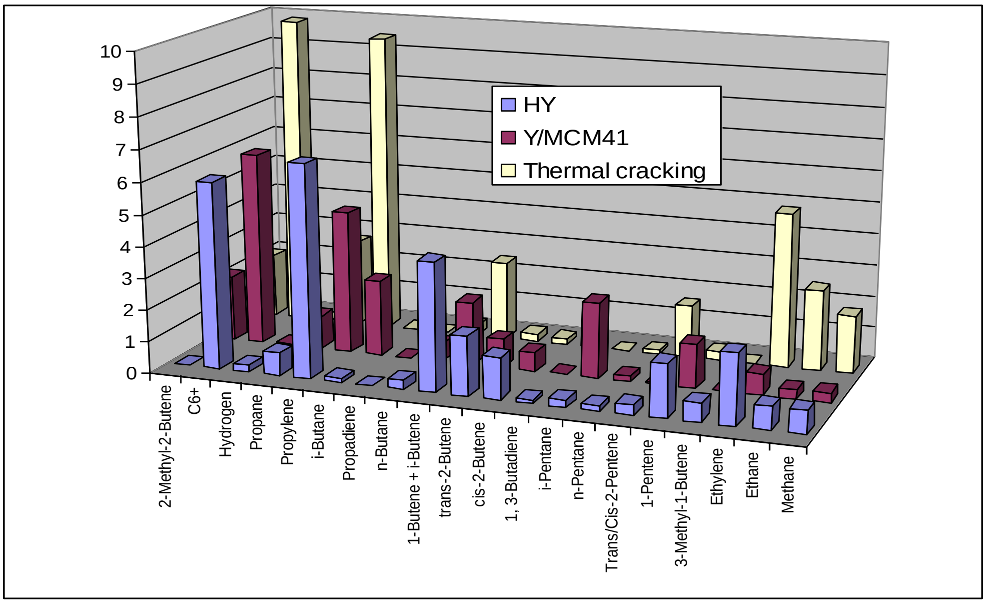


Figure 48, Comparison of dry gases in the final products.

Figure 48 compares the total dry gases obtained from the waste oil cracking reaction over HY/MCM-41 and HY and by thermal cracking. Thermal cracking gives more ethylene, ethane and methane and also C_6+ and propylene products. As indicated in **Figure 46**, less total dry geses are btained over HY/MCM-41 than over HY. Over HY, more also C_6+ , propylene, n and iso-butenes and ethylene. Over HY/MCM-41 more C_6+ and propylene, n-butane and iso-pentane products.

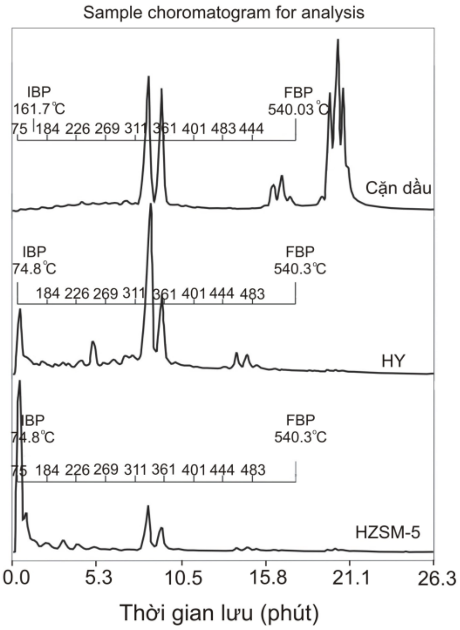


Figure 49, Liquid product of cracking reaction over HY/MCM-41 and NM-ZSM-5 (c) catalysts and for comparison Waste oil sludge (b)

The liquid product of cracking reaction is analysed by SIMDIST GC ThermoElectro system. The composition of liquid fraction is measured via the distribution of boiling point (**Figure 49**). It shows that the vegetable oil sludge has three areas of boiling point. All of them are over 343^{0}C corresponded with the segments of HCO and LCO. The spectrum of the catalytic cracking reaction over MP-HY showed the peaks occur at near of 75 °C and 343 °C. The intensity of the peaks which are near 75 °C is lower than the peaks are near 343 °C. It proves that the unconverted segments still exist in liquid product with high content. On the contrary, in the spectrum of the catalytic cracking reaction over MP-HZSM-5, peaks occur at near 75 °C have the intensity is much higher than that occur at near 343 °C. This presents that the total of LPG and gasoline is much higher than the total of HCO and LCO. It also showed that the conversion of vegetable oil in the cracking reaction over MP-ZSM-5 is much higher than that over MP-HY. The obtained results are completely in agreement with previous results. Once again, MP-ZSM-5 proved its priority over MP-HY as mentioning above.

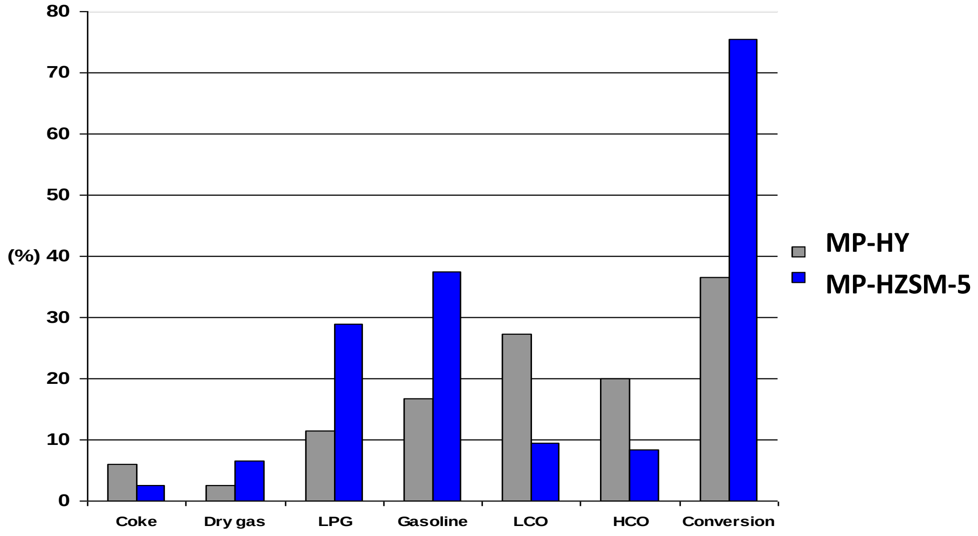


Figure 50, Comparison on the products formation over NMZSM-5 and HY/MCM-41 catalysts

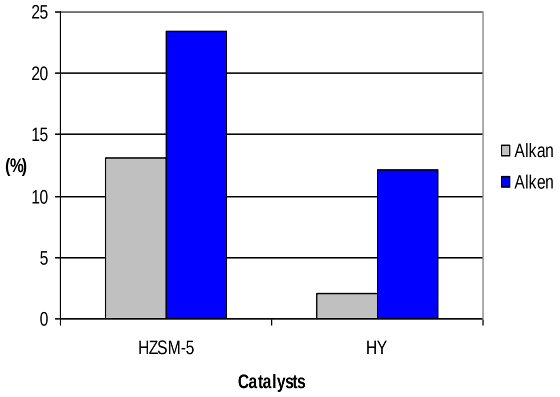


Figure 51, Comparison on the production of alkens over NMZSM-5 and HY/MCM-41 catalysts

Figure 50 describes the obtained products of the catalytic cracking reaction over MP-HY and MP-ZSM-5 catalyst materials in the shaped of column chart. It clearly shows that the total of

LPG, gasoline (desired products) and conversion of the catalytic cracking reaction over MP-ZSM-5 is nearly twice as high as that over MP-HY. On the contrary, the total of coke, HCO and LCO (undesired products) over MP-ZSM-5 is half of that over MP-HY. This result proves the priority of the MP-ZSM-5 over MP-HY in the cracking reaction of vegetable oil sludge.

The conversion of the cracking reaction using MP-ZSM-5 is over 75%, the total of LPG and gasoline is 4 times as high as the total of HCO, LCO and coke. This indicates that MP-ZSM-5 has very high selectivity with desired products and high activity for the cracking reaction of vegetable oil sludge to produce biodiesel. On the other hand, the conversion over MP-HY is only 37% (half of MP-HZSM-5). The total of desired products (LPG, gasoline) is half of undesirous products (HCO, LCO and coke). MP-ZSM-5 proved its priorities in comparison with MP-HY not only conversion but also selectivity in the catalytic performance.

The obtained products of the cracking process are classified of gas, liquid and solid (coke) types. Gas product is analysed by gas chromatography system. The yield of obtained gases of the catalytic cracking reaction over MP-ZSM-5 is much higher than that over MP-HY. This proved that the acidity of MP-ZSM-5 is much stronger than that of MP-HY.

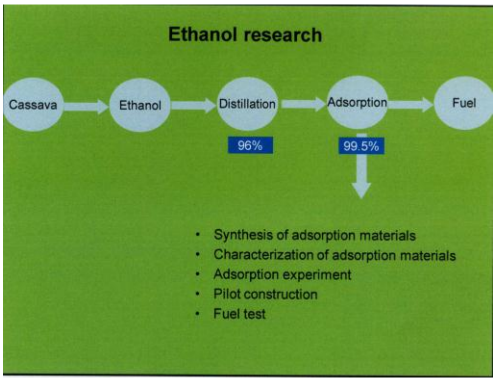
On the other hand, from the obtained composition of gas product, the quantity of alkane and alkene can be calculated and the mechanism of the cracking reaction over catalysts can be determined. The calculated data is presented in **Figure 51**, it shows that the quantity of obtained alkene is much more than alkane. This result allows to devise that the mechanism of the cracking reaction of vegetable oil sludge over MP-HY and MP-ZSM-5 catalysts is carbenium.

The conclusion is that the best catalyst is NMZSM-5 catalyst.

2.3.3. Work Package 3,

First period: November 2006-April 2007

(Tasks 2.1, 2.2, 2.4 and 2.5): Production of alcohols from fermentation of rice, sugarcane and cassava (Vietnamese agro-products) by distillation; Construction and evaluation of the purification system (Microreactor); Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period; First analysis with BP for the selection of the first series of adsorbents (See Task 1.12); Concentration of alcohols (concentration>99.5%) by using selective adsorbents (from BP–CMI labolatory) as well as zeolites prepared from Kaolin of Vietnam. First screening of the adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques;


Ethanol research

- Synthesis of adsorption materials
- Characterization of adsorption materials
- Adsorption experiment
- Pilot construction
- Fuel test

Fig. 52, Rude ethanol produced from Cassava by distillation with a concentration of 96.5%

The ethanol has been obtained from Vietnamese agro products by distillation. However the concentration reached is only 96.5%. It is indispensable to concentrate this rude ethanol by adsorption process using new nanoporous materials prepared by partner BP. At this stage, VP2 partner constructed a microreactor for adsorption of ethanol to further concentrate ethanol. The pilot for a large scale is under construction. VP2 partner used a zeolite adsorbent produced from Kaolin of Vietnam to test the microreactor.

Fig. 53, Microreactor for the concentration of ethanol by adsorption on zeolite adsorbent

<u>Second period: May 2007- October 2007</u>

3.2 Construction and evaluation of the purification system (Microreactor)

The microreactor for the concentration of ethanol by adsorption process was successfully constructed and tested. The first test using zeolite 3A adsorbent showed that the microreactor gives correct results.

3.3 Establish the technology of absolute alcohols production for use as “clean fuel” with capacity of 100litters/day

This has been completed since the technology for the centration of ethanol by adsorption process has been chosen.

3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period

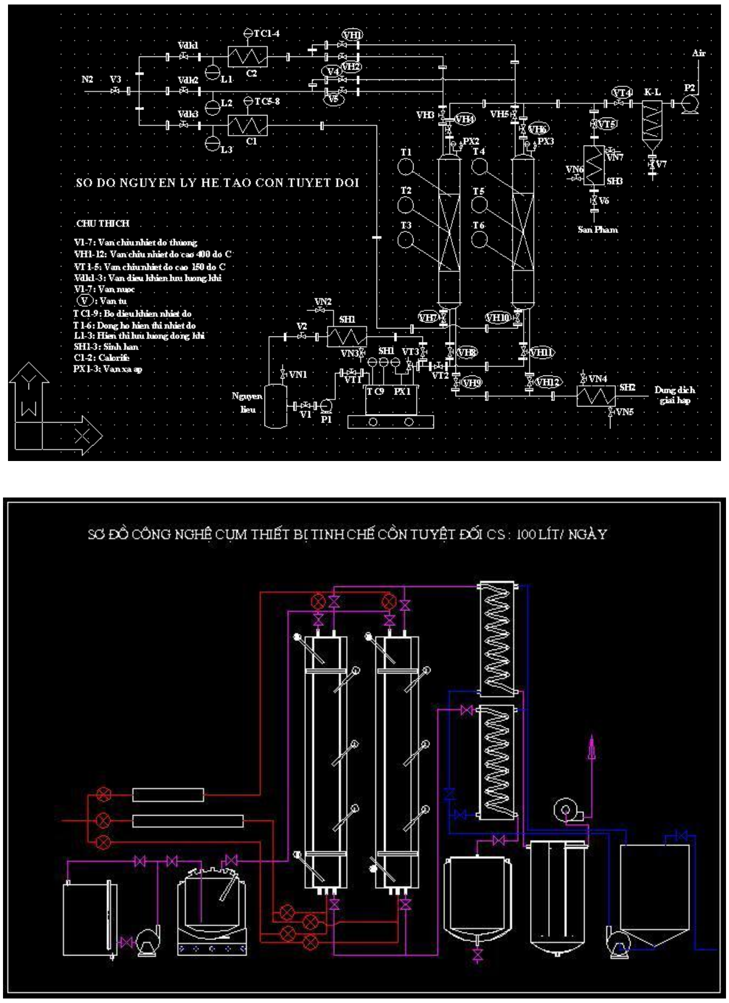
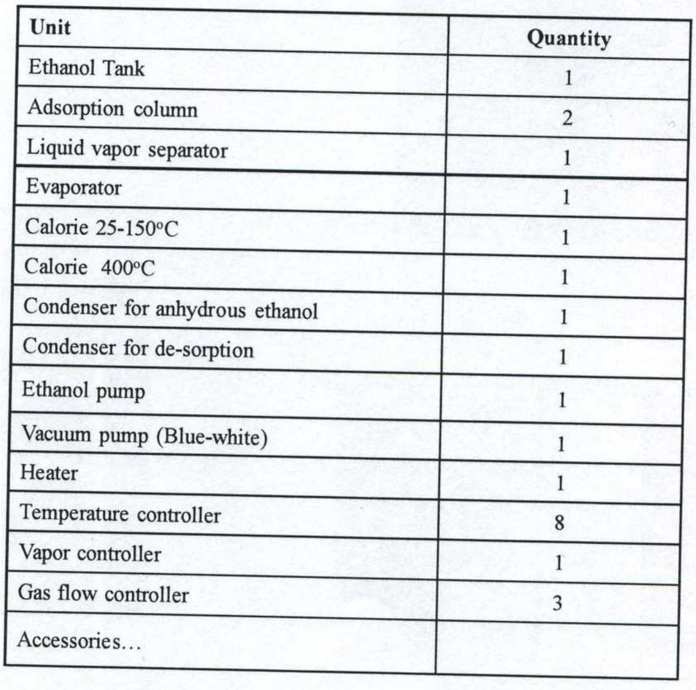


Figure 54, Scheme of pilot for concentration of ethanol by adsorption process

Table 10, Materials necessary for the construction of Pilot



Unit	Quantity
Ethanol Tank	1
Adsorption column	2
Liquid vapor separator	1
Evaporator	1
Calorie 25-150°C	1
Calorie 400°C	1
Condenser for anhydrous ethanol	1
Condenser for de-sorption	1
Ethanol pump	1
Vacuum pump (Blue-white)	1
Heater	1
Temperature controller	8
Vapor controller	1
Gas flow controller	3
Accessories…	

Figure 55, Evaporator (left), ethanol pump (center) and ethanol fuel stock tank (right) with liquid-vapor separator

Different devices used for the construction (**Table 10**) of pilot for the concentration of ethanol by adsorption process have been assembled.

3.5 First analysis with **BP** for the selection of the first series of adsorbents (**See Task 1.12**),
3.6 Concentration of alcohols (concentration>99.5%) by using selective adsorbents (from **BP**–CMI labolatory) as well as zeolites prepared from Kaolin of Vietnam. First screening of the adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques,
3.7 Evaluation of the quality of alcohols produced with adsorbents supplied by **BP** by using difference techniques,
3.8 Establishment of the criteria for the selection of the best adsorbents with the participation of **BP** (**See Task 1.13**),
3.9 The information obtained from 3.6 and 3.7 will be supplied to Belgian partner to modify porous adsorbents,
3.10 Adsorption Testing of the modified porous adsorbents supplied by Belgian partner (**BP**) and characterization of used adsorbents by a series of physico-chemical techniques,

These six Tasks will be discussed together. In the first **Semiannual Report**, a microreactor was constructed by VP2. To evaluate this microreactor, VP2 used zeolite A as adsorbent to start the research work since no materials were ready from BP due to the late setting-up of the project and the late engagement of researchers. The justification to use this zeolite is due to its pore size of 0.4 nm, very close to the molecular size of ethanol (0.44 nm). Furthermore, it is a long term study to develop a new and good adsorbent for ethanol concentration by adsorption from our study since the powder can not be used in the concentration process. Powdery products should be made in form of pellet. The choice of binder, size of pellet, form of pellet, all these need a detailed study. It could be more practical to use Zeolite A (3, 4 or 5A) adsorbent to solve the urgent problem in Vietnam. That is why VP2 will focus the evaluation of zeolite A adsorbent for ethanol concentration. The **Tasks 3.5, 3.6, 3.7, 3.8, 3.9 and 3.10 have been modified to**

3.5 First analysis with **BP** using Zeolite A adsorbent,
3.6 Concentration of alcohols (concentration>99.5%) by using zeolites prepared from silicas extracted from rice husks and Kaolin of Vietnam. First test of the adsorbents in

microreactor and characterization of used adsorbents by a series of physico-chemical techniques,

3.7 Evaluation of the quality of alcohols produced with zeolite A adsorbents,

3.8 Synthesis of zeolite A using silica extracted from rice husks with the participation of **BP** (**See Task 1.13**),

3.9 Characterization of zeolkite A adsorbents,

3.10 Adsorption Testing of the modified zeolite A adsorbents and characterization of used adsorbents by a series of physico-chemical techniques

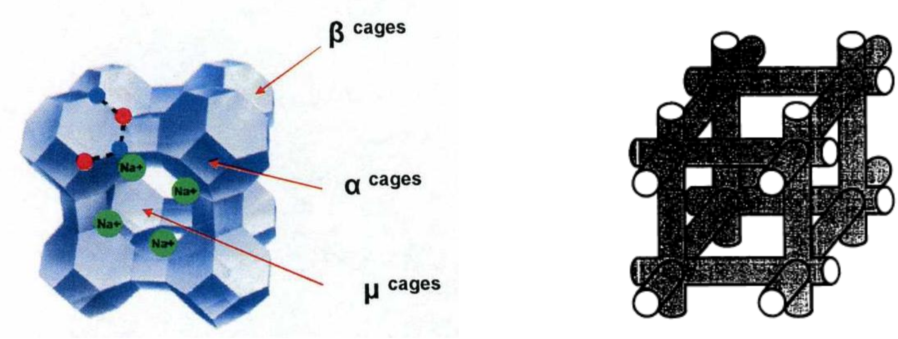


Figure 56, Schematic representation of zeolite A, different cages (left) and structure (right)

The VP2 partner synthesized a series of zeolite A using silica extracted from rice husks and then prepared in the form of spheres (**Taks 3.8 and 3.9**). **Figure 57** shows the XRD pattern of the product obtained, indicating the successful synthesis of zeolite A and **Figure 58** depicts the zeolite A adsorbent in form of spheres.

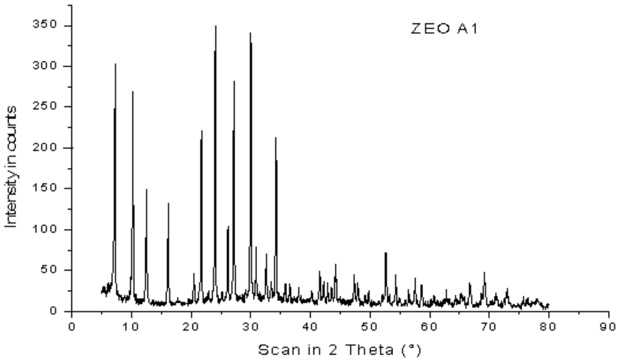


Figure 57, XRD pattern of zeolite A synthesized with Kaolin-Vietnam

Figure 58, Photograph of Zeolite A adsorbent

3.11 Evaluation of the quality of alcoholic products by using different techniques.

Third period: November 2007-April 2008

3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period,
3.8 Synthesis of zeolite A using silica extracted from rice husks with the participation of **BP** (**See Task 1.13**),
3.9 Characterization of zeolite A adsorbents,
3.11 Evaluation of the quality of alcoholic products by using different techniques
3.12 Establishment of the correlation between the characteristics of adsorbents and the purification behaviour in order to further modify or functionalize the modified porous nanoadsorbents : **Removed from the project**
3.13 Alcohol concentration test of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.15**) and characterization of used adsorbents by a series of physico-chemical techniques: **Removed from the project**
3.14 Evaluation of the quality of alcohol products by using different techniques,
3.15 Selection of the best adsorbents for the long period catalytic testing on the basis of the information obtained from 3.13 and 3.14 with the participation of **BP**: **Removed from the project**.

As the primary objective, VP2 continues the construction of pilot for the concentration of ethanol by adsorption process (**Task 3.4**). Two adsorption columns have been constructed (**Figure 59**). The electrical devices have been assembled (**Figure 60**).

Figure 59, Adsorption columns

Figure 60; Electrical devices for the Pilot

A protocol for the synthesis of Zeolite A using silica extracted from rice husks and kaolin of Vietnam has been developed (**Figure 61**) (**Tasks 3.8 and 3.9**). Infra-Red spectroscopy (**Figure 62**) and ^{27}Al MAS NMR (**Figure 64**) characterization show that a well crystallized zeolite A was formed. XRD technique (**Figure 63**) confirms the zeolite A structure.

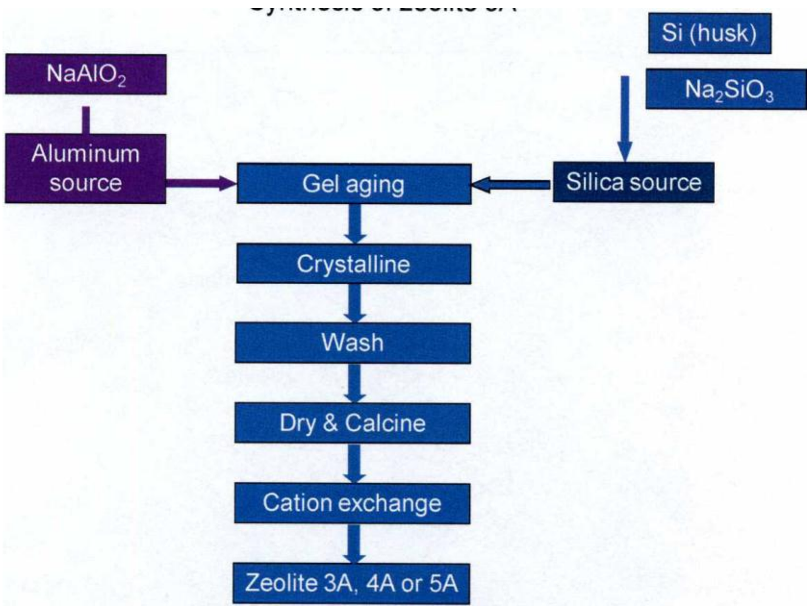


Figure 61, Synthesis protocol of Zeolite A using silica extracted from rice husks and Kaolin of Vietnam as binder

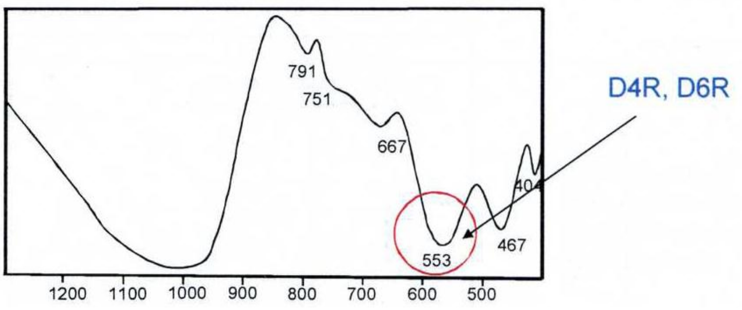


Figure 62, IR spectroscopic characterization of zeolite structure

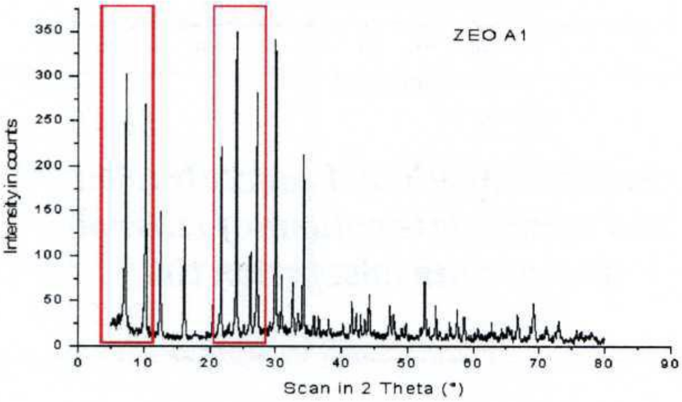


Figure 63, XRD pattern of material obtained from the synthesis using silica extracted from rice husks

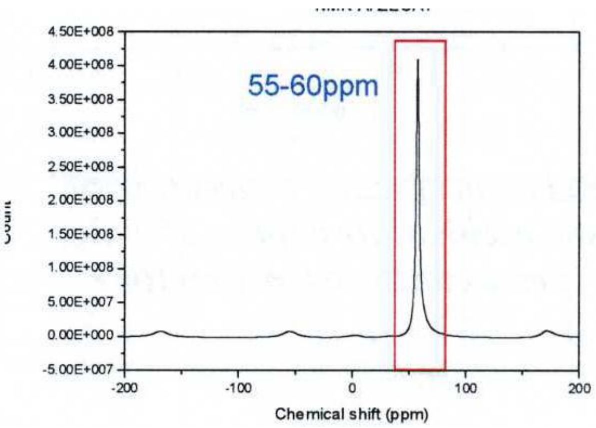


Figure 64, ^{27}Al MAS NMR spectrum of material synthesized using silica extracted from rice husks

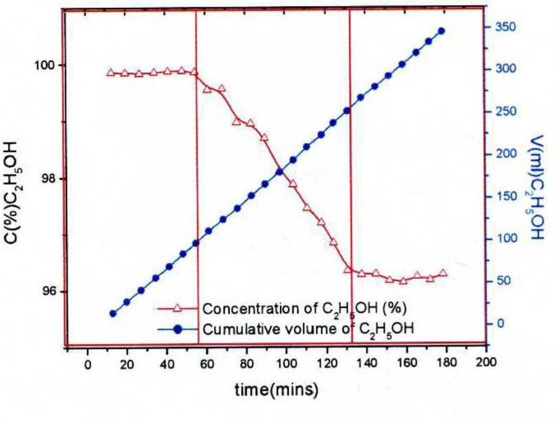


Figure 65, Relation of ethanol concentration and accumulate volume of ethanol versus with adsorption time

Figure 65 depicts the variation of ethanol concentration (red line) as a function of adsorption time (**Tasks 3.11 and 3.14**). It is clearly shown that at initial adsorption time (less than 60 minutes), a highly pure ethanol can be obtained. Above 60 minutes, the concentration of ethanol starts to decrease to reach a constant at around 130 minutes of adsorption. This means that the adsorbent is saturated by water and we have ethanol with a concentration of around 96%. The ethanol forms an azeotropic mixture with water, giving this typical azeotropic concentration of ethanol. This suggests that zeolite A adsorbent can not continue to concentrate ethanol by removing the water. The regeneration of zeolite adsorbent is necessary.

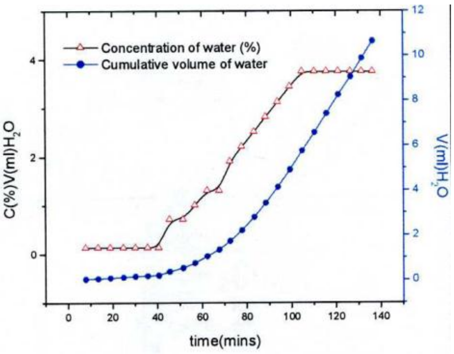


Figure 66, Relation of water concentration and accumulate volume of water versus with adsorption time

Figure 66 demonstrates the variation of water concentration in the product (**Tasks 3.11 and 3.14**). It is clear that at the beginning of adsorption, all the water has been adsorbed by adsorbent and removed from ethanol flow. After 40 minutes adsorption, zeolite adsorbent is saturated by water. The water concentration in ethanol product increases to reach an azeotropic concentration of ethanol with around 4% of water and 96% of ethanol. The results in Figures 16 and 17 are quite in good agreement.

The above results showed that each 40 minutes adsorption, a regeneration of zeolite adsorbent becomes indispensable to get highly concentrated ethanol.

<u>**Fourth period: April 2008-November 2008**</u>

3.4 Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period: **Completed**
3.12 Establishment of the correlation between the characteristics of adsorbents and the purification behaviour in order to further modify or functionalize the modified porous nanoadsorbents : **Completed**
3.14 Evaluation of the quality of alcohol products by using different techniques: **Completed**
3.16: Purification testing in a pilot with large quantity of catalysts and characterization of used adsorbents by a series of physico-chemical techniques: **Completed**
3.17: Evaluation of the quality of alcohol products by using different techniques: **Completed**

Figure 67 gives different views of constructed Pilot. The Pilot after a long time construction is completely built and used for the first concentration of ethanol by adsorption process using zeolite A adsorbent (**Task 3.4**). The Pilot contains two main columns with zeolite A adsorbents, a tank for the storage of rude ethanol, the pump for the injection of ethanol,

Figure 67, Pilot constructed. Front view (up) and side view (down)

Figure 68 shows the percentage of ethanol at different injection volumes of rude ethanol as a function of adsorption times. At high injection volumes of rude ethanol, the ethanol concentration obtained decreases sharply due to the presence of water and a constant concentration of 96 % of ethanol is obtained. This concentration corresponds to the azotropic concentration of ethanol and water. At lower injection volumes, this concentration attains at longer adsorption times. **Table 11** gives water adsorption at different vapor velocity of rude ethanol injection. Higher velocity of rude ethanol injection, more water adsorption during the full adsorption process whilst higher velicity of rude ethanol injection, less first adsorption of water on material. **Figure 68** gives a global view of the different steps of ethanol concentration process by adsorption.

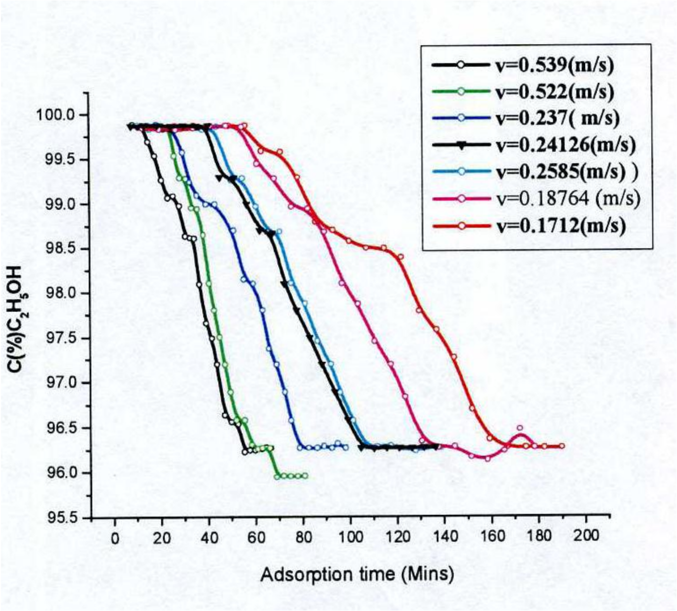
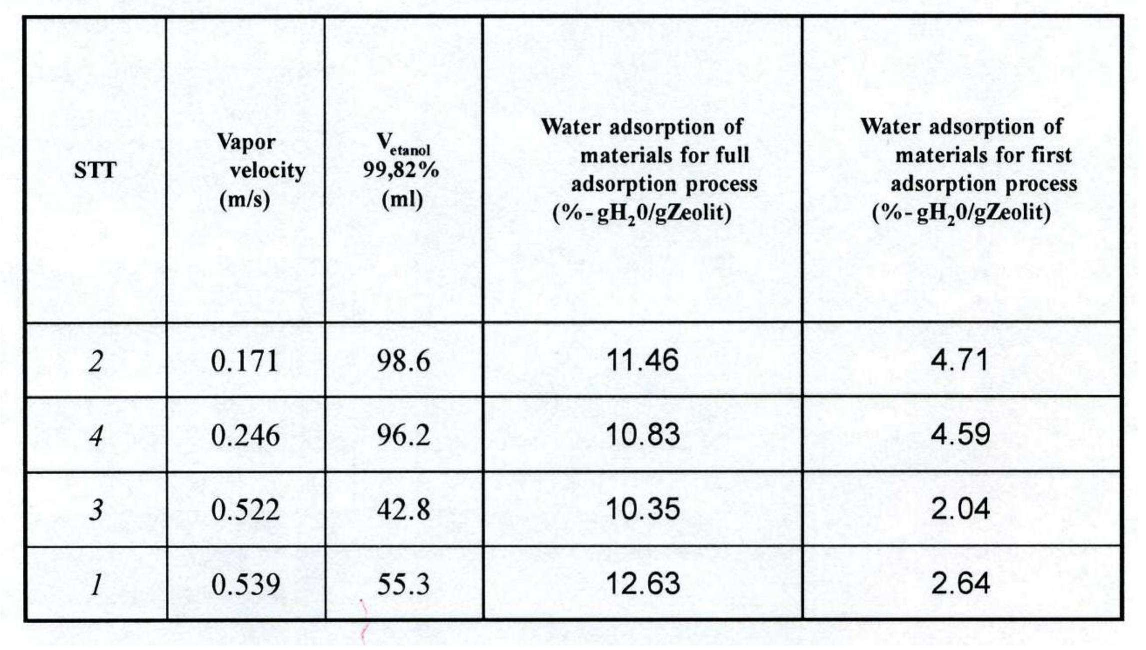


Figure 68, Quality evaluation of ethanol with different injection volume of rude ethanol

Table 11, Water adsorption at different vapor velocity of rude ethanol injection



STT	Vapor velocity (m/s)	V_{etanol} 99,82% (ml)	Water adsorption of materials for full adsorption process (%-$gH_20/gZeolit$)	Water adsorption of materials for first adsorption process (%-$gH_20/gZeolit$)
2	0.171	98.6	11.46	4.71
4	0.246	96.2	10.83	4.59
3	0.522	42.8	10.35	2.04
1	0.539	55.3	12.63	2.64

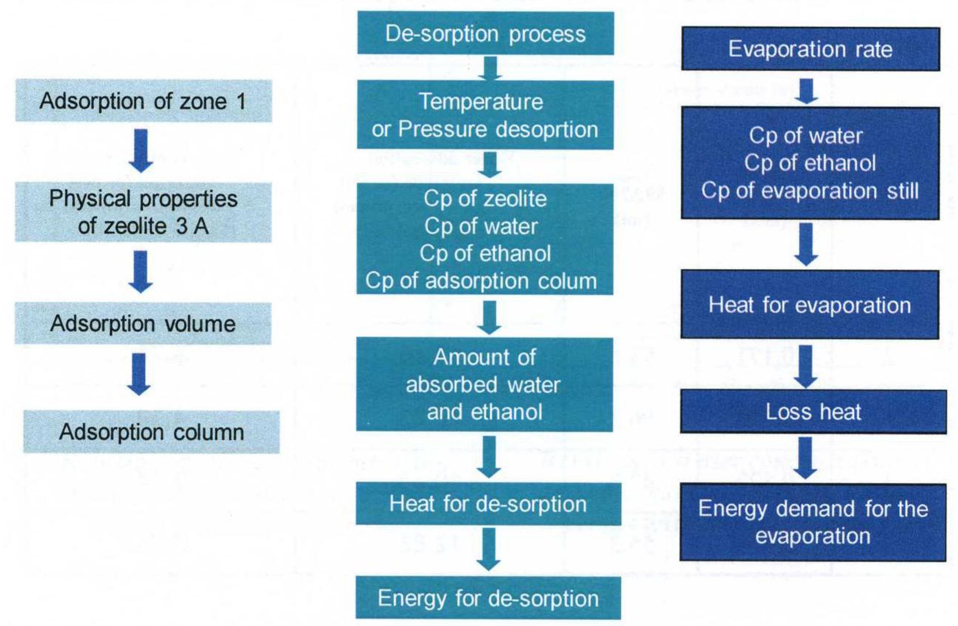


Figure 69, Different steps of the process for the concentration of ethanol by adsorption using zeolite A adsorbent

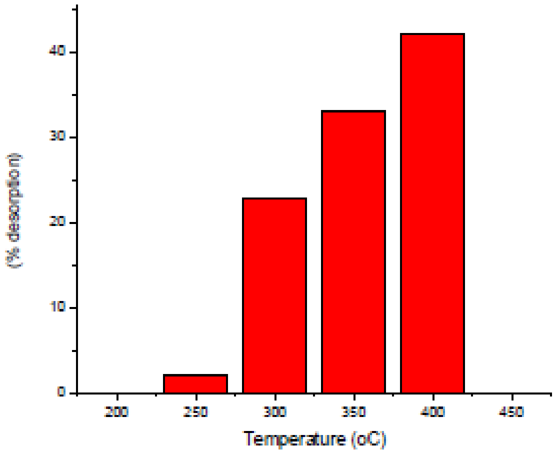


Figure 70, variation of desorption as a function of temperature

Figure 70 gives the variation of desorption as a function of temperature (left) at atmospheric pressure and as a function of temperature at high pressure (right). With increasing temperature, more water is desorbed.

2.3.4. Conclusion

First period: November 2006-April 2007

BP partner was quite successful in their first synthesis. Ordered nanoporous material involving microporous materials (ZSM-5) and mesoporous materials (MCM-41, Al-MCM-41, and SBA-3) has been successfully synthesized using extracted silicon by RHs as silicon source. Furthermore, heteroatoms such as Al and Ti species have been easily introduced into the mesoporous and microporous walls of MCM-41 and ZSM-5 by simple mixture of extracted silicon with aluminum or titanium source in initial reaction gel. This part of results from this period demonstrated that rice husks can be a good precursor for the production of high value added materials.

In collaboration with Belgian partner, VP1 partner made the first analysis using the first series of nanoporous zeolites and mesoporous materials as catalysts which showed very promising results that materials using rice husks as precursors are more active than commercial catalysts in the cracking of n-Hexane and TIPB. This part of results from this period demonstrated that rice husks can be a good precursor for the production of high value added materials. All the tasks from the WP2 have been completed on the basis of time schedule.

In the collaboration with Belgian partner, VP2 partner obtained the rude ethanol by distillation with a concentration of 96.5%. In the framework of the project, a microreactor to screen the best adsorbents has been constructed. A zeolite adsorbent produced from Kaolin of Vitenam has been used to test the microreactor.

Second period: May 2007-October 2008

In this period, BP continued to develop new extraction methods and to use extracted silica s precursor to synthesize new nanoporous materials. A very efficient and very innovative method to extract silica from rice husks has been developed. This method can help us to reach two goals by only one process: extraction of silica and sunthesize the nanoporous carbon nanomaterials. By using KOH of different concentrations, silica can be extracted from rice husks, leaving a very nice porous carbon network with very high surface area from 2000-2500 m2/g (**Tasks 1.6, 1.7, 1.8 and 1.11**). By controlling the KOH concentrations, we can tailor the pore size of nanoporous carbon materials. Using extracted silica, a large series of advanced materials have been synthesized and fully characterized. These materials have been evaluated by VP1 in the cracking reaction of n-Hexane, TIPB and waste oil sludge (**Tasks 2.4, 2.5, 2.7 and 2.8**). On the basis of these evaluations, it is revealed that catalysts with zeolite structure containing mesoporosity are the most efficient catalysts, better than thermal cracking and the standard ECAT catalysts. We then focused to synthesize and modify the protocol to synthesize zeolites with mesoporosity such as ZSM-5 zeolite and materials containing ZSM-5 zeolite structure with the presence of mesoporosity (**Tasks 1.12 and 1.13 and 2.8 and 2.10**). These new materials have been characterized (**Task 1.11**). Due to the time limit and due to the fact that using rice husks as direct silica source is not reasonable for the synthesis and that carbon nanotubes and silicon carbide are not suitable for cracking reactions, **Tasks 1.9 and 1.10** have been removed from the project. The microreactor has been completely constructed by VP1 partner and used for the evaluation of catalysts prepared in this project (**Task 2.3**) The cracking products have been largely analyzed (**Tasks 2.6 and 2.9**). VP2 partner finished the construction of microreactor (**Task 3.2**). Zeolite A has been used to evaluate this microreactor, demonstrating the microreactor works in good conditions. Due to the time limit, the construction of pilot will take much time. It is not possible to construct the pilot and to evaluate all the materials prepared by BP (two years project). The construction of pilot becomes the priority and main objective of VP2 partner. Different **Tasks 3.5, 3.6, 3.7, 3.10 and 3.12** have been modified to accommodate this change. The adsorbent selected for ethanol concentration by adsorption process is Zeolite A. This zeolite has been synthesized using Kaolin of Vietnam as rude material. The construction is on road. The concentrated ethanol obtained has been evaluated.

Third period: November 2007-April 2008

A new series of micro-mesoporous zeoite ZSM-5 catalysts by variation of hydrothermal treatment times have been synthesized and characterized by a series of techniques (IR, XRD, SEM, TEM) (**BP**) and have been evaluated in the waste oil sludge cracking reaction and compared with thermal cracking. All the results have been also compared with a pure ZSM-5 catalyst synthesized from silica extracted from rice husks. The results showed that the catalyst with ZSM-5 zeolite structure with the highest crystallinity and a mesoporosity gives the highest conversion, the highest amount of desired products (Gasoline and LPG), more propylene and butenes and less coke. The products distribution in gas products and in liquid products has been analyzed. Pyrolysis gives more paraffinic hydrocarbons and catalytic cracking gives more aromatic hydrocarbons (**VP1**).

As described in **Semiannual Report**, VP2 modified the objective and put the construction of pilot as the primary goal. Instead to waiting for the synthesis of different zeolites by BP as adsorbents and then to selecting the best adsorbent, it is decided to use zeolite A as adsorbent due to the pore size of this zeolite is quite similar to that of ethanol. In fact due to the time limit (two years project), it is not possible to finish the selection of a best adsorbent with different steps in two years term (synthesis, characterize, adsorption testing and pelletization). At the end of the project, it is necessary to deliver a technology for the concentration of ethanol, becoming urgent due to the society need. The modification the objective and the use of zeolite A as adsorbent are fully justified. As a consequence, different Tasks of VP2 have been modified.

A new protocol to synthesize zeolite A using silica extracted from rice husks has been developed. The zeolite A obtained has been characterized by using a large series of techniques such as XRD, IR, ^{27}Al solid state MAS NMR. The behavior of zeolite in ethanol concentration by adsorption process and the quality of ethanol obtained have been evaluated.

Fourth period: May 2008-October 2008

BP synthesized HY and HY/MCM-41 catalysts using silica extracted from rice husks and characterized these new materials.

BP One-Pot Synthesized Catalytically Stable and Active Nanoreactors by the encapsulation of Size-Controlled Nanoparticles within a Hierarchically Macroporous Core@Ordered Mesoporous Shell System. The results are quite interesting and published ina TOP journal “**Advanced Materials**”, a great success for the project.

VP1 evaluated HY and HY/MCM-41 catalysts synthesized during this period in the waste oil sludge catalytic cracking and compared with thermal cracking. This study shows that the presence of a mesoporosity is favorable to crack heavier fraction.

From this project on the basis of the catalytic cracking reaction of waste oil sludge over a large series of catalysts synthesized, the best catalyst is a material with larger acidity (ZSM-5) and the presence of a mesoporosity.

The Pilot after a long time construction is completely built and used for the first concentration of ethanol by adsorption process using zeolite A adsorbent. The Pilot contains two main columns with zeolite A adsorbents, a tank for the storage of rude ethanol, the pump for the injection of ethanol,

All the Tasks and modified Tasks have been completed. All the objectives have been reached.

2.4. General Conclusions

First period: November 2006-April 2007

The project was officially started by a kicking off meeting which was held in Hanoi Vietnam on 15 April 2007 during the visit of Prof. Bao-Lian Su to Vietnam. During the kicking off meeting, all the tasks have been reviewed. Belgian partner, to realize all the tasks, engaged Dr. Xiao-Yu Yang, an expert in the synthesis of nanomaterials and Mr. Thomas Ligot as technician.

Ordered nanoporous material involving microporous materials (ZSM-5) and mesoporous materials (MCM-41, Al-MCM-41, and SBA-3) has been successfully synthesized using extracted silicon by RHs as silicon source. Furthermore, heteroatoms such as Al and Ti species have been easily introduced into the mesoporous and microporous walls of MCM-41 and ZSM-5 by simple mixture of extracted silicon with aluminum or titanium source in initial reaction gel. This part of results from this period demonstrated that rice husks can be a good precursor for the production of high value added materials.

The first analysis using the first series of nanoporous zeolites and mesoporous materials as catalysts showed very promising results that materials using rice husks as precursors are more active than commercial catalysts in the cracking of n-Hexane and TIPB. This part of results from this period demonstrated that rice husks can be a good precursor for the production of high value added materials.

The rude ethanol was obtained by distillation with a concentration of 96.5%. A microreactor to screen the best adsorbents has been constructed. A zeolite adsorbent produced from Kaolin of Vitenam has been used to test the microreactor.

Second period: May 2007-October 2007

During this period, Dr. Xiao-Yu Yang, Mr. Thomas Ligot (three months) and Mrs. Hadj Sadok have been engaged for a best realization of the project.

This period is of great success with a huge amount of materials and results have been obtained. A very efficient and innovative silica extraction process from rice husks has been developed to give simulataneously silica and a very nice nanoporous carbon network. This process has never previously been reported. It is shown that by adjusting the base concentration, the porosity and surface area of nanoporous carbon materials can be tailored. A large series of zeolite and mesoporous materials (such as Nano-mesoporous ZSM-5, Al-MCM-41, Si-SBA-15, HY, HY/MCM-441 and ZSM-5/MCM-41) have been obtained, characterized and evaluated by VP1.

The evaluation results by VP1 have been very helpful to select the best catalysts. After first analysis, we have concentrated this period on the synthesis, characterization of mesoporous ZSM-5 catalysts. More information on these catalysts will be given in next period report. The cracking products have been evaluated and analyzed by VP1 using the microreactor they constructed using n-hexane, TIPB and waste oil sludge as reagents. A comparison has been made with a standard catalyst (ECAT) and also with thermal cracking. It is shown that our materials are more performant that ECAT and thermal cracking. VP1 partner realized a great work on the valuation of catalysts and also the quality of cracking products.

After construction of microreactor for the concentration of ethanol by adsorption process and evaluation of this microreactor by using Zeolie A as adsorbent, VP2 concentrated their work on the construction of pilot. Due to the time limit (2 years project), VP2 modified their objective on the construction of pilot which needs more time. Differn Tasks have been accordingly modified to accommodate to the new objective. We selected Zeolite A as the adsorbent of test for the concentration of ethanol. This choice was based on the pore size of Zeolite A. This zeolite can be synthesized using Kaolin of Vietnam as detailed in the project. After designing, the construction of Pilot for the concentration of ethanol by adsorption process has been started and different devices have been constructed.

All the Tasks defined initially in the project and modified after kicking off the project have been successfully accomplished. In spite of some modifications in Tasks, the objective of this period has been reached. A very good collaboration has been established between partners.

Third period: November 2007-April 2008

This period is very rich in scientific exchange and also in results. A large amount of results have been obtained.

The first **Annual Meeting** has been held in Namur from 31st October to 6th November 2007 to exchange the information and for the discussion of next steps.

During this period, Mr. Do Xuan Dong made a scientific stay in Namur following the program initially defined.

BP engaged Dr. Xiao-Yu Yang and Mrs. Hadj Sadok for a better realisation of the project.

A new series of micro-mesoporous zeoite ZSM-5 catalysts by variation of hydrothermal treatment times have been synthesized and characterized by a series of techniques (IR, XRD, SEM, TEM) (**BP**) and have been evaluated in the waste oil sludge cracking reaction and compared with thermal cracking. All the results have been also compared with a pure ZSM-5 catalyst synthesized from silica extracted from rice husks. The results showed that the catalyst with ZSM-5 zeolite structure with the highest crystallinity and a mesoporosity gives the highest conversion, the highest amount of desired products (Gasoline and LPG), more propylene and butenes and less coke. The products distribution in gas products and in liquid products has been analyzed. Pyrolysis gives more paraffinic hydrocarbons and catalytic cracking gives more aromatic hydrocarbons (**VP1**).

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Fourth period: May 2008-OOctober 2008

Second Annual Meeting has been held in Namur September 2008 to analysis the research state of the project, to modify some tasks following the situation and to prepare the closing of the project. A **General Meeting** has been organized by Belspo on 16 June 2008 in Brussels. BP presented the project progress. This meeting gathered Vietnamese partners and Belgian partners involved in different Belgo-Vietnamese cooperation projects. Mr. Tran Quong Vinh and Mrs. Le Thi Kim Lan made their scientific stay from 26 August to 12 September in Namur to prepare and characterize new materials.

BP, VP1 and VP2 presented the results obtained from this Belgo-Vietnamese bilateral Cooperation project by two poster presentations in The 6th International Mesostructured Materials Symposium has been held in Namur from 8th to 12th September 2008.

The **Closing Meeting of the project** has been organized in Hanoi, Viet Nam at the beginning of 2010 and September 2011 in Namur, Belgium, separately for Vietnamese partners and for Belgian partners. The **Closing Meeting** in Namur, Belgium was organized from 11-14 September 2011 with the participation of Viet Names partners, Prof. Le Thi Hoai Nam from Institute of Chemistry and Dr. Van Dinh Son Tho from University of technology Hanoi.

BP synthesized HY and HY/MCM-41 catalysts using silica extracted from rice husks and characterized these new materials.

BP One-Pot Synthesized Catalytically Stable and Active Nanoreactors by the encapsulation of Size-Controlled Nanoparticles within a Hierarchically Macroporous Core@Ordered Mesoporous Shell System. The results are quite interesting and published ina TOP journal "**Advanced Materials**", a great success for the project.

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From this project on the basis of the catalytic cracking reaction of waste oil sludge over a large series of catalysts synthesized**, the best catalyst is a material with larger acidity (ZSM-5) and the presence of a mesoporosity**.

The Pilot after a long time construction is completely built and used for the first concentration of ethanol by adsorption process using zeolite A adsorbent. The Pilot contains two main columns with zeolite A adsorbents, a tank for the storage of rude ethanol, the pump for the injection of ethanol,

All the Tasks and modified Tasks for this period from point of view of time schedule have been completed. All the objectives of this period have been reached.

Annexe 1. Repartition of tasks

Tasks	BP	VP1	VP2
WP 1 :			
1.1: Furniture of rice husk by Vietnamese partner,	X	X	X
1.2: Bibliographic research	X		
1.3: Chemical analysis of rice husks obtained from different regions of Vietnam. Chemical or physical extraction of silica from rice husk. This work will be performed during the whole period of the project,	X	X	X
1.4: Using extracted silica as starting silica source to synthesize silica based nanostructures such as pure siliceous mesoporous materials,	X		
1.5: Using extracted silica as starting silica source and other synthetic inorganic sources to synthesize silicoaluminate, metallosilicate mesoporous materials,	X		
1.6: Chemical or physical extraction of carbon from rice husk. This work will be performed during whole period of the project.	X	X	X
1.7: Using extracted carbon as starting carbon source to synthesize carbon based nanostructures such as porous carbon materials and carbon nanotubes,	X		
1.8: Using directly rice husk as carbon source to synthesize porous carbon materials and carbon nanotubes,	X		
1.9: Using directly rice husk as silica source and other synthetic inorganic source to synthesize silicoaluminate, metallosilicate mesoporous materials,	X		
1.10: Using directly rice husk as silica and carbon sourcse to synthesis Si carbide materials,	X		
1.11: Characterization of these new nanomaterials synthesized from rice husk,	X	X	X
1.12: Preparation of the first series of catalysts and adsorbents on the basis of the information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.4 and 3.5**),	X	X	X
1.13: Modification of our porous nanostructures as catalysts and adsorbents on the basis of scientific results (catalytic reactions and purification) and information from Vietnamese partners (**VP1** and **VP2**) (**See Tasks 2.7 and 3.9**),	X		
1.14: Characterization of these modified nanomaterials by a series of physico-chemical techniques,	X		
1.15: Remodification and Functionalization of our as prepared porous materials and our modified porous nanomaterials on the basis of the test results supplied by Vietnamese partners (**VP1** and **VP2**) (**See tasks 2.10 and 3.12**) and characterization of these re-modified and functionalized porous nanomaterials by a series of physico-chemical techniques,	X	X	X
1.16: After testing by **VP1** and **VP2** (**See Tasks 2.13 and 3.15**), production in large quantity of the best catalyst and adsorbent by **BP** and use of these materials by **VP1** and **VP2** for testing long period in Viet Nam . The characterization of these porous nanomaterials produced in large quantity by a series of physico-chemical techniques.	X	X	X
WP 2 :			
2.1: Bibliographic research		X	X
2.2: Determination of main characteristics of vegetable oil sludge as	X	X	X

boiling point, heavy metal contents, iodine index …etc,			
2.3: Construction and evaluation of the catalytic testing system (Microreactor),		X	X
2.4: First analysis with **BP** for the selection of the first series of catalysts (**See Task 1.12**),	X	X	X
2.5: Production of biodiesel by pyrolysis and catalytic cracking, using catalysts from Belgium partner (**BP**-CMI laboratory) as well as zeolites catalysts from Vietnamese partners. First screening of the catalysts in microreactor by **VP1 and VP2** and the characterization of used catalysts by a series of physico-chemical techniques by **BP**,	X	X	X
2.6: Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscocity index, Acid number.. etc		X	
2.7: Establishment of the criteria for the selection of the best catalysts with the participation of **BP** (**See Task 1.13**),	X	X	X
2.8: Catalytic Testing of the modified porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.13**). The characterization of used catalysts by a series of physico-chemical techniques will be done by **BP**,	X	X	
2.9: Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscosity index, Acid number.. etc		X	
2.10: Establishment of the correlation between the characteristics of catalysts and the catalytic behaviour with the participation of **BP** in order to further modify or functionalize the modified porous nanocatalysts (**See Task 1.15**),	X	X	X
2.11: Catalytic Testing of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**Task 1.15**) and characterization of used catalysts by a series of physico-chemical techniques by **BP**,	X	X	
2.12: Evaluation of the quality of biodiesel products by using diferrence techniques : Cetane number, viscosity index, Acid number.. etc,		X	
2.13: Selection of the best catalyst for the long period catalytic testing with the participation of **BP**.	X	X	X
2.14: Catalytic testing with large quantity of catalysts by **VP1**, the characterization of used catalysts by a series of physico-chemical techniques by **BP**,	X	X	
2.15: Evaluation of the quality of biodiesel products by using difference techniques : Cetane number, viscosity index, Acid number.. etc		X	
WP 3:			
3.1: Production of alcohols from fermentation of rice, sugarcane and cassava (Vietnamese agro-products) by distillation.		X	X
3.2: Construction and evaluation of the purification system (Microreactor),		X	X
3.3: Establish the technology of absolute alcohols production for use as “clean fuel” with capacity of 100litters/day.		X	X
3.4: Construction and evaluation of a pilot system for the evaluation of adsorbents in a large quantity and a long period,		X	X
3.5: First analysis with **BP** using Zeolite A adsorbent	X	X	X
3.6: Concentration of alcohols (concentration>99.5%) by using zeolites prepared from Kaolin of Vietnam. First screening of the	X		X

adsorbents in microreactor and characterization of used adsorbents by a series of physico-chemical techniques,			
3.7: Evaluation of the quality of alcohols produced with zeolite A adsorbents,	X	X	X
3.8: Establishment of the criteria for the selection of the best adsorbents with the participation of **BP** (**See Task 1.13**),	X	X	X
3.9: The information obtained from 3.6 and 3.7 will be supplied to Belgian partner to modify porous adsorbents,	X	X	X
3.10: Adsorption Testing of the modified zeolite A adsorbents and characterization of used adsorbents by a series of physico-chemical techniques,	X		X
3.11: Evaluation of the quality of alcoholic products by using different techniques,			X
3.12: Establishment of the correlation between the characteristics of adsorbents and the purification behaviour in order to further modify or functionalize the modified porous nanoadsorbents ,	X	X	X
3.13: Alcohol concentration test of the re-modified and functionalized porous nanomaterials supplied by Belgian partner (**BP**) (**See Task 1.15**) and characterization of used adsorbents by a series of physico-chemical techniques,	X		X
3.14: Evaluation of the quality of alcohol products by using different techniques,			X
3.15: Selection of the best adsorbents for the long period catalytic testing on the basis of the information obtained from 3.13 and 3.14 with the participation of **BP**,	X	X	X
3.16: Purification testing in a pilot with large quantity of catalysts and characterization of used adsorbents by a series of physico-chemical techniques,		X	X
3.17: Evaluation of the quality of alcohol products by using different techniques.		X	X

Annexe 2. Time Schedule

Tasks	***N***	***D***	***J***	***F***	***M***	***A***	***M***	***J***	***J***	***A***	***S***	***O***	***N***	***D***	***J***	***F***	***M***	***A***	*M*	*J*	*J*	*A*	*S*	*O*
WP 1																								
1.1	**X**																							
1.2	**X**	**X**	**X**																					
1.3			**X**	**X**	**X**	**X**	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1.4				**X**	**X**	**X**	X																	
1.5					**X**	**X**	X	X																
1.6							X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
1.7									X	X	X	X	X	X										
1.8										X	X	X	X	X	X	X	X							
1.9											X	X	X	X	X	X	X							
1.10												X	X	X	X	X	X							
1.11				**X**	**X**	**X**	X	X	X	X	X	X	X	X	X	X	X	X	X					
1.12					**X**	**X**	X	X	X	X	X	X	X	X										
1.13										X	X	X	X	X	X	X	X	X	X					
1.14														X	X	X	X	X	X	X				
1.15																X	X	X	X	X	X	X		
1.16																				X	X	X	X	X
WP2																								
2.1	**X**																							
2.2		**X**	**X**	**X**																				
2.3				**X**	**X**	**X**	X	X	X	X	X													
2.4	**X**	**X**	**X**	**X**	**X**	**X**	X																	
2.5						**X**	X	X	X	X	X													
2.6							X	X	X	X	X	X												
2.7								X	X	X	X	X	X											
2.8										X	X	X	X	X	X	X								
2.9											X	X	X	X	X	X	X							
2.10												X	X	X	X	X	X	X	X					
2.11																	X	X	X	X	X			
2.12																		X	X	X	X	X		
2.13																			X	X	X	X	X	
2.14																				X	X	X	X	X
2.15																				X	X	X	X	X
WP3																								
3.1	**X**	**X**	**X**																					
3.2		**X**	**X**	**X**	**X**	**X**	X																	
3.3					**X**	**X**	X	X	X	X	X	X												
3.4					**X**	**X**	X	X	X	X	X	X												
3.5	**X**	**X**	**X**	**X**	**X**	**X**	X																	
3.6						**X**	X	X	X	X	X													
3.7							X	X	X	X	X	X												
3.8								X	X	X	X	X	X	X	X									
3.9									X	X	X	X	X	X	X	X								
3.10											X	X	X	X	X	X	X							
3.11												X	X	X	X	X	X	X						
3.12													X	X	X	X	X	X	X					
3.13																X	X	X	X	X	X			
3.14																		X	X	X	X	X		
3.15																		X	X	X	X	X	X	
3.16																				X	X	X	X	X
3.17																					X	X	X	X

Annex 3

List of publications, patents and presentations by this joint project

1. Le Thi Hoai Nam, Nguyen Dinh Tuyen, Nguyen Ngoc Triu, Nguyen Thanh Loan, Tran Quang Vinh, Van Dinh Son Tho, Bao-Lian Su. "Study on synthesis of ZSM-5 zeolites using vietnamese rice husk in vegetable oil sludge cracking reaction" Journal of Chemistry, P.1-6, Vol.45(6A), 2007
2. Le Thi Hoai Nam, Nguyen Dinh Tuyen, Nguyen Thi Thanh Loan, Tran Quang Vinh, Nguyen The Anh, Van Dinh Son Tho, Le Thi Kim Lan, Bao-Lian Su. "Synthesis of biofuel by catalytic cracking of vegetable oil sludge in the presence pf nano-meso ZSM-5 catalyst". 6th International mesostructured materials Symposium (poster). Belgium, 2008.
3. Le Thi Hoai Nam, Nguyen Dinh Tuyen, Tran Quang Vinh, Nguyen Thi Thanh Loan, Nguyen Ngoc Triu, Van Dinh Son Tho, Do Xuan Dong, Le Thi Kim Lan, Nguyen The Anh, Le Quang Du, Vu Thi Minh Hong, Xiao-Yu Yang, Zoulika Hadj-Sadok, Bao-Lian Su. "Synthesis, characterization and catalytic properties of HY and HZSM-5 Zeolites Synthesized by Using silica Resource from Vietnamese rice husk in the cracking reaction of vegetable oil slugde". Proceedings of International scientific conference on "chemistry for development and integration". P.1097-1109. Ha Noi, 2008.
4. Le Thi Hoai Nam, Tran Quang Vinh, Nguyen Thi Thanh Loan, Bao-Lian Su. "Study on synthesis, characterization of HZSM-5 zeolites using rice husk". Journal of Chemistry, Vol. 47 (1), p.47-53, 2009
5. Do Xuan Dong, Le Thi Hoai Nam, Le Quang Du, Chu Van Giap, Tran Thi Nhu Mai, Bao lian Su, "Study on synthesis Si-C materials with mesoporous sizes using Si-C sources from Vietnamese rice husk", Journal of Chemistry, Vol. 47 (2A), p.352-357, 2009.
6. Le Thi Hoai Nam, Nguyen Ngoc Triu, Tran Quag Vinh, Bao-Lian Su. "Study on synthesis, characterization of HY zeolites using rice husk", Journal of Science and Technology, 2009.
7. Patent: Le Thi Hoai Nam, Bao-Lian Su, Nguyen Dinh Tuyen, Do Xuan Dong, Van Dinh Son Tho, Nguyen Thi Thanh Loan, Le Thi Kim Lan, Tran Quang Vinh, Xiao-Yu

Yang, “The synthesis procedure of Nano-meso ZSM-5 multi-porous material using silica source from rice husk” (2008)

8. Le Thi Hoai Nam, Tran Quang Vinh, Nguyen Thi Thanh Loan, Van Dinh Son Tho, Xiao-Yu Yang, Bao Lian Su, Preparation of bio-fuels by catalytic cracking reation of vegetable oil sludge , Fuel 90 (2011) 1069-1075
9. Le Thi Hoai Nam, Nguyen Thi Thanh Loan, Tran Quang Vinh, Le Thi Kim Lan, Le Quang Du, Bao Lian Su, Effect of crystallization time on forming structure of new useful multiporous material “Nano-meso ZSM-5” and its application, Journal of Experimental Nanoscience (JEN), p.1-12, 2011
10. Xiao-Yu Yang, Yu Li, Feng-Shou Xiao, Gustaaf Van Tendeloo, Bao-Lian Su, One-Pot Synthesis of Catalytically Stable and Active Nanoreactors: Encapsulation of Size-Controlled Nanoparticles within a Hierarchically Macroporous Core@Ordered Mesoporous Shell System, Adv. Mater. 2009, 21, 1368–1372

Fuel 90 (2011) 1069–1075

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Preparation of bio-fuels by catalytic cracking reaction of vegetable oil sludge

Le Thi Hoai Nam [a,*], Tran Quang Vinh [a], Nguyen Thi Thanh Loan [a], Van Dinh Son Tho [b], Xiao-Yu Yang [c], Bao-Lian Su [c,*]

[a] Institute of Chemistry, Vietnamese Academy of Science and Technology, Hanoi, Viet Nam
[b] Hanoi University of Technology, Viet Nam
[c] FUND University of Namur, Bruxelles, Namur, Belgium

ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form 14 October 2010
Accepted 15 October 2010
Available online 24 November 2010

Keywords:
Biofuel
Multi-porous catalyst
Catalytic cracking
Rice husk
Vegetable oil sludge

ABSTRACT

Biofuel production from vegetable oil is potentially a good alternative to conventional fossil derived fuels. Moreover, liquid biofuel offers many environmental benefits since it is free from nitrogen and sulfur compounds. Biofuel can be obtained from biomass (e.g. pyrolysis, gasification) and agricultural sources such as vegetable oil, vegetable oil sludge, rubber seed oil, and soybean oil. One of the most promising sources of biofuel is vegetable oil sludge. This waste is a major byproduct of vegetable oil factories. It consists of triglycerides (61%), free fatty acid (37%) and impurities (2%). The hydrocarbon chains of triglycerides and free fatty acid are mainly made up of C_{16} (30%) and C_{18} (36%) hydrocarbons. The others consist of C_{12}–C_{17} hydrocarbon chains. Transesterification can help in converting vegetable oil sludge into biofuel. The disadvantage of this method is that a large amount of methanol is required. The alternative method for this conversion is catalytic cracking. The objective of this research is to evaluate and compare the pyrolysis process with cracking catalytic reaction of vegetable oil sludge by Micro-activity test MAT 5000 of Zeton-Canada.

A ZSM-5/MCM-41 multiporous composite (MC-ZSM-5/MCM-41), was successfully synthesized using silica source extracted from rice husk. The material has the MCM-41 mesoporous structure, and its wall is constructed by ZSM-5 nanozeolite crystals. The porous system of the material includes pores of the following sizes: 5 Å (ZSM-5 zeolite), 40 Å (MCM-41 mesoporous material), and another porous system whose diameter is in the range of 100–500 Å (mesoporous system) formed by the burning of organic compounds that remain in the material during the calcination process. This pore system contributes to an increase in the catalytic performance of synthesized material.

The results of vegetable oil sludge cracking reaction show that the product consists of fractions such as dry gas, liquefied petroleum gas (LPG), gasoline, light cycle oil (LCO), and (heavy cycle oil) HCO, which are similar to those of petroleum cracking process.

MC-ZSM-5/MCM-41 catalyst is efficient in the catalytic cracking reaction of vegetable oil sludge as it has higher conversion and selectivity for LPG and gasoline products in comparison to the pyrolysis process. Product distribution (% of oil feed) of cracking reaction over MC-ZSM-5/MCM-41 is coke (3.4), total dry gas (7.0), LPG (31.1), gasoline (42.4), LCO (8.9), HCO (7.2); and that of pyrolysis are coke (19.0), total dry gas (9.3), LPG (16.9), gasoline (28.8), LCO (13.7), and HCO (12.3).

These results have indicated a new way to use agricultural waste such as rice husk for the production of promising catalysts and the processing of vegetable oil sludge to obtain biofuel.

1. Introduction

Nowadays, the energy consumption is drastically increasing due to the rapid growth of population combined with increased economic development and the dependency on the earth's natural resources (such as fossil fuels). This is considered as the main reason for the increased pollution of the atmosphere and the resulting potential for climate change [1]. Out of the total energy consumed as fossil fuels (80.3%), the transport sector, which is the main contributor to air pollution, accounts for 57.7% [1]. In addition, the exhaustion of fossil derived gas and oil resources is also the serious problem in energy security.

Biodiesel fuels are attracting increasing attention worldwide as blending components or as direct replacements for fuel in vehicle

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* Corresponding authors. Tel.: +84 4 22192481; fax: +84 4 38361283 (L.T.H. Nam), tel.: +32 81 72 45 31 (Direct), +32 81 72 54 16 (Secretary); fax: +32 81 72 54 14 (B.-L. Su).

E-mail addresses: namlht2005@yahoo.com (L.T.H. Nam), bao-lian.su@fundp.ac.be (B.-L. Su).

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doi:10.1016/j.fuel.2010.10.060

engines [2]. There are several methods for the conversion of vegetable oils to biofuels, such as pyrolysis, gasification, transesterification processes, catalytic cracking reaction, and hydrocracking reaction [3–7]. Among these methods, the catalytic cracking of vegetable oils to produce biofuels has been widely studied by many researchers over the world [8–11]. However, the use of this method on the industrial scale is limited by the high cost and availability of vegetable oil feedstock (75% of the total manufacturing cost). This restriction causes the production costs to reach approximately 1.5 times higher than that for diesel [12,13]. Therefore, to solve this problem, waste vegetable oil and vegetable oil sludge are used as raw materials because they are considerably cheaper than virgin vegetable oil [14,15]. Further, we studied their cracking reaction as a potential process for the production of biofuels.

Currently, the amount available of vegetable sludge is not much in Vietnam (approximately 0.6 million tons/year), because vegetable oil plants almost import purified vegetable oil and they only continue to purify more by the request of customer. The price of import purified vegetable oil is expensive. The price of crude vegetable oil is much cheaper than purified one. But the treatment of vegetable oil sludge is complicate. So, by the obtained result of this research, Vietnam now may import cheap crude vegetable oil to produce purified type. The vegetable oil sludge could be more available and applied for the field of biofuel production.

In this article, we report the results of a MC-ZSM-5/MCM-41 synthesized using silica extracted from Vietnamese rice husk. This material is the combination of ZSM-5 zeolite and MCM-41 mesoporous material and has some different names that were shown in some papers such as MCM-41/ZSM-5 composites [16,17], meso-ZSM-5 composite zeolite [18], ZSM-5-MCM-41 micro-mesoporous molecular sieve [19]. All of these materials have multiporous system (micropore system of ZSM-5 zeolite and mesopore system of MCM-41 material), and are formed by nano crystals of ZSM-5 zeolite. Beside this, the new MC-ZSM-5/MCM-41 also have a new feature that was formed by the special feature of silica source extracted from rice husk. Its catalytic activity has been investigated in the vegetable oil sludge catalytic cracking reaction; this process has been then compared with the pyrolysis process. The results show that the catalytic cracking reaction over MC-ZSM-5/MCM-41 catalyst is more efficient than pyrolysis, especially with regard to the selectivity of LPG and gasoline products.

2. Experimental

2.1. Extraction of silica from rice husk

Silica was extracted from rice husk (for 30 min) using 1% sodium hydroxide solution at a temperature of 80 °C. The resulting Si-containing solution was used as a silica source. The compostion of extracted solution included SiO_2: 9 g/l, Na_2O: 7.8 g/l and others. This solution was used together with other synthetic inorganic materials to synthesize MC-ZSM-5/MCM-41.

2.2. Synthesis of MC-ZSM-5/MCM-41

The typical synthesis process is described as follows.

The first step: ZSM-5 seed was prepared by using Si-containing solution, $Al_2(SO_4)_3.18H_2O$, templating agent tetrapropyl ammonium bromide (TPABr) and sulfuric acid. The reaction mixture was stirred for 2 h to form a homogenous gel. The resulting gel was then transferred into an autoclave, and the temperature was maintained under 150 °C for 10–15 h by stirring to form ZSM-5 zeolite seed.

The second step: ZSM-5 zeolite seed was added to cetyltrimethylammonium bromide (CTMABr) and stirred vigorously at room temperature for 1 h. The resulting homogenous mixture was transferred into an autoclave, and the temperature was maintained under 150 °C for 10–15 h. The solid product was filtered and washed using deionized water to pH 7, dried at 100 °C for 12 h, and calcined at 540 °C for 5 h to remove the template. Then, product was ion exchanged with NH_4NO_3 2 M, washed, dried, and calcined again to form NM-HZSM-5. A white powder is obtained, which was used as the sample.

2.3. Characterization

X-ray diffraction (XRD): powder X-ray diffraction patterns were recorded on a HUT-PCM-Bruker D8 Advance instrument diffractometer system equipped with Ni-filtered Cu Kα radiation (operating at 40 kV, 40 mA, wavelength λ = 0.154 nm). The patterns were recorded at room temperature (298 K); 2θ values ranged from 0.1° to 5° and 5° to 50°, and the scanning speeds were 1°min^{-1} and 2°min^{-1}. Transmission electron microscopy (TEM) was performed using a Philips Tecnai-10 microscope at 100 kV. Scanning electron microscopy (SEM) was carried out using a Jeol JSM-7500F instrument. Sample was dried, mounted on a thin plate and coated by a thin gold layer before recording. The FT-IR spectra were recorded using a IMPACT-410 (Germany) Infrared Spectrophotometer at room temperature in the range 1300–400 cm^{-1} on thin wafer of KBr in which 1% (w/w) of sample was dispersed. Nitrogen adsorption/desorption isotherms: the BET surface area and pore volume were measured by using nitrogen adsorption/desorption isotherms by using ASAP2010 equipment (Micrometrics-USA). The sample was treated in vacuum of 10^{-6} mmHg, at 120 °C for 4 h and at 350 °C for 9 h. Presence of aluminum within the framework was detected through ^{27}Al Solid state magic angle spinning (MAS)-NMR method. The spectrum was obtained using a Bruker MSL400 spectrometer for ^{27}Al (at 104.3 MHz).

2.4. Catalytic cracking reaction

The vegetable oil sludge was obtained from Vietnamese Van Dao Company. Its composition is as follows: triglycerides (61%), free fatty acid (37%) and impurities (2%). The hydrocarbon chains of triglycerides and free fatty acid are mainly C_{16} (30%) and C_{18} (36%) hydrocarbon. The others consisted of C_{12}–C_{17} hydrocarbon chain.

Micro-activity test (MAT 5000) system of Zeton-Canada was used for catalytic cracking. ASTM D5154 testing method was applied on the procedures of catalytic cracking; the main parameters of catalytic cracking and pyrolysis processes are described in Table 1. The coke formation was evaluated in situ by combustion with air and then quantifying the released CO_2 using an infra-red gas analyzer (1440 Gas Analyzer – Servomex). The gas product was collected in a brine water glass bottle and analyzed by using Refinery gas analyzer – Trace GC – Thermo Electro. The boiling distribution of the liquid product was determined by a SIMDIST system linked with a

Table 1
The main parameters of pyrolysis and catalytic cracking conditions.

Parameters	Pyrolysis	Catalytic cracking
Weight of catalyst, g		4.1
Catalyst bed cracking, °C	600	483
Cat./oil (C/O) ratio		4
WHSV, l/h		12
Total N_2 flow rate (pre-purge), ml/s	50	50
Total N_2 flow rate (reaction), ml/s	5	5
Total N_2 flow rate (stripping), ml/s	25	25
Oil feed temperature, °C	50	50
Oil feed density at 50.0 °C, g/ml	0.9	0.9
Actual volumetric oil feed, ml	1.2	1.2
N_2 pre-purge time, min	15	15
N_2 reaction time, sec	75	75
N_2 stripping time, min	10	10

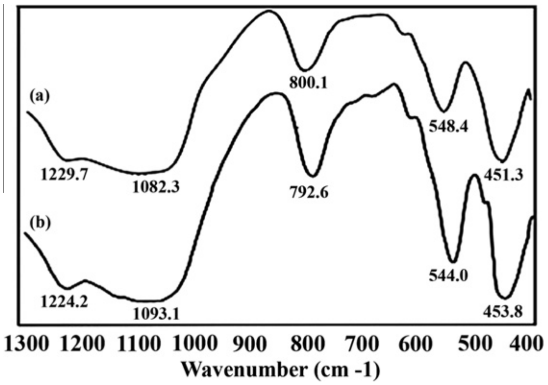


Fig. 1. IR spectra of the samples. IR spectrum of ZSM-5 Standard sample (a) and IR spectrum of MC-ZSM-5 (b).

GC Thermo Electro system, detector FID integrated TriPlus autosampler. The calibration gas is RGA standard of MESA International Technologies, Inc. The calibration liquid for distillation simulation is ASTM D2887 Calibration mix (RESTEK). The composition of the liquid fraction from the cracking of the vegetable oil sludge was determined by GC–MS (GC-HP HEWLETT 5890 PACKARD SERIES II; MS-HEWLETT 5989B PACKARD).

3. Results and discussion

3.1. Characterization of MC-ZSM-5/MCM-41

3.1.1. Infrared spectroscopy (IR)

Fig.1 shows the IR spectra (range: 400–1300 cm^{-1}) of ZSM-5 standard sample (Fig. 1a) and MC-ZSM-5/MCM-41 sample using silica source from rice husk (Fig. 1b). From the observed spectra, we can see that the IR spectrum of MC-ZSM-5/MCM-41 synthesized using rice husk silica sample completely agrees with that of the ZSM-5 standard sample. No other phase occurred in the spectrum of the synthesized material. The peak at 550 cm^{-1} is attributed to the fluctuation of five-membered rings in ZSM-5 structure, and it is typical for the crystalline status of ZSM-5 zeolite. According to [20], the crystallinity of the synthesized material is 100% if the intensity ratio of 550 cm^{-1} peak to 450 cm^{-1} peak is 0.8. The calculated ratio in our case is 0.8; this confirmed that the crystallinity of the synthesized material reaches approximately 100%.

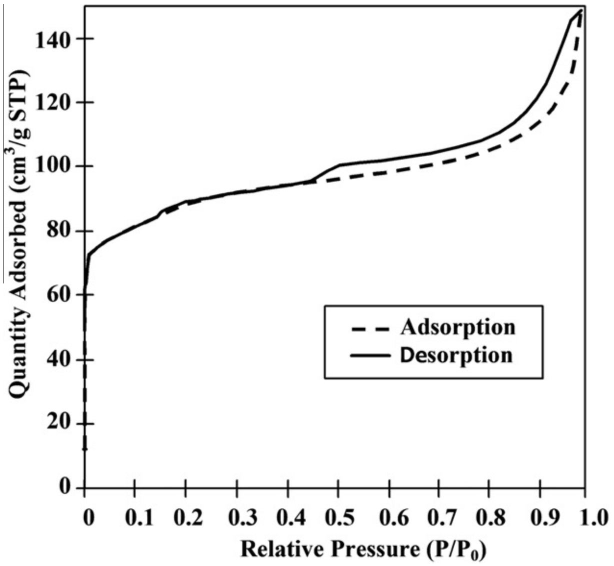


Fig. 3. N_2 adsorption/desorption isotherms.

3.1.2. X-ray diffraction

The XRD pattern of ZSM-5 standard sample is shown in Fig. 2a and the XRD patterns of MC-ZSM-5/MCM-41 are shown in Fig. 2b and Fig. 2c. The XRD pattern with large angle (5°–40°, Fig. 2b) shows very strong intensive peaks, and no odd peaks are found in comparison to the XRD pattern of ZSM-5 standard sample (Fig. 2a). The MFI structure (ZSM-5) of the sample was confirmed by observing the intense typical reflection peaks at 2θ at 9.1° and 24.1° [20]. This result shows that the sample has high content of crystalline phase and high purity. Moreover, the XRD pattern with small angle (Fig. 2c) indicates the presence of a peak at 2θ region of 0–2° ($\sim$0.5°). This peak is attributed to mesophase [21]. The XRD

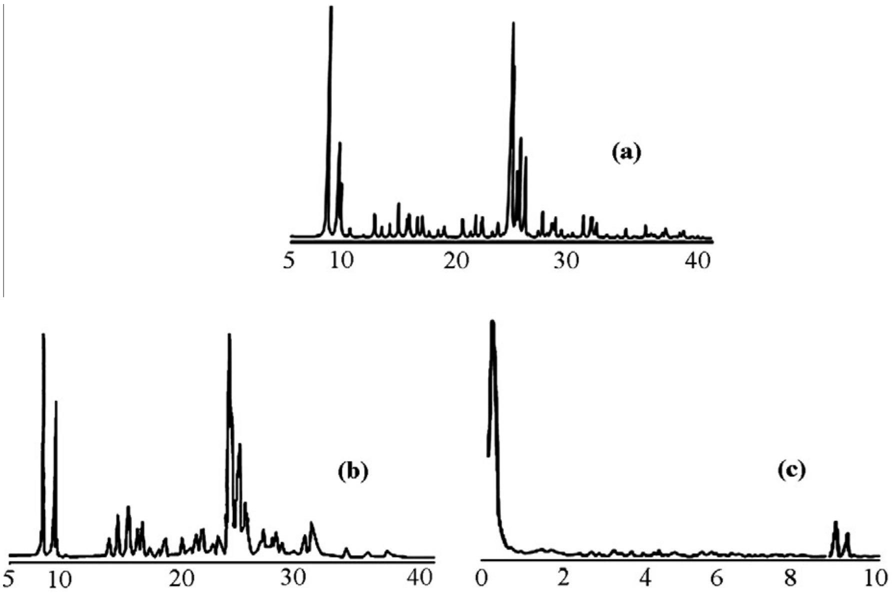


Fig. 2. XRD pattern of ZSM-5 standard sample at large angle (5–40°) (a), XRD pattern of MC-ZSM-5 at large angle (5–40°) (b) and XRD pattern of MC-ZSM-5 at small angle (0–10°) (c).

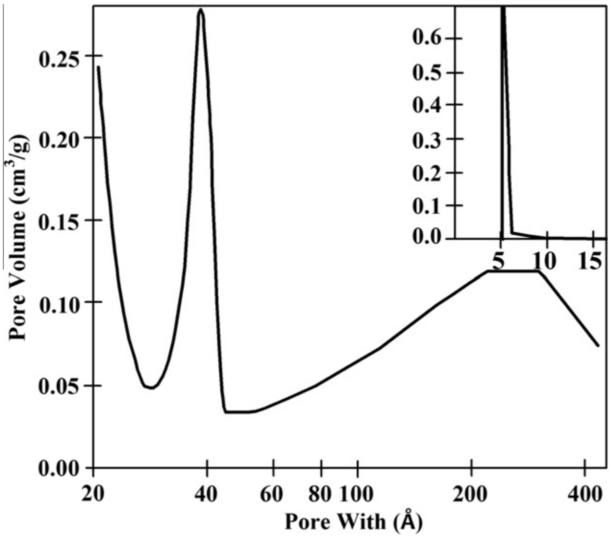


Fig. 4. Pore size distribution.

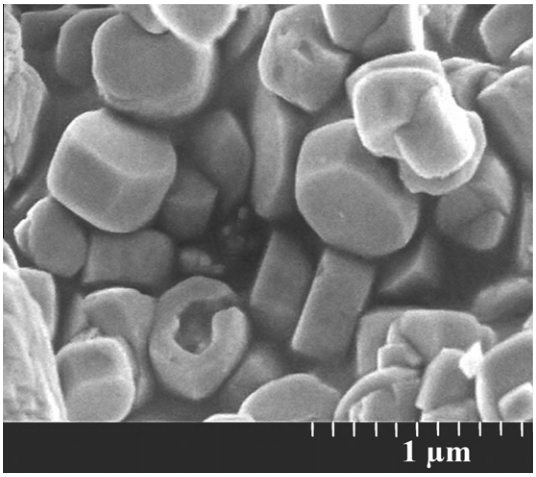


Fig. 5. SEM image.

patterns at small and large angles indicate that the structure of the synthesized sample contains both microphase (ZSM-5 zeolite) and mesophase (MCM-41).

3.1.3. BET characterization

The mesostructure of MC-ZSM-5/MCM-41 sample was also confirmed by N_2 adsorption/desorption isotherms. Fig. 3 shows the appearance of a wide hysteresis loop. This typical shape is characterized as mesoporous structure [21]. The result shows that the sample has two porous systems: micropores with size of 6 Å and mesopores with size of 40 Å and 200 Å, The specific surface area is ~477 m^2/g (Fig. 4).

3.1.4. SEM and TEM images

The SEM and TEM images show the morphology of MC-ZSM-5/MCM-41 sample (Figs. 5 and 6). The images clearly indicate the existence of long-range mesophase. The zeolite seeds assembled to create MCM-41 ordered mesoporous structure under the direction of the organic template. From the result, it is evident that MC-ZSM-5/MCM-41 with a size of 0.5 µm was formed.

In addition, the observed TEM image shows a very interesting feature of the synthesized sample. Besides the MCM-41 mesoporous system (size: 4 nm), there is another porous system which has diameter in range of 10–50 nm. The existence of this pore system can be explained by the presence of organic substances (in extracted silica solution), which are removed in calcination process. As a result of the removal of organic substances, an additional mesoporous system in the synthesized material is formed, and this result is in good agreement with that obtained from the BET method.

3.1.5. Nuclear magnetic resonance ^{27}Al NMR method

The existence of Al^{3+} ion in zeolite framework relates to the acidity of material due to the tetrahedral coordination of Al^{3+} ion for the formation of Bronsted and Lewis acidic sites in the zeolite. In order to determine the distribution of Al^{3+} ion in the synthesized material, the ^{27}Al-NMR method was used. Fig. 7 shows the ^{27}Al-NMR of MC-ZSM-5/MCM-41.

The ^{27}Al-NMR of MC-ZSM-5/MCM-41 gives a signal at 55 ppm with high intensity, which is ascribed to Al unit connected to the nearest-neighboring Si tetrahedra [22,23]. However, it also shows one more signal at 0 ppm with very low intensity, which is negligible in comparison to the intensity of signal at 55 ppm. According to references [22,23], this signal is attributed to Al^{3+}, which is not presented in zeolite framework. This indicates that most of the aluminum ions are presented in the zeolite framework.

3.2. Catalytic performance

In order to evaluate the catalytic activity of synthesized material, the vegetable oil sludge cracking reaction was performed.

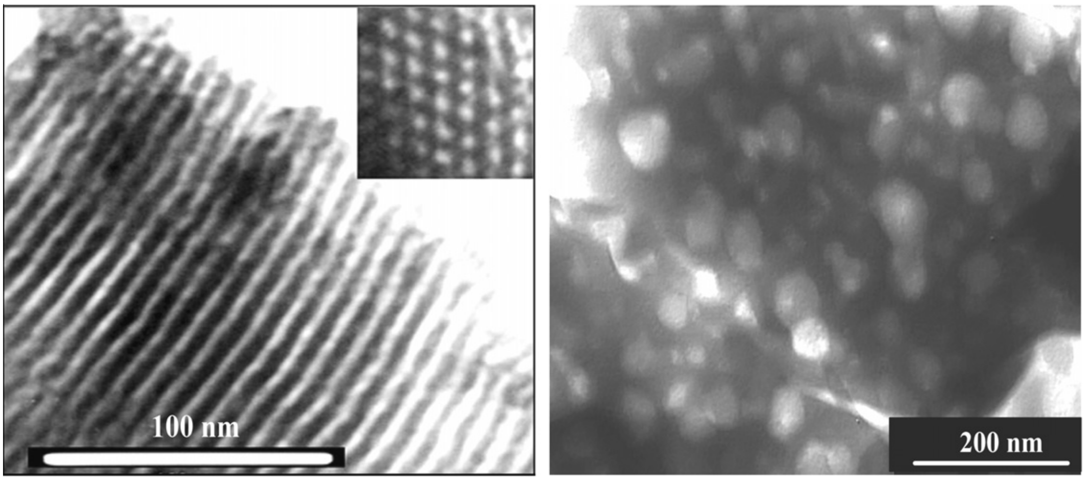


Fig. 6. TEM images.

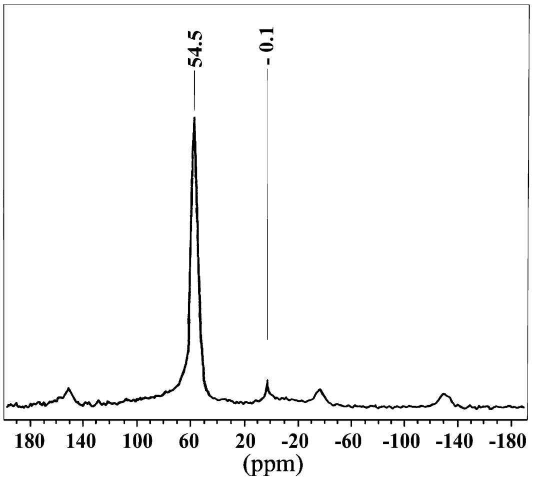


Fig. 7. ^{27}Al-NMR of MC-ZSM-5.

The reaction was carried out using an MAT 5000 system; the input parameters are listed in Table 1.

The catalytic activity is measured via product yield and conversion of the cracking reaction. The main products of the cracking reaction are as follows:

- Dry Gases mainly consisted of H_2, CO, CO_2, CH_4, C_2H_6, and C_2H_4 gases
- Liquefied Petroleum Gas (LPG): consisted of C3—C4 (C3, C3=, *i*C4, *n*C4, C4=, Propadien)
- Gasoline: initial boiling point (IBP) is less than 221 °C and also consisted of C_5^+ gases in gas product.
- LCO (light cycle oil): IBP ranges between 221 °C and 343 °C
- HCO (heavy cycle oil): IBP is more than 343 °C and it consists of other fragments of the vegetable oil sludge that did not undergo cracking.
- Coke.

Table 2 describes the products obtained after pyrolysis (thermal cracking) and after the cracking of vegetable oil sludge by using MC-ZSM-5/MCM-41 as catalyst. The results indicate that MC-ZSM-5/MCM-41 is effective for the cracking of vegetable oil sludge reaction to obtain the biofuel. Both conversion and the total yield of LPG and gasoline (desirous products) of the catalytic cracking reaction over MC-ZSM-5/MCM-41 are much higher than that of pyrolysis process. In contrast, the total yield of coke, HCO and LCO (undesirous products) also in catalytic cracking is considerably lower that that of pyrolysis.

Gas product was analyzed by gas chromatography system (Refinery gas analyzer – Trace GC – Thermo Electro). Table 3 describes the composition of the gas product. The total quantity of gas product of the cracking reaction over MC-ZSM-5/MCM-41 catalyst is higher than that of the pyrolysis. It indicates that the catalytic cracking underwent more deeply than the pyrolysis did. Moreover, the presence of *i*-Butane in gas product of catalytic cracking over MC-ZSM-5/MCM-41 shows that there is an isomerization occurred.

The liquid product of the cracking reaction was analyzed by using SIMDIST GC Thermo Electro system. The composition of liquid fraction is measured via the distribution of boiling point (Fig. 8). The chromatogram of vegetable oil sludge shows that it has three areas of boiling point. All the boiling points that are above 343 °C correspond to the segments of HCO. After the catalytic cracking reaction and pyrolysis, the components are cracked

Table 2
Product composition of vegetable oil sludge cracking reaction and pyrolysis.

Composition	MC-ZSM-5/MCM-41 (wt% of oil feed)	Pyrolysis (wt% of oil feed)
Conversion	81.9	56.7
Coke	3.4	19.0
Dry gas	7.0	9.3
LPG	31.1	16.9
Gasoline	42.4	28.8
LCO	8.9	13.7
HCO	7.2	12.3

Table 3
Composition of gas product.

Composition	MC-ZSM-5/MCM-41 (wt% of oil feed)	Pyrolysis (wt% of oil feed)
2-Methyl-2-butene	1	1.6
Hydrogen	0.1	0.0
Propane	8.6	2.1
Propylene	6.8	7.3
i-Butane	5.4	0.0
n-Butane	2.9	0.2
1-Butene + *i*-butene	3.8	1.9
trans-2-Butene	1.6	0.2
cis-2-Butene	1.2	0.1
1,3-Butadiene	0	1.1
Ethylene	4.8	3.8
Ethane	1.1	2.0
Methane	0.8	1.4
Total	38.1	21.7

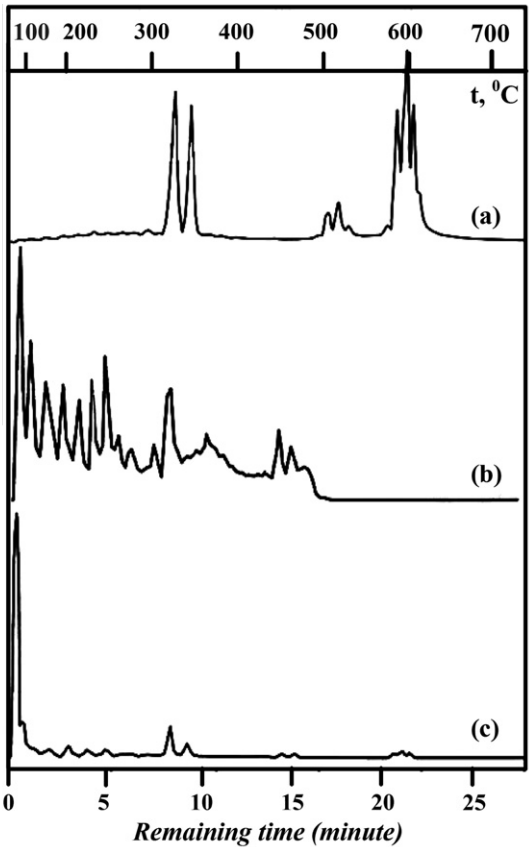


Fig. 8. The distribution of liquid product with respect to the boiling point. Vegatable oil sludge (a), thermal cracking (b) and catalytic cracking using MC-ZSM-5/MCM-41 (c).

Table 4
Some main products of pyrolysis of vegetable oil sludge.

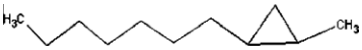
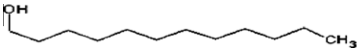
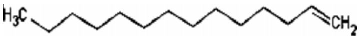
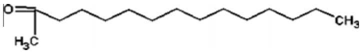
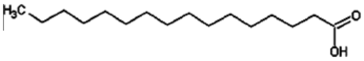
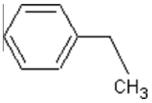
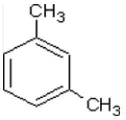
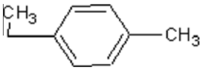
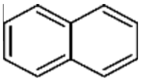
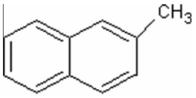
No.	Substance	Structure formula
1	1-Hexyl-2-methyl-cyclopropane	
2	Dodecanol	
3	1-Tetradecene	
4	Pentadecane	
5	1-Pentadecane	
6	2-Pentadecanone	
7	Hexadecanoic acid	

Table 5
Some main products of catalytic cracking of vegetable oil sludge by using MC-ZSM-5/MCM-41 as catalyst.

No.	Substance	Structure formula
1	Ethyl-benzene	
2	1,3-dimethyl-benzene	
3	1,4-dimethyl-benzene	
4	4-Ethyl-toluene	
5	Napthalene	
6	2-Methyl-napthalene	

to form the lighter products (LPG, gasoline, etc.). The chromatogram of the catalytic cracking reaction over MC-ZSM-5/MCM-41 shows the peaks near 75 °C and 343 °C; the intensity of peaks near 75 °C are higher than that of the peaks near 343 °C. This shows that the total yield of LPG and gasoline was higher than that of the total yield of HCO and LCO after the cracking reaction over this catalyst. This result is not clearly shown in the spectrum of thermal cracking (pyrolysis process). There are many peaks in range of 75–343 °C. This proves that the product selectivity of catalytic cracking reaction over MC-ZSM-5/MCM-41 is much better than that of the pyrolysis process.

Tables 4 and 5 describe some main products of the catalytic cracking of vegetable oil sludge over MC-ZSM-5/MCM-41 catalyst and the pyrolysis process. The results show that main products of pyrolysis are the derivatives of paraffinic hydrocarbon and that of the catalytic cracking are polycyclic aromatic hydrocarbons. The aromatic hydrocarbons are the desirous components because they lead to high octane number of gasoline. Moreover, they are the suitable initial feed for the petrochemistry.

The results show that the quantity of coke obtained from pyrolysis is high because the pyrolysis takes place via radical mechanism. The formation of radicals leads to the formation of coke [24]. The total coke formed in the pyrolysis process is higher than that formed in catalytic cracking reaction. On the other hand, this result also confirms that the mechanism involved in catalytic cracking reaction over MC-ZSM-5/MCM-41 catalyst is carbenium with aromatization process [25]. The existence of long-range dimensional mesophase and microphase is the advantage of MC-ZSM-5/MCM-41. Then, the easier diffusion of feed and product is going to increase the conversion of cracking reaction. Due to the pore structure and acidity of MC-ZSM-5/MCM-41, the temperature of the catalytic cracking reaction is lower than that of pyrolysis but the product yield is higher.

The priority of catalytic cracking over MC-ZSM-5/MCM-41 in comparison to pyrolysis could be explained by the advantage of multiporous structure of MC-ZSM-5/MCM-41 catalyst. The big molecules contained in feedstock are cracked via two steps. At the first step, they move to the mesopore systems and to be cracked to smaller molecules. At the second step, these smaller molecules are continued to move to the micropore system and to be cracked to light molecules. In addition, the presence of the aromatics in the liquid product also shows the effect of ZSM-5 and MCM-41 structure of MC-ZSM-5/MCM-41 on the catalytic performance of this catalyst.

4. Conclusion

The catalyst MC-ZSM-5/MCM-41 was successfully synthesized from rice husk silica. In addition to the ZSM-5 microporous system and the MCM-41 mesoporous system with a pore size of 5 Å and 4 nm, respectively, there is another pore system. Its pore diameter is in the range of 10–50 nm (mesoporous system); these pores are formed due to the burning of organic compounds remaining in material during the calcination process.

MC-ZSM-5/MCM-41 proved that it is a good catalyst in the catalytic cracking reaction of vegetable oil sludge to produce biofuel. The obtained results have found a new way not only to salvage the agricultural waste – rice husk, but also to produce biofuel from vegetable oil sludge, thereby replacing the natural petroleum oil resource which is being exhausted by humans.

Acknowledgement

This work was supported by Belgium Federal Government (Belspo) and Vietnam Ministry of Science and Technology (Most) bilateral cooperation project (BL/13/V11) and by Vietnam Ministry of Industry and Trade (Moit).

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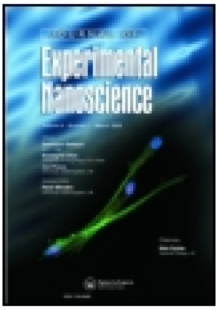

Journal of Experimental Nanoscience
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tjen20

Study on the structural formation of new useful multiporous material ‘nano-meso ZSM-5’ and its application in producing biofuel

Le Thi Hoai Nam [a], Nguyen Thi Thanh Loan [a], Tran Quang Vinh [a], Le Kim Lan [a], Le Quang Du [a], Van Dinh Son Tho [b] & Bao Lian Su [c]

[a] Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

[b] Department of Petrochemical Technology, Faculty of Chemical Technology, Hanoi University of Technology, Hanoi, Vietnam

[c] Laboratory of Inorganic and Materials Chemistry, University of Namur (FUNDP), Namur, Belgium

To cite this article: Le Thi Hoai Nam, Nguyen Thi Thanh Loan, Tran Quang Vinh, Le Kim Lan, Le Quang Du, Van Dinh Son Tho & Bao Lian Su (2011): Study on the structural formation of new useful multiporous material ‘nano-meso ZSM-5’ and its application in producing biofuel, Journal of Experimental Nanoscience, DOI:10.1080/17458080.2010.529170

To link to this article: http://dx.doi.org/10.1080/17458080.2010.529170

Journal of Experimental Nanoscience
2011, 1–12, iFirst

Study on the structural formation of new useful multiporous material 'nano–meso ZSM-5' and its application in producing biofuel

Le Thi Hoai Nam[a]*, Nguyen Thi Thanh Loan[a], Tran Quang Vinh[a], Le Kim Lan[a], Le Quang Du[a], Van Dinh Son Tho[b] and Bao Lian Su[c]

[a]*Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam;* [b]*Department of Petrochemical Technology, Faculty of Chemical Technology, Hanoi University of Technology, Hanoi, Vietnam;* [c]*Laboratory of Inorganic and Materials Chemistry, University of Namur (FUNDP), Namur, Belgium*

(*Received 22 January 2010; final version received 24 September 2010*)

New 'nano–meso ZSM-5' (NM-ZSM-5) material was successfully synthesised by hydrothermal treatment using silica derived from rice husk. The synthesis of the material involves two steps of crystallisation, including the formation of ZSM-5 zeolite seed and mesoporous structure. The effect of crystallisation time on the formation of mesoporous structure was studied in the range 0–40 h. Samples were characterised by X-ray diffraction, infrared spectroscopy, transmission electron microscopy, Brunauer–Emmett–Teller and ^{27}Al-NMR methods. The results show that the best time for crystallisation is 14 h. The synthesised material has a multiporous structure, including micropore system of ZSM-5 zeolite, mesopore system of MCM-41 and another pore system which has a diameter in the range 10–50 nm (mesoporous system) due to the burning of organic compounds that remain in the material during the calcination process. In addition, the synthesised NM-ZSM-5 achieves crystallinity of approximately 100%. The catalytic performance of NM-ZSM-5 material was evaluated by the catalytic cracking reaction to produce biofuel from vegetable oil sludge. The research proved that NM-ZSM-5 is one of the most suitable catalysts for this process. The catalytic cracking reaction over NM-ZSM-5 yields products that are similar to those of the petroleum cracking process, such as dry gases, liquefied petroleum gas, gasoline, light cycle oil and heavy cycle oil.

Keywords: multiporous material; rice husk; biofuel; synthesis method

1. Introduction

ZSM-5 zeolite is a very active additive used in fluid catalytic cracking during the petroleum cracking process for the production of fuel. In order to improve the catalytic performance of this additive, many worldwide researches, such as synthesising MCM-41 mesoporous material based on ZSM-5 zeolite and synthesising ZSM-5/MCM41 composite by adding ZSM-5 on the MCM-41 matrix [1,2], have been conducted. These materials have

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*Corresponding author. Email: namlht2005@yahoo.com

ISSN 1745–8080 print/ISSN 1745–8099 online

DOI: 10.1080/17458080.2010.529170
http://www.informaworld.com

multiporous structure (both microporous and mesoporous phases) and are more active in comparison to ZSM-5 zeolite.

Tetraethylorthosilicate (TEOS), Ludox, water glass and Si-containing solutions are the resources of silica that are used in the synthesis of nano–meso ZSM-5 (NM-ZSM-5). Among them, TEOS and Ludox are very expensive. Beside water glass, the Si-containing solution from rice husk was considered. The results showed that silica extracted from rice husk has a very good quality that is required to synthesise the catalyst [3–6].

This study mentions the effect of the crystallisation time on the formation of NM-ZSM-5 synthesised using silica extracted from rice husk. Samples are characterised by modern techniques such as infrared spectroscopy (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 isothermal adsorption/desorption and ^{27}Al-NMR. The catalytic activity of material is evaluated by the catalytic cracking reaction of vegetable oil sludge to produce biofuel.

2. Experimental

2.1. *Extraction of silica from rice husk*

Silica was extracted from rice husk (for 30 min) using 1% sodium hydroxide solution at a temperature of 80°C. The resulting Si-containing solution was used as a silica source. The composition of the extracted solution included 9.03 g/L of SiO_2 and 7.77 g/L of Na_2O among others. This solution was used together with other synthetic inorganic materials to synthesise NM-ZSM-5.

2.2. *Synthesis of NM-ZSM-5*

A typical synthesis process of NM-ZSM-5 is described as follows:

Step 1: ZSM-5 seed was prepared using silica from rice husk, $Al_2(SO_4)_3 \cdot 18H_2O$, template agent tetrapropyl ammonium bromide (TPABr) and sulphuric acid. The reaction mixture was stirred for 2 h, then transferred into an autoclave and kept at a temperature of 135°C for 10 h with stirring.

Step 2: The obtained solution of ZSM-5 zeolite seed was added to cetyltrimethylammonium bromide (CTMABr) and stirred vigorously at ambient temperature for 1 h. The final mixture was transferred into an autoclave and kept at a temperature of 135°C for different crystallisation times. The solid product was filtered and washed with deionised water to a pH of 7, dried at 100°C for 12 h and calcined at 540°C for 5 h to remove template (the final calcination temperature was reached using a ramp of 5°C/min). The obtained sample was a white-coloured powder.

2.3. *Characterisation*

IR spectroscopy was measured using an IMPACT-410 (Germany) at room temperature. Wave numbers are in the range 400–1300 cm^{-1}. Sample was wafered with KBr.

Powder XRD patterns were recorded on a HUT-PCM-Bruker D8 Advance instrument diffractometer system equipped with Ni-filtered Cu-Kα radiation (operating at 40 kV, 40 mA, wavelength $\lambda = 0.154$ nm). The patterns were recorded at room temperature (298 K), 2θ values were from 0.1° to 5° and 5° to 50°, and the scanning speeds were 1 and 2 degrees/min.

TEM was performed on a Philips Tecnai-10 microscope at 100 kV.

SEM was carried out on a Jeol JSM-7500F instrument. Sample was dried, mounted on a thin plate and coated by a flimsy platinum layer before recording.

The Brunauer–Emmett–Teller (BET) surface area and pore volume were measured by nitrogen adsorption/desorption isotherms method using ASAP2010 equipment (Micrometrics, USA). The sample was treated in vide pressure at 120°C for 4 h and at 350°C for 9 h.

The presence of aluminium within the framework has been evaluated through ^{27}Al solid state magic angle spinning-NMR method. Spectrum was obtained with a Bruker MSL400 spectrometer for ^{27}Al (at 104.3 MHz).

2.4. *Catalytic cracking reaction*

The vegetable oil sludge was obtained from Van Dao, a Vietnamese Company. The composition is as follows: triglycerides (61%), free fatty acid (37%) and impurities (2%). The hydrocarbon chains of triglycerides and free fatty acid are mainly C_{16} (30%) and C_{18} (36%), the others consisted of C_{12}–C_{17} hydrocarbon chains.

Micro-activity test (MAT 5000) system of Zeton, Canada, was used for catalytic cracking. The procedures of catalytic cracking applied ASTM D5154 testing method and the main parameters of catalytic cracking and pyrolysis processes are given in Table 1.

The coke formation was evaluated *in situ* by combustion with air and quantified by CO_2 infrared analyser (1440 Gas Analyser, Servomex).

The gas product was collected in a glass bottle containing brine water and analysed by refinery gas analyser (TRACE GC, Thermo Electron).

The distribution of boiling point (BP) of the liquid product was determined by SIMDIST GC (Thermo Electron) system, flame ionisation detector integrated

Table 1. Main parameters of pyrolysis and catalytic cracking conditions.

Parameters	Pyrolysis	Catalytic cracking
Weight of catalyst (g)		4.06
Catalyst bed cracking (°C)	600	483
Catalyst/oil (C/O) ratio		4
WHSV (L/h)		12
Total N_2 flow rate (prepurge, mL/s)	50	50
Total N_2 flow rate (reaction, mL/s)	5	5
Total N_2 flow rate (stripping, mL/s)	25	25
Oil feed temperature (°C)	50	50
Oil feed density at 50°C (g/mL)	0.87	0.87
Actual volumetric oil feed (mL)	1.16	1.16
N_2 pre-purge time (min)	15	15
N_2 reaction time (s)	75	75
N_2 stripping time (min)	10	10

TriPlus auto-sampler. The gas was calibrated according to RGA standard of MESA International Technologies, Inc., while the liquid for distillation simulation was according to ASTM D2887 Calibration mix (RESTEK).

The composition of the liquid fraction of vegetable oil sludge cracking reaction was analysed by GC–MS method (GC-HP HEWLETT 5890 PACKARD SERIES II; MS-HEWLETT 5989B PACKARD).

3. Results and discussion

3.1. *Synthesis of NM-ZSM-5*

Temperature and time of the crystallisation are the key factors which have a considerable influence on the formation of the porous inorganic materials. We investigated the influence of the crystallisation time of step 2 on the synthesis of NM-ZSM-5. The synthesis conditions are given in Table 2.

3.2. *Characterisation of NM-ZSM-5*

3.2.1. *IR spectra*

Figure 1 shows the IR spectra of the ZSM-5 seed and the NM-ZSM-5 samples with silica source extracted from rice husk. Spectra range from 400 to 1300 cm^{-1}.

The IR spectra of all samples show peaks that are similar to those of the standard ZSM-5 sample [4]. The peak at 550 cm^{-1} is attributed to the fluctuation of 5-1 rings in ZSM-5 structure, which is typical for the crystalline status of a material and is usually used as a standard band to determine the content of the crystalline phase. According to Kulkarni et al. [7], the crystallinity of synthesised material is 100% if the intensive ratio of the peaks at 550 to 450 cm^{-1} is 0.8. Figure 1 shows that the ratio of the samples increase from M1 to M4 and then decrease from M4 to M7. In addition, the ratio of the peaks at 550 to 450 cm^{-1} of M4 is approximately 0.8. Consequently, these results show that the

Table 2. The crystallisation conditions of NM-ZSM-5 samples.

	Crystallisation conditions		
		Time (h)	
Sample	Temperature (°C)	Step 1	Step 2
Seed	135	10	0
M1	135	10	2
M2	135	10	5
M3	135	10	8
M4	135	10	14
M5	135	10	22
M6	135	10	30
M7	135	10	40

crystallinity of the M4 sample is the highest in comparison to other samples and reaches approximately 100%.

3.2.2. *X-ray diffraction*

The results obtained from IR method can be proved again more clearly by XRD method. The XRD patterns of the NM-ZSM-5 samples are shown in Figure 2(a) (wide-angle X-ray) and Figure 2(b) (small-angle X-ray). The ZSM-5 structure of the samples was confirmed by the presence of the peaks at 9.05° and 24.05° which characterise the MFI structure [7].

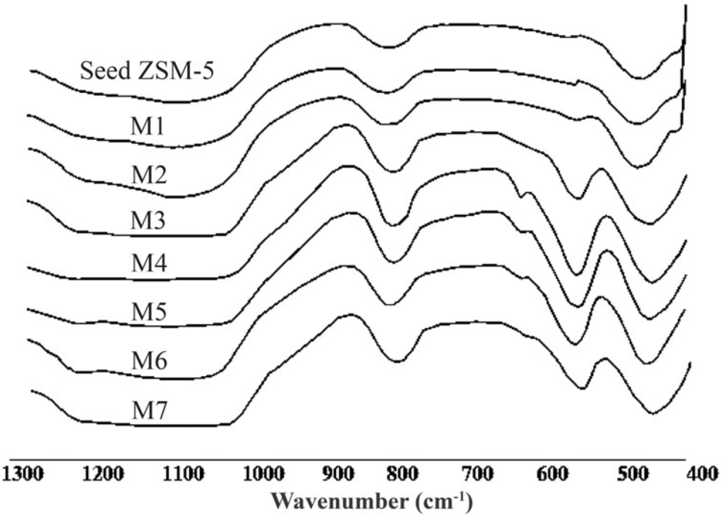

Figure 1. IR spectra of samples.

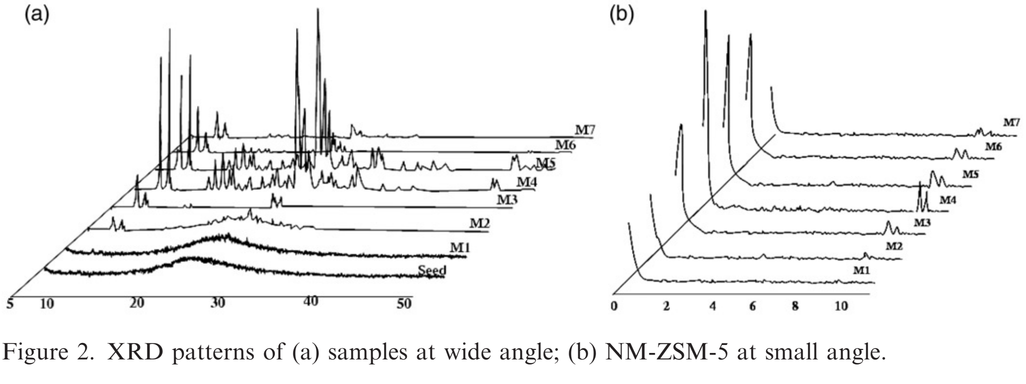

Figure 2. XRD patterns of (a) samples at wide angle; (b) NM-ZSM-5 at small angle.

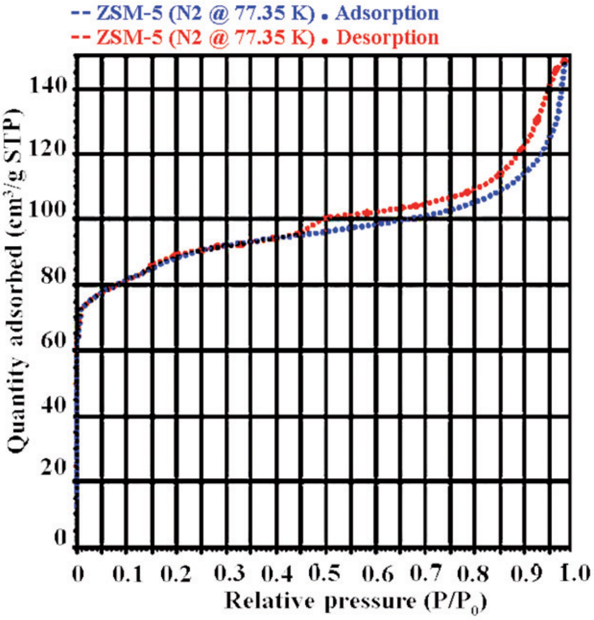

Figure 3. N_2 adsorption/desorption isotherms of NM-ZSM-5.

On the other hand, the XRD patterns also show that the M4 samples have the highest content of crystalline phase. This consideration is in good agreement with the above-mentioned IR result.

The XRD patterns (Figure 2(b)) show the presence of the peaks at 2θ region of 0–2°, which are characteristic of mesophase [8]. Also, the M4 sample has the highest intensity of peaks. The obtained results prove that the optimum crystallisation time for NM-ZSM-5 synthesis is 24 h (step 1: 10 h; step 2: 14 h).

3.2.3. *BET characterisation*

The mesostructure of the NM-ZSM-5 sample was also observed by N_2 adsorption/desorption isotherms. Figure 3 shows the appearance of a wide hysteresis loop. This typical shape is characteristic of mesoporous structure [8]. Figure 4 shows that the sample has two pore systems: micropore with a size of 5.5 Å and mesopore of around 40–200 Å; and the specific surface area is ~522 m^2/g.

3.2.4. *SEM and TEM images*

The SEM and TEM images show the morphology of NM-ZSM-5 sample. The SEM images (Figure 5) clearly indicate that MCM-41 formed with a uniform size of 350 nm in the shape of hexagons. The ZSM-5 zeolite seeds assembled to create MCM-41-ordered mesoporous structure under direction of the organic template.

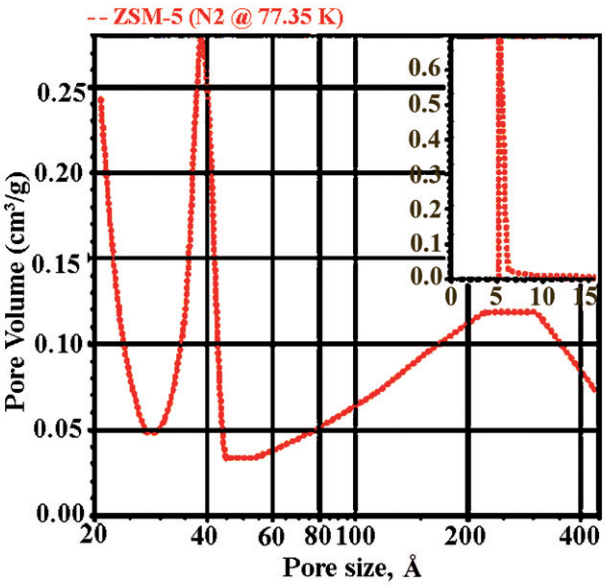

Figure 4. Pore size distribution of NM-ZSM-5.

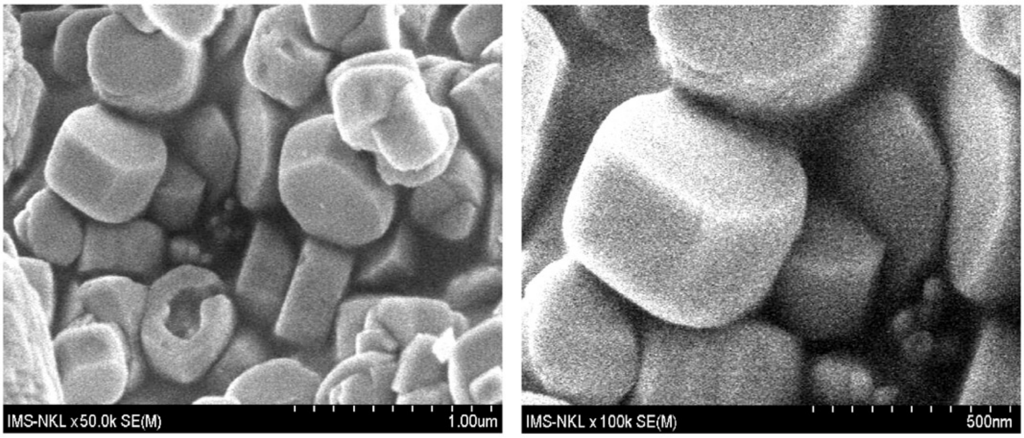

Figure 5. SEM images of NM-ZSM-5.

The existence of long-range dimensional mesophase of the material is shown in the TEM image (Figure 6). The mesopores in the structure of MCM-41 are uniform with a size of 4 nm.

In addition, the observed TEM image shows a very interesting feature of the synthesised sample. Besides the MCM-41 mesoporous system, there is another porous system which has a diameter in the range 10–50 nm. The exits of this pore system can be explained by the carbon that is present in the treated rice husk, which is still being removed

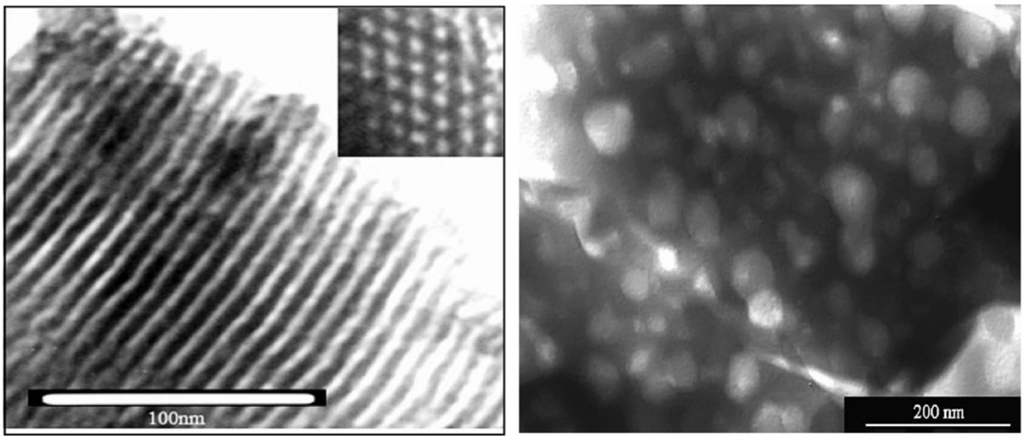

Figure 6. TEM images of NM-ZSM-5.

in the calcination process. The removal of carbon formed special mesoporous system of synthesised material and this result tally with the result obtained from BET method in the pore distribution chart.

3.2.5. *Nuclear magnetic resonance-^{27}Al-NMR*

The exits of Al^{3+} ion in zeolite framework relates with the acidity of the material (due to Al^{3+} ion tetrahedrally coordinated in the framework of zeolite). From the obtained result, the acidity of the material can be indirectly measured via the determination of the presence of Al^{3+} in zeolite framework. So, to determine the distribution of Al^{3+} ion of synthesised material, the ^{27}Al-NMR method was applied. Figure 7 shows the ^{27}Al-NMR of NM-ZSM-5.

The ^{27}Al-NMR of NM-ZSM-5 gives rise to one resonance only at 55 ppm with high intensity due to the presence of aluminium in a tetrahedrally coordinated environment, which is typical for aluminium zeolitic framework [7,8]. However, it also shows one more resonance at 0 ppm with very low intensity and it is negligible in comparison with the intensity of resonance at 55 ppm. According to Jiao et al. [9] and Hunger and Brunner [10], this resonance is attributed to Al^{3+} which is not present in zeolite framework. This indicates that the quantity of aluminium used is almost present in zeolite framework.

3.3. *Catalytic performance*

In order to evaluate the catalytic activity of the synthesised material, the vegetable oil sludge cracking reaction was performed. The reaction was carried out on a MAT5000 system of Hanoi University of Technology (Vietnam) with input parameters listed in Table 1.

The catalytic activity is measured via product yield and conversion of the cracking process. Main products of the cracking reaction are as follows:

- Dry gasses: mainly consisting of H_2, CO, CO_2, CH_4, C_2H_6 and C_2H_4.

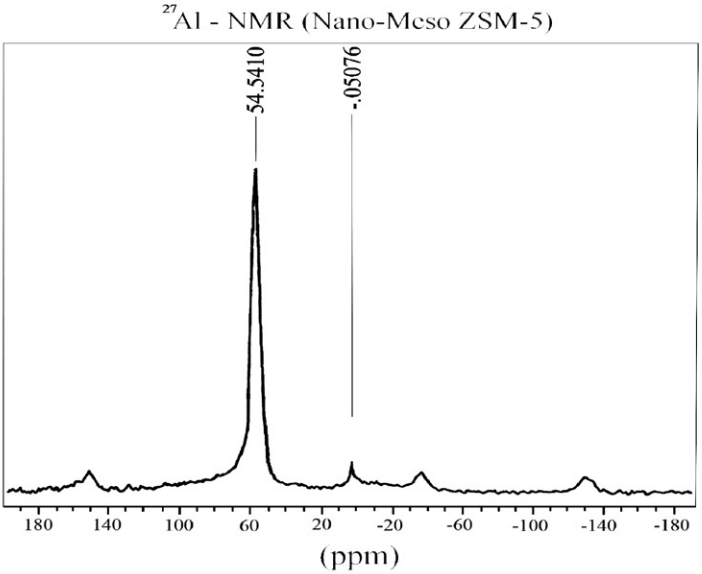

Figure 7. ^{27}Al-NMR of NM-ZSM-5.

- Liquefied petroleum gas (LPG): consisting of C_3–C_4 (C_3, C_3=, iC_4, *n*C_4, C_4=, propandien).
- Gasoline: BP is less than 221°C and also consisting of C_5^+ gases in gas product.
- Light cycle oil (LCO): BP ranges between 221°C and 343°C.
- Heavy cycle oil (HCO): BP is more than 343°C and other fragments which are not converted from initial vegetable oil sludge.

Figure 8 shows the products obtained from the catalytic cracking reaction over NM-ZSM-5 and HZSM-5 catalyst materials in the form of a bar chart. The result indicates that both NM-ZSM-5 and HZSM-5 are very active for the vegetable oil sludge cracking reaction to produce biofuel. On the other hand, it shows that the total of LPG, gasoline (desirous products) and conversion of the catalytic cracking reaction over NM-ZSM-5 is higher than that of HZSM-5. On the contrary, HCO and LCO (undesirable products) of NM-ZSM-5 are lower than that of HZSM-5.

The products obtained from the cracking reaction are classified into gas, liquid and solid (coke) types. Gas product is analysed by gas chromatography system (refinery gas analyser; TRACE GC, Thermo Electron). Table 3 describes the gas product of catalytic cracking over HZSM-5 and NM-ZSM-5 and of pyrolysis. The total quantities of gas product of the cracking reaction over HZSM-5 and NM-ZSM-5 catalysts are higher than that of the pyrolysis. It indicates that the catalytic cracking underwent more deeply than the pyrolysis did. Moreover, the presence of *i*-butane in gas product of catalytic cracking over NM-ZSM-5 shows that an isomerisation has occurred.

The liquid product of the cracking reaction is analysed by SIMDIST GC Thermo Electron system. The composition of liquid fraction is measured via the distribution of BP (Figure 9). It shows that the vegetable oil sludge has three areas of BP. All of them are over

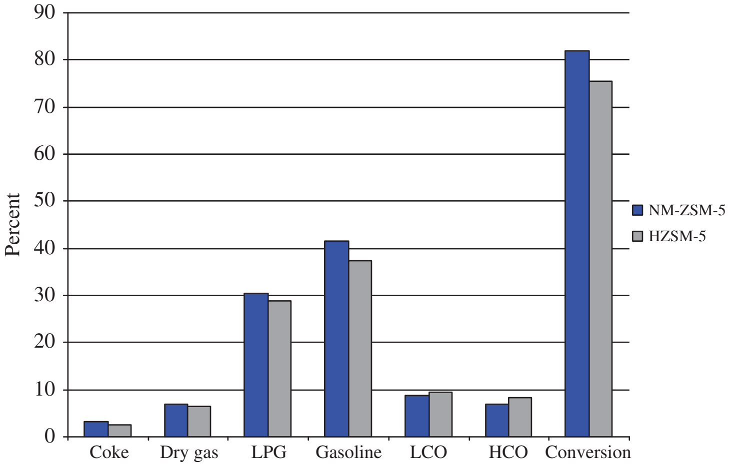

Figure 8. Products and conversion of vegetable oil sludge cracking reaction over HZSM-5 and NM-ZSM-5.

Table 3. The composition of gas product.

Composition	Formula	H-ZSM-5 (%)	NM-ZSM-5 (%)	Pyrolysis (%)
2-Methyl-2-butene	2M2C4=	0.56	0.97	1.56
Hydrogen	H2	0.11	0.13	0.00
Propane	C3	6.52	8.88	2.12
Propylene	C3=	8.61	7.06	7.30
i-Butane	*i*C4	**3.14**	**5.49**	**0.00**
Propadiene	Propadiene	0.00	0.00	0.00
n-Butane	*n*C4	1.90	2.94	0.24
1-Butene + *i*-butene	1C4 = +*i*C4=	4.85	3.86	1.92
trans-2-Butene	T2C4=	2.36	1.70	0.18
cis-2-Butene	C2C4=	1.59	1.20	0.14
1,3-Butadiene	1,3-Butadiene	0.00	0.00	1.11
3-Methyl-1-butene	3M1C4=	0.57	0.44	0.00
Ethylene	C2=	4.84	4.88	3.76
Ethane	C2	0.99	1.14	1.96
Methane	CH4	0.55	0.83	1.42

343°C, corresponding to the segments of HCO and LCO. The spectra of the catalytic cracking reaction over both HZSM-5 and NM-ZSM-5 also show that the peaks occur near 75°C and 343°C; the intensity of the former being much higher than that of the latter. It shows that the cracking reaction over these catalysts have a total of LPG and gasoline that is much higher than those of HCO and LCO. However, the intensity of peaks at near 343°C in the spectra of NM-ZSM-5 is lower than that of HZSM-5 and the ratio of peaks at 75°C to 343°C is much higher than that of HZSM-5. This indicates that the obtained gasoline and LPG fractions in the product of cracking reaction over NM-ZSM-5 is higher than that of HZSM-5.

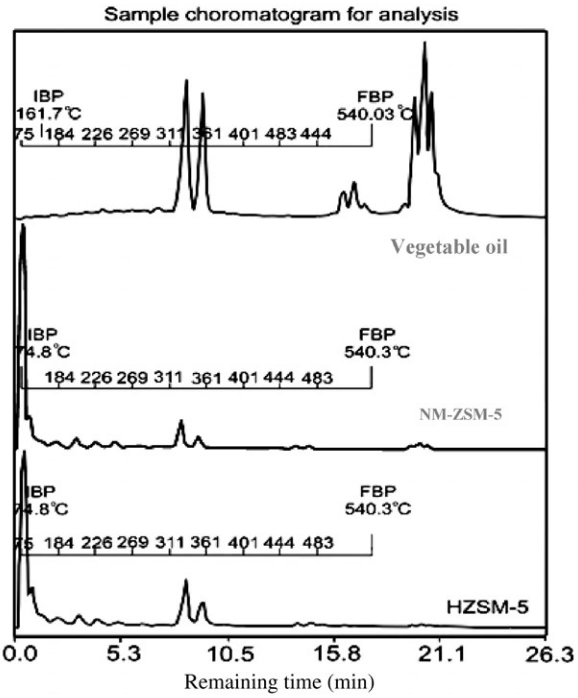

Figure 9. The distribution of liquid product of catalytic cracking reaction over HZSM-5 and NM-ZSM-5 by the BP.

4. Conclusion

NM-ZSM-5 catalyst was successfully synthesised from rice husk silica. The results prove that the optimum crystallisation time for the synthesis of NM-ZSM-5 is 24 h. Besides the ZSM-5 microporous and the MCM-41 mesoporous systems with a size of 5 Å and 4 nm, respectively, there is another porous system which has a diameter in the range 10–50 nm (mesoporous system) due to the burning of organic compounds that remain in the material during the calcination process.

NM-ZSM-5 proved that it is a good catalyst in the cracking reaction of vegetable oil sludge with higher conversion and selectivity for LPG and gasoline products in comparison to HZSM-5 zeolite. The obtained results have found a new way in the salvage of agricultural waste to produce promising catalysts which can be applied not only to catalysis and adsorption fields, but also to produce biofuel from vegetable oil sludge replacing the exhausted natural petroleum oil resource.

Acknowledgements

The authors are thankful to the Vietnamese Ministry of Science and Technology, the Vietnamese Ministry of Industry and Trade and the Belgian Federal Science Policy Office for providing financial support.

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One-Pot Synthesis of Catalytically Stable and Active Nanoreactors: Encapsulation of Size-Controlled Nanoparticles within a Hierarchically Macroporous Core@Ordered Mesoporous Shell System

By *Xiao-Yu Yang, Yu Li, Gustaaf Van Tendeloo, Feng-Shou Xiao,* and *Bao-Lian Su**

Core/shell structures of nanoporous materials have received a lot of attention in recent years owing to the great versatility of the combined functionalities of cores and shells and their potential application in drug and biomolecule delivery, separation science, and confined-space catalysis.[1,2] Colloidal templating has been extensively explored in the production of various core/shell or hollow capsule structures of various chemical compositions, from inorganic materials, polymers, and carbon structures to composites.[3] A layer-by-layer approach was also shown to be a suitable fabrication method.[4] Recent tendencies have focused on the replacement of the amorphous disordered core with ordered porous cores, such as mesoporous materials and zeolites. This has yielded mesoporous cores within polymer/nanocrystal shells, and zeolitic cores within polymer/colloidal/mesoporous shells.[5] However, direct synthesis of a hierarchically bimodal nanoporous core/shell structure is still a great challenge.[3–5] Furthermore, most research in this area has been focused on the development of synthetic methodologies, and very little attention has been directed toward the functionalization of core/shell materials for nanoreactor applications.[4]

Here, we present the synthesis of bimodal nanoporous aluminosilicates with a hierarchically macroporous core inside an ordered mesoporous shell via a one-pot reaction. This is achieved through a combination of the surfactant templating and the self-formation phenomenon of porous hierarchy,[6] using a mixture of an aluminosilicate ester, di-s-butoxyaluminoxytriethoxysilane ($(Bu^sO)_2$–Al–O–Si–$(OEt)_3$) and tetramethyl orthosilicate (TMOS). Most interestingly, the method of core/shell-structure synthesis was precisely applied to nanoreactor design, to generate new functionalities by in situ encapsulation of metal oxide nanoparticles inside the core/shell structure. One of the ultimate advantages of this new core/shell structure is that a mesoporous shell allows the diffusion of chemical reagents toward the inside of the structure, and prevents leaching of the metal oxide nanocrystals that are formed inside the macroporous core. Other advanced properties can be exploited in the design of magnetic devices, sensors, and rechargeable lithium batteries. In addition, other active species, such as metallic nanoparticles, organometallics, and even biological species, can be encapsulated by this one-pot-synthesis strategy.

Scanning electron microscopy (SEM) images of the as-synthesized sample show that the spheres are homogeneously sized, with a diameter of around 500 nm (Fig. 1a). Transmission electron microscopy (TEM) studies confirm the uniform sizes of these sub-micrometer spheres (Fig. 1b). Interestingly, foamlike hierarchically macroporous cages of sizes 50–80 nm are observed inside these spheres (Fig. 1b–d). A higher-magnification image (Fig. 1d and inset) shows very good regularity in the denser shells of the spheres, which were formed by the ordered 2D hexagonal (*P6mm*) mesostructure covering the foamlike macroporous cores. The thickness of the shells is around 80 nm. More importantly, the TEM image shows that the macroporous cages are interconnected with uniformly ordered mesopores, which would be valuable for the fast diffusion of reactants and products in catalysis. Meanwhile, X-ray diffraction (XRD) pattern of the as-synthesized sample (Fig. 2a) clearly exhibits well-resolved peaks that can be indexed as the (100), (110), and (200) diffractions associated with the *p6mm* hexagonal symmetry with a lattice constant $a_0 = 4.32$ nm. After calcination in air at 500 °C for 4 h, the three diffraction peaks of the sample became sharper due to the removal of surfactant molecules (Fig. 2b), showing good thermal stability of the ordered hexagonal mesostructure in the shell.

Figure 3 shows N_2 isotherms of the calcined sample and its pore-size distribution. Notably, the sample calcined at 500 °C for 4 h exhibits a typical IV-type isotherm, assigned to a 2D hexagonal (*P6mm*) mesostructure. The N_2 adsorption isotherm gives a Brunauer–Emmett–Teller (BET) surface area of 892 $m^2\ g^{-1}$ and pore volume of 0.68 $cm^3\ g^{-1}$. Interestingly, the sample isotherm exhibits two inflections (Fig. 3). The first one (a type H1 hysteresis loop at $0.30 < P/P_0 < 0.70$) gives a pore-size distribution in the range of 1–10 nm, with one sharp maximum centered at around

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[*] Prof. B.-L. Su, Dr. X.-Y. Yang, Dr. Y. Li
Laboratory of Inorganic Materials Chemistry (CMI)
University of Namur (FUNDP)
61, rue de Bruxelles, B-5000 Namur (Belgium)
Fax: (+32)-81-725414
E-mail: bao-lian.su@fundp.ac.be

Prof. G. Van Tendeloo
EMAT, University of Antwerp
Groenenborgerlaan 171
B-2020 Antwerpen (Belgium)

Prof. F.-S. Xiao
College of Chemistry, Jilin University
Changchun 130023 (China)

DOI: 10.1002/adma.200802914

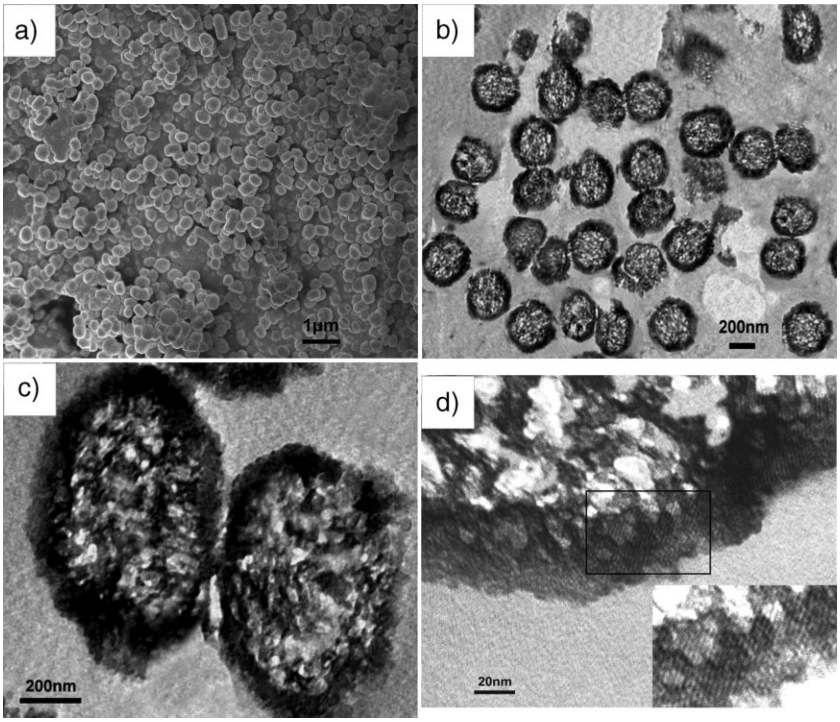

Figure 1. a) SEM image of as-synthesized and b–d) TEM images of calcined sample.

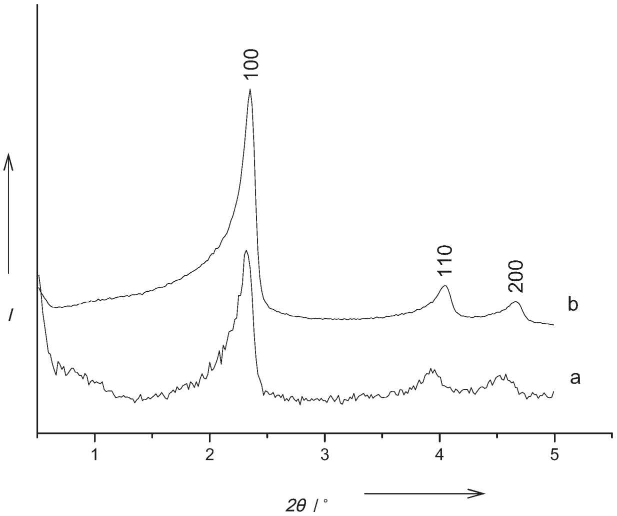

Figure 2. XRD patterns of a) as-synthesized and b) calcined sample.

2.4 nm and another less visible maximum at 5.7 nm. These result from a CTMAB-templated mesoporous shell with mesoporous size of 2.4 nm and disordered mesopores in macroprous cores with a pore size of around 5.7 nm,[7] respectively. The second inflection (a hysteresis loop at $0.70 < P/P_0 < 0.98$) indicates the presence of a significant amount of large pores, with a relatively large pore-size distribution in the range of 40–100 nm (inset of Fig. 3). These results also show that the material presents both mesoporous and macroporous pore-size distributions, in good agreement with the TEM data. The existence of mesopores of 2.4 nm is also in good agreement with XRD results.

The use of an aluminosilicate ester with two alkoxide groups and different hydrolysis rates renders the precise control of this novel structure possible. The rupture, at least partly, of Al–O–Si linkage of Al–Si ester is unavoidable. The hydrolysis of the $\text{Al–(Bu}^{s}\text{O)}_2$ group is very rapid.[6,7] It easily self-aggregates to form an interior macroporous structure, which was attributed to microphase-separated regions of metal oxide and solvent, established by the flow of the solvent across the membrane to the alkoxide interface. The key point of this novel synthetic process is that although the hydrolysis of the Si–(OEt)_3 group is relatively slow,[7] these unhydrolyzed –Si(OEt)_3 of aluminsilicate ester can still be enriched around the surface of the core formed by –Al(OEt)_2, due to the unique molecular structure of the aluminosilicate ester (the oxygen atom bridges –Si(OEt)_3 and –Al(OEt)_2 group). And then these –Si(OEt)_3 groups can assemble themselves, together with TMOS, around surfactant micelles (CTMAB), to form denser, ordered mesoporous structures around the macroporous core, which in fact hinder the formation of channel-like macroporous structures,[6] therefore obtaining the novel sub-micrometer spheres with a foamlike macroporous core and ordered mesoporous shell. The higher Al content observed in the core and the lower Al content observed in the shell (S-Fig. 1 of Supporting Information) suggest that the formation of macropores was mostly attributed to the fast hydrolysis and polymerization of the aluminosilicate ester, and the ordered mesoporous shell can only be formed via a surfactant-templating mechanism.

The present core/shell structure provides a unique system for investigating nanoreactors, with the shell designed for a better

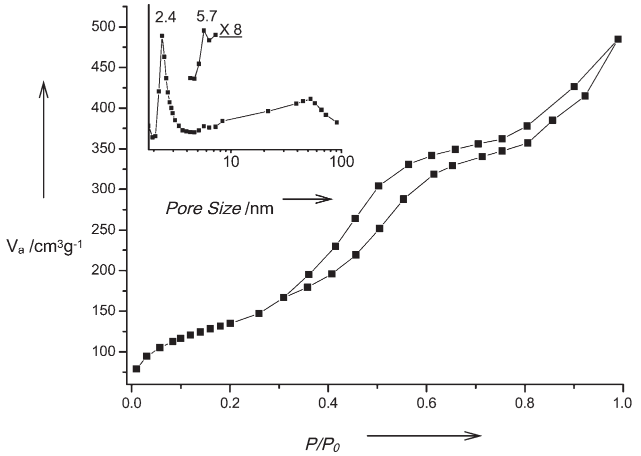

Figure 3. N_2 isotherm and the corresponding pore-size distribution (inset) of calcined sample.

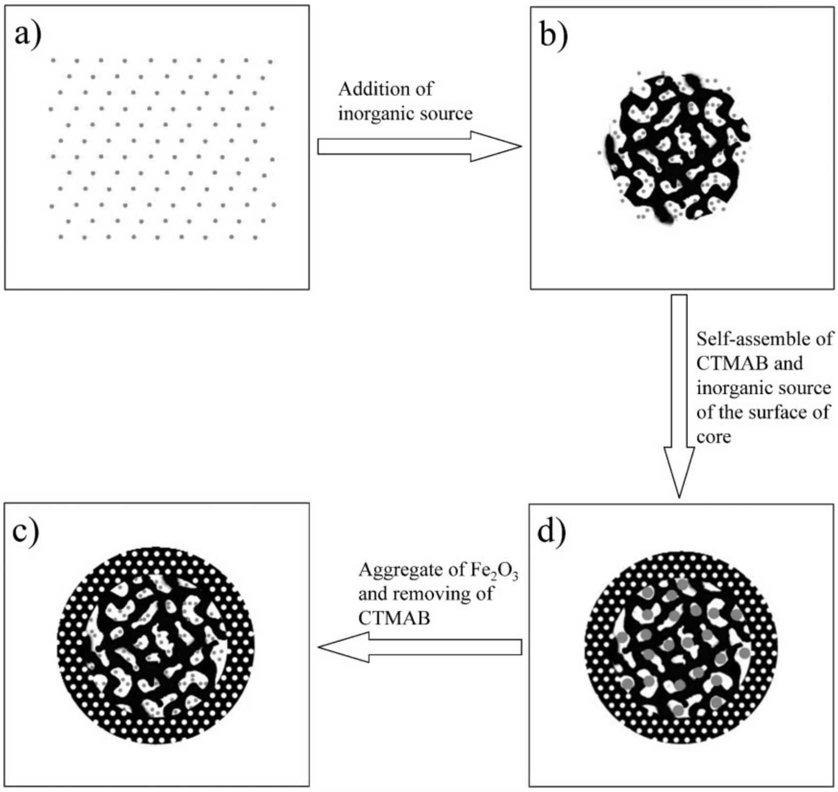

Figure 4. Proposed structure for the formation of macroporous core@mesoporous shell sample. a) The aqueous solution containing iron species, b) formation of foamlike macroporous core containing iron, c) formation of mesoporous shell in surface of macroporous core, and d) nanoreactor with Fe_2O_3 nanoparticles.

diffusion of reactants and products, and the core for encapsulation of active sites, such as metallic nanoparticles. As an example of the introduction of the catalytically active sites into the internal macroporous cores, the above synthetic strategy has been employed in the presence of an iron-ion-complex solution (Fig. 4). An aluminosilicate ester and TMOS, with a defined ratio, were added to an aqueous solution of $(NH_4)_3[Fe(CN)_6]$ (pH 11). The almumino-silicate ester and TMOS in the presence of CTMAB in the solution instantaneously created a foamlike macroporous core containing iron species, and a denser, ordered mesoporous shell as discussed above. Meanwhile, the surfactant molecules could not only avail to the formation of a mesoprous shell, but it would also be useful to stabilize $[Fe(CN)_6]^{3-}$ ions without the precipitation at pH 11, and to avoid the leaching of the Fe species involved in macropores in the synthesis of the nanoreactor. Some iron species can also be embedded in the mesoporous shells. After calcination, the encapsulated iron species aggregated to form Fe_2O_3 nanoparticles, and the organic templates within the mesoporous channels were removed, resulting in the formation of a nanoreactor with an ordered mesoporous shell and the macroporous core containing active Fe_2O_3 nanoparticles. The successful entrapment of Fe_2O_3 nanoparticles into the macroporous core was confirmed by TEM, XRD, and high-resolution (HR)TEM studies. As shown in Figure 5, the Fe_2O_3 nanoparticles had a uniform size of 12 nm (Fig. 5a). The size larger than the entrance of the mesoporous channels indicates that the nanoreactors can effectively prevent leaching of the active sites. The size of Fe_2O_3 nanoparticles of two samples synthesized with various concentrations of iron species was further determined by TEM images (Fig. 5). Interestingly, the particle size was tailored from 12 to 8 nm by varying the Fe/CTMAB molar ratio. More importantly, the size ratio between two samples was in good agreement with the concentrations of iron species. This indicates that the size of Fe_2O_3 nanoparticles could be efficiently tailored by controlling the concentration of iron species in the initial mixture of reactants. Meanwhile, the XRD peaks are characteristic of Fe_2O_3 crystals with high degree of crystallinity (JCPDS card, No. 87–1166), and were mainly located in the center of the macroporous cages (S-Fig. 2 of Supporting Information). High-resolution observations of the Fe_2O_3 nanoparticles further display direct evidence of crystalline degree and sizes of the encapsulated Fe_2O_3 nanoparticles synthesized with various concentrations of iron species (Fig. 5c and d). The Fe_2O_3 nanoparticles synthesized with various concentrations of iron show high degree of crystallinity, and the lattice fringes of 0.185 and 0.250 nm correspond to the (024) and (110) crystal planes of hematite structures of Fe_2O_3 (JCPDS card, No. 87–1166), respectively. Furthermore, these HRTEM images clearly show that the sizes of the Fe_2O_3 nanoparticles are gradually reduced with decreasing the concentration of iron in the initial mixture of reactants. It is clear that the main Fe_2O_3 particles are located in the cores. Fe_2O_3 particles in the mesochannels should be very small in size and relatively low in amount, since our HRTEM did not clearly show the presence of Fe_2O_3 particles in the mesochannels of the shell. One possible reason is the low quantity of such particles.[8]

Catalytic activities for hydroxylation of phenol with H_2O_2 over the encapsulated Fe_2O_3 nanoparticles (12 nm) are presented in Table 1. For comparison of catalytic activity, reference catalysts MCM-41, Fe-MCM-41, and α-Fe_2O_3 were synthesized according to the published literature.[9] As expected, encapsulated Fe_2O_3 nanoparticles are very active for the catalytic conversion of phenol. It is also noteworthy that recycled, encapsulated Fe_2O_3 nanoparticles still show comparable activities to that of the initial ones. For example, after five cycles, the encapsulated Fe_2O_3 still Exhibits 90% of the initial activity (Table 1). In contrast, Fe-MCM-41 and free Fe_2O_3 nanoparticles, often used as reference catalysts for similar reactions, show relatively low activities. The encapsulated Fe_2O_3 nanoparticles are stable, reusable, and active. The great efficiency of the encapsulated Fe_2O_3 nanoparticles can be attributed to this unique core/shell nanoreactor design. The nanosized particles were well dispersed, and the macroporous structure of the core can minimize the aggregation of Fe_2O_3 nanoparticles, whilst the mesoporous shell can prevent the active sites from leaching and favor the diffusion of the reagents and products.

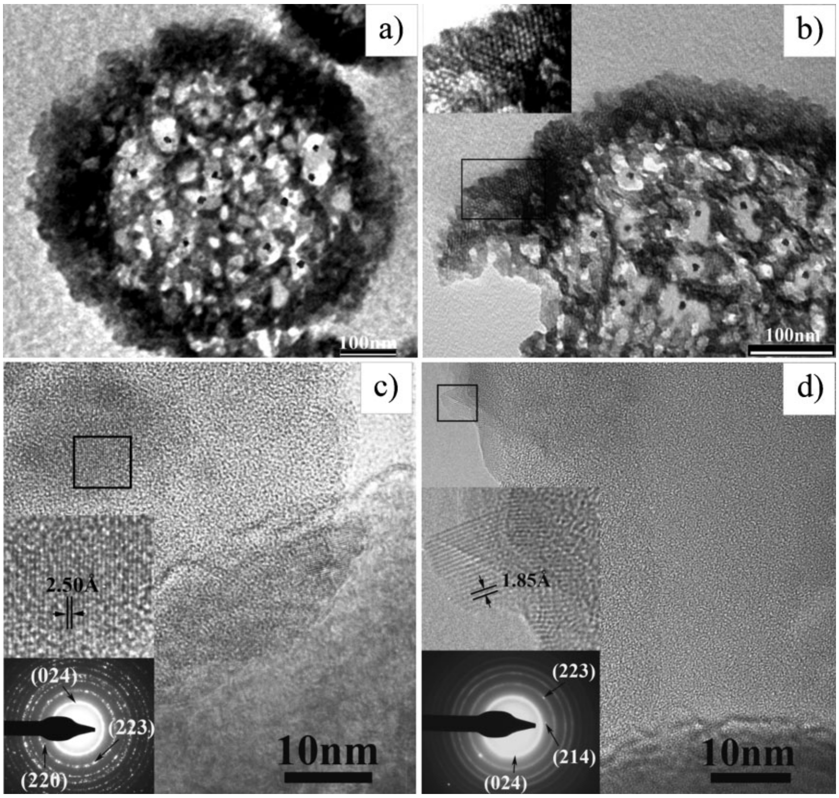

Figure 5. TEM and HRTEM images of calcined encapsulated Fe_2O_3 particles synthesized using various iron concentrations (Fig. 5a and c, Fe/CTAB = 10; Fig. 5b and d, Fe/CTAB = 5, molar rate). The insets in the HRTEM images are the corresponding selected-area electron diffraction (SAED) patterns taken from many particles.

Table 1. Composition, surface area, and catalytic activity [a].

Samples	Si/Fe	S_{sample} [$m^2\ g^{-1}$]	Phenol conv. [%]	H_2O_2[b] conv. [%]	Select[c] [% BQ]	Select [% CAT]	Select [% HQ]
Encapsulated Fe_2O_3 (1)[d]	78	821	22.5	78.6	5.8	61.1	33.1
Encapsulated Fe_2O_3 (5)	81	619	20.4	74.3	4.8	63.7	31.5
MCM-41[e]		1023	0	0	0	0	0
Fe-MCM-41	59	905	7.1	25.3	1.8	52.1	46.1
Fe_2O_3		29	7.3	63.2	9.0	57.9	33.1

[a] Reaction conditions: water as a solvent, temperature 80 °C, phenol/H_2O_2 = 3:1 (molar ratio), reaction time for 4 h, catalyst/phenol = 5% (weight ratio). [b] The conversion of H_2O_2 was calculated as follows: H_2O_2 conversion = 100 × H_2O_2 (moles) consumed in formation of diphenols and benzoquine/total H_2O_2 (moles) added. [c] CAT: catechol, HQ (hydroquinone), and BQ (benzoquinone). The product of tar is not included, and the product selectivity is CAT (or HQ or BQ)/(CAT + HQ + BQ). [d] Encapsulated Fe_2O_3 (*X*) denotes encapsulated Fe_2O_3 by our method, and *X* is the number of recycles. [e] MCM-41, Fe-MCM-41, and Fe_2O_3 were prepared according to the method reported in Ref. [8].

The high activity, stability, and excellent recycling behavior of the encapsulated nanoparticles in the samples should be directly attributed to the unique core/shell synthesis of nanoporous materials with integral macro- and mesoporosities. We believe that this method may open an exciting avenue for the preparation of hierarchically bimodal nanoporous materials with core/shell structures, and for the design of nanoreactors with combined functionalities in the cores and the shells.

Experimental

Di-s-butoxyaluminoxytriethoxysilane ($(Bu^sO)_2$–Al–O–Si–$(OEt)_3$) was purchased from Gelest, and other chemicals from Aldrich. In a typical synthesis of foamlike macroporous core@ordered hexagonal mesoporous shell aluminosilicates, the following procedure was used: i) the mixture of 6 g Di-s-butoxyaluminoxytriethoxysilane and 6 g TMOS was introduced into 56 g CTAB solution (2.2 g of CTAB dissolved in 56 g of aqueous ammonia (pH 11)) under stirring. ii) After stirring at room temperature for 24 h, the solution was transferred to Teflon lined autoclaves and aged for 72 h at 80 °C. iii) After the solid product was filtered, calcination of the product was carried out at 500 °C for 4 h in a flow of oxygen, to remove the organic templates. For comparison, Fe_2O_3, Fe-MCM-41, and MCM-41 were synthesized according to published literatures [8].

XRD patterns were obtained using a Panalytical X'Pert diffractometer using Cu Kα radiation. SEM experiments were performed using a JSM-6700F electron microscope (JEOL, Japan). TEM experiments were performed using a Philips TECNAI-10 at with an acceleration voltage of 100 kV. HRTEM experiments were performed using a JEM-4000EX (JEOL, Japan) with an acceleration voltage of 400 kV. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010M system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution for mesopores was calculated using the Barrett–Joyner–Halenda (BJH) model.

EDX results and XRD patterns are given in the Supporting Information.

Acknowledgements

This work was supported by the Belgian Federal Government (Belspo PAI-IAP project, INANOMAT, P6/17, and Belgium-Viet Nam bilateral cooperation project, BL/13/V11). X.-Y. Y. thanks the University of Namur for a doctoral fellowship and FNRS (Fonds National de la Recherche Scientifique in Belgium) for a ''Chargé de recherche'' position. Supporting Information is available online from Wiley InterScience or from the author.

Received: October 2, 2008
Revised: October 30, 2008

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PRODUCING BIOFUEL BY CRACKING VEGETABLE OIL SLUDGE OVER NANO-MESO ZSM-5 CATALYST

Le Thi Hoai Nam[1], Nguyen Dinh Tuyen[1], Nguyen Thi Thanh Loan[1], Tran Quang Vinh[1], Nguyen The Anh, Le Thi Kim Lan[1], Xiao-Yu Yang[2], Bao Lian Su[2]

[1] Institute of Chemistry, Vietnamese Academy of Science and Technology, [2]University of Namur (Belgium)

ABSTRACT

New "Nano-meso ZSM-5"(NM-ZSM-5) materials was successfully synthesized by hydrothermal treatment using silica derived from rice husk. The obtained samples were characterrized by different techniques such as XRD, IR, TEM, BET and ^{27}Al-NMR. The catalytic property was tested on the vegetable oil sludge cracking reaction to produce biofuels. NM-ZSM-5 proved that it is very active in the cracking reaction of vegetable oil sludge.

INTRODUCTION

Bio-fuel can be obtained from biomass (e.g. pyrolysis, gasification) and from agricultural sources such as vegetable oil, cat fish, rubber seed oil, soybean oil … One of the potential sources could be able to convert to biofuel is a vegetable oil sludge. This waster is a major by-product of vegetable oil factory.

Vietnam achieves approximately the annual rice production of 30 million ton, among them the rice husk composition occupies 15 – 20 % weight with content of silica 15 – 20 %. Study on using silica from rice husk for synthesis of high quality materials was interested by a large of scientists over the world.

In this article, we report results of the synthesis and characterization of a new nano-meso ZSM-5 material using silica source from Vietnam rice husk. The new material has got both of microstructure and mesostructure which are formed by ZSM-5 nano particles with size of 5nm. The catalytic activity in vegetable oil sludge cracking reaction to form renewable bio-based products suitable for use in fuel and chemical applications...

Table 1. *The input parameters*

Catalytic cracking condition	
Weight of catalyst	4.0600 (g)
Catalyst Bed Cracking	483.0 (°C)
Total N_2 Flowrate (Prepurge)	50(ml/s)
Total N_2 Flowrate (Reaction)	5 (ml/s)
Total N_2 Flowrate (Stripping)	25(ml/s)
Oil Feed Temperature	50.0 (°C)
Oil Feed Density @ 50.0°C	0.8747 (g/ml)
Actual Volumetric Oil Feed	1.1600 (ml)
N_2 Pre-purge Time	15.0 (min)
N_2 Reaction Time	75 (sec)
N_2 Stripping Time	10.0 (min)

Table 2: *Products of cracking reaction*

Product	NM-ZSM-5	Pyrolysis
Coke	3.275	14.546
Dry gases	6.818	7.139
LPG	30.430	13.008
Gasoline	41.451	22.070
LCO	8.721	10.504
HCO	7.035	9.410

CONCLUSION

NM-ZSM-5 catalyst was successfully synthesized from rice husk silica. Besides the microporous and the MCM-41 mesoporous system with size of 5A^0 and 4nm respectively, there is another pores system which has diameter in range of 10-50nm (mesoporous system) due to the burning of organic compounds remain in material during the calcination process.

NM-ZSM-5 proved that it is a good catalyst in the cracking reaction of vegetable oil sludge to produce biofuels. The obtained results have found a new way not only to the salvage of agricultural waste but also to produce biodiesel from vegetable oil sludge replacing the exhausted natural petroleum oil resource.

EXPERIMENTAL

A. Extraction of silica from rice husk

B. Synthesis of "Nano-meso ZSM-5"

A typical synthesis process is described via 2 steps as follows:

The first-step: Preparation of ZSM-5 seed

The second-step: Synthesis of ZSM-5 zeolite

C. Characterization

The product was characterized by methods such as XRD (HUT- PCM- Bruker D8); TEM (TEM 1010), SEM (Jeol JSM-7500F), IR (IMPACT-410), Nitrogen adsorption/desorption isotherms (ASAP 2010 equipment [Micrometrics-USA]).

D. Catalytic cracking reaction

The composition of vegetable oil sludge is triglyceride (61%), free fatty acid (37%) and impurities (2%). The hydrocarbon chains of triglyceride and free fatty acid are mainly C_{16}(30%) and C_{18} (36%) hydrocarbon. The others consisted of C_{12}-C_{17} hydrocarbon chain.

Micro-activity test MAT 5000 of Zeton-Canada was used for catalytic cracking. The procedures of catalytic cracking were applied ASTM D5154 testing method and main parameters of catalytic cracking condition were described in table 1.

The coke formation was measured by 1440 Gas Analyzer – Servomex. The gas product was analyzed by Refinery gas analyzer – Trace GC - ThermoElectro. The boiling distribution of the liquid product was determined by SIMDIST GC ThermoElectro system, detector FID integrated TriPlus auto-sampler. The calibration gas is RGA standard of MESA International Technologies, Inc. The calibration liquid for distillation simulation is ASTM D2887 Calibration mix (RESTEK)

RESULTS AND DISCUSSION

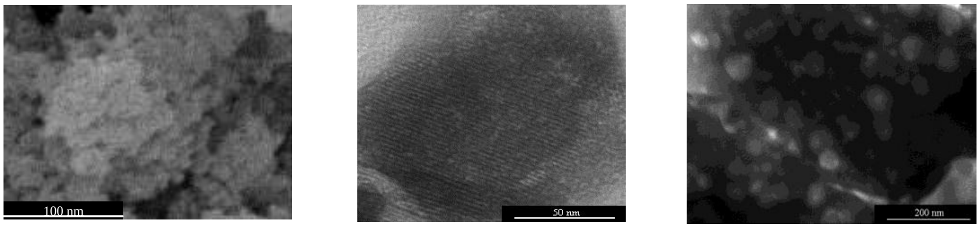


Figure 1: SEM and TEM images of NM-ZSM-5

PRODUCING BIOFUEL

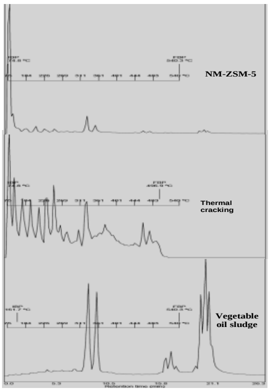


Figure 2: *The distribution of liquid product by the boiling points*

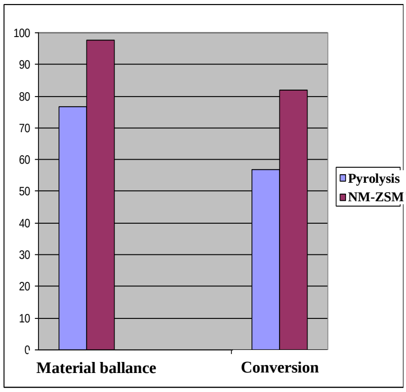


Figure 3: *Material balance and conversion*

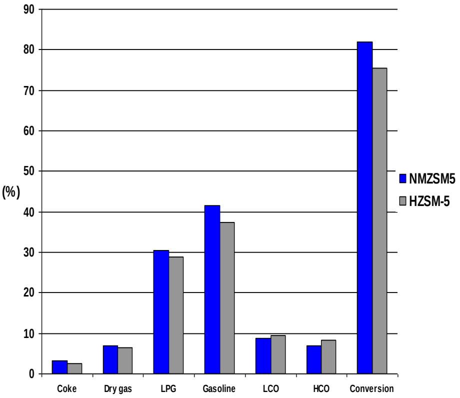
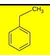
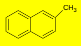
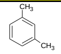
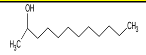
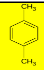
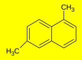
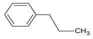
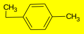
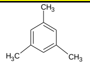
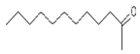
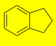
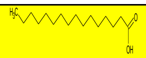
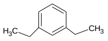
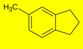
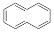


Figure 4: *Products and conversion of vegetable oil sludge cracking reaction over catalysts*

Table 3: *Liquid product fragment*

N_0	Product's name	Formular	%	N_0	Product's name	formular	%
1	Ethyl-benzene		3.25	11	2-Methyl-naphthalene		7.79
2	1,3-dimethyl-benzene		13.13	12	2-Dodecanol		2.37
3	1,4-dimethyl-benzene		4.35	13	1,6-dimethyl-naphthalene		2.18
4	Propyl-benzen		1.03	14	1,3-dimethyl-naphthalene		1.2
5	4-Ethyl-toluene		8.18	15	Heptadecane		3.46
6	1,3,5-Trimethyl-benzene		2.73	16	2-Dodecanone		1.23
7	2,3-dihydro-1H- indene		1.50	17	Hexadecanoic acid		23.44
8	O-diethyl benzene		1.82	18	2-Propenyl-decanoate		3.09
9	2,3-dihydro-5-methyl-1H- Indene		1.52	19	Tridecanol		2.50
10	Napthalene		3.89		Others (<1%)		

Acknowledgment: The authors thank the Vietnamese Ministry of Science and Technology and the Begian federal science policy office for financial support.

SYNTHESIS, CHARACTERIZATION AND CATALYTIC PROPERTIES OF HY AND HZSM-5 ZEOLITES SYNTHESIZED BY USING SILICA RESOURCE FROM VIETNAMESE RICE HUSK IN THE CRACKING REACTION OF VEGETABLE OIL SLUDGE

Le Thi Hoai Nam[1], Nguyen Dinh Tuyen[1], Nguyen Ngoc Triu[1], Tran Quang Vinh[1], Vu Thi Minh Hong[1], Van Dinh Son Tho[2], Do Xuan Dong[1], Xiao- Yu Yang[3], Zoulika Hadj-Sadok[3], Bao-Lian Su[3]

1. Institute of Chemistry, Vietnamese Academy of Science and Technology, 2 Hanoi University of Technology, 3University of Namur (Belgium)

Abstract

HY and HZSM-5 zeolites were successfully synthesized by hydrothermal treatment using silica derived from rice husk silica. The samples were characterized by XRD, IR, SEM, TEM and 27Al-NMR methods. Their catalytic activities were tested on the vegetable oil sludge cracking reaction to produce biodiesel. Characterization results revealed that materials synthesized from rice husk silica have crystallinity and acidity as high as standard samples. In the same conditions of the cracking reaction, HZSM-5 showed its priority of catalytic performance compares to that of HY in terms of conversion and yield of liquid fuel gasoline fraction

INTRODUCTION

Biodiesel which is produced by the transformation of vegetable oil, oil sludge, oil heavy segment or polymer waste is one of solutions that scientists are being interested in and the obtained results are very promising. The optimum technology for this transformation is catalytic cracking process. Two of the most used catalysts are Y and ZSM-5 zeolites because they have high thermal-hydrothermal durability and are suitable for the condition of cracking reaction.

Rice husk is the milling byproduct of rice and is a major waste material of the agricultural industry. In Viet Nam, annual rice husk quantity is 5 million tons. However, rice husk has little or no commercial application. Therefore, the reusing of rice husk with high value is interested by many researchers. Rice husk has the main composition are metal oxides. In there, SiO_2 is over 20% and was proved that it is very good quality of silica source.

In this study, we report results of the synthesis and characterization of HY and HZSM-5 zeolites synthesized from rice husk silica and compare their catalytic activity in vegetable oil sludge cracking reaction to form renewable bio-based products suitable for use in fuel and chemical applications...

EXPERIMENTAL

1. Slica-source preparation: Silica-source for the synthesis of ZSM-5 was extracted from rice husk by using solution NaOH 1% at 80^0C for 30 minutes.

2. HZSM-5 preparation: ZSM-5 material was synthesized using TPABr as template. The obtained gel was crystallized at 170^0C for 24 hours. The product was washed, dried at 100^0C and calcined at 550^0C for 5 hours to remove all template. Then, product was ion exchanged with NH_4NO_3 2M, washed, dried and calcined again to form HZSM-5.

3. HY preparation: Gel has molar ratio as follows: $28NaOH \times 1Al_2O_3 \times 20SiO_2 \times 300H_2O$. Gel was aged at ambient temperature for 72 hours and hydrothermal crystallized at 100^0C for 24 hours. After that, the obtained product was washed, dried and calcined at 500^0C for 3 hours. Product continues to be ion exchanged with NH_4NO_3 2M, washed, dried and calcined again to form HY.

4. Characterization methods: Infrared spectrum (IR), XRD pattern, SEM and TEM and ^{27}Al Solid state magic angle spinning (MAS)-NMR method.

5. Catalytic cracking reaction: The vegetable oil sludge's composition is triglyceride (61%), free fatty acid (37%) and impurities (2%). The hydrocarbon chains of triglyceride and free fatty acid are mainly C_{16}(30%) and C_{18} (36%) hydrocarbon. The others consisted of C_{12}-C_{17} hydrocarbon chain.

Micro-activity test MAT 5000 of Zeton-Canada was used for catalytic cracking. with ASTM D5154 testing method. Main parameters were described in table 1.

The coke formation was in-situ evaluated by 1440 Gas Analyzer – Servomex. The gas product was analyzed by Refinery gas analyzer–Trace GC-ThermoElectro. The liquid product was determined by SIMDIST GC ThermoElectro system, detector FID integrated TriPlus auto-sampler. The calibration gas is RGA standard of MESA International Technologies, Inc. The calibration liquid for distillation simulation is ASTM D2887 Calibration mix (RESTEK). The composition detail of the liquid fraction of the vegetable

RESULTS AND DISCUSSION

Table 1. ***The input parameters***

Catalytic cracking condition	
Weight of catalyst	4.0600 (g)
Catalyst Bed Cracking	483.0 (ºC)
Total N_2 Flowrate (Prepurge)	50(ml/s)
Total N_2 Flowrate (Reaction)	5 (ml/s)
Total N_2 Flowrate (Stripping)	25(ml/s)
Oil Feed Temperature	50.0 (°C)
Oil Feed Density @ 50.0°C	0.87 (g/ml)
Actual Volumetric Oil Feed	1.16 (ml)
N_2 Pre-purge Time	15.0 (min)
N_2 Reaction Time	75 (sec)
N_2 Stripping Time	10.0 (min)

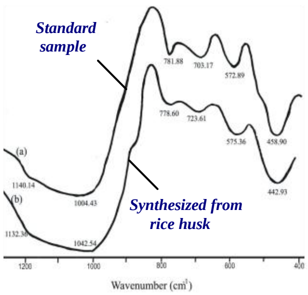


Figure 1: ***: IR spectrums of Y zeolites***

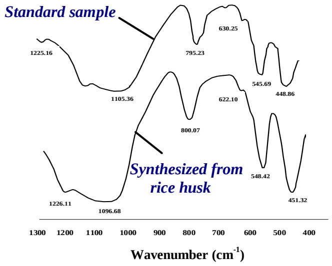


Figure 2: ***IR spectrums of ZSM-5 zeolite***

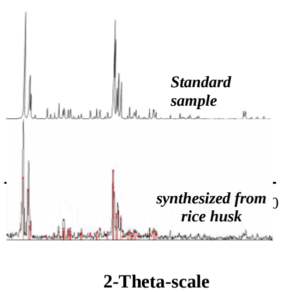


Figure 3: ***XRD patterns of ZSM-5 zeolites***

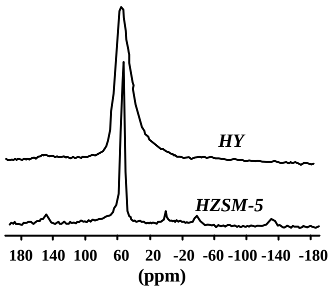


Figure 4. ***^{27}Al-NMR of materials***

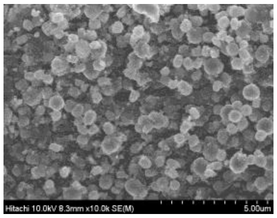


Figure 5: ***SEM image of HY***

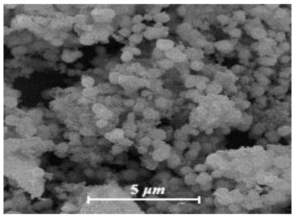


Figure 6: ***SEM image of HZSM-5***

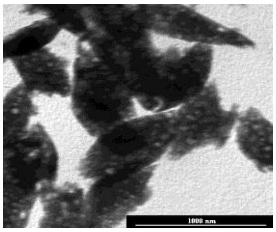


Figure 7: ***TEM image of HZSM-5***

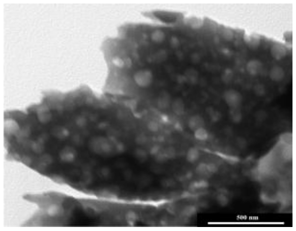


Figure 8: ***TEM image of HY***

CATALTYTIC PERFORMANCE perfomance

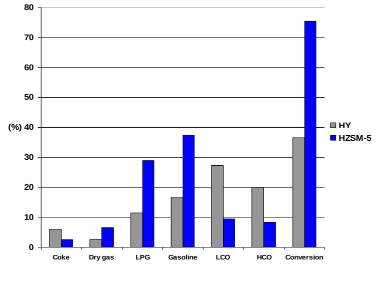


Figure 9: ***Products and conversion of vegetabl sludge cracking reaction***

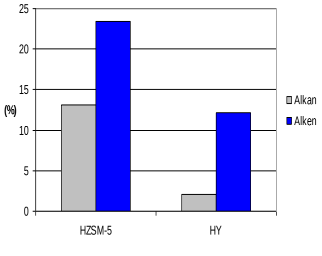


Figure 10. ***Distribution chart of alkane and alkene products***

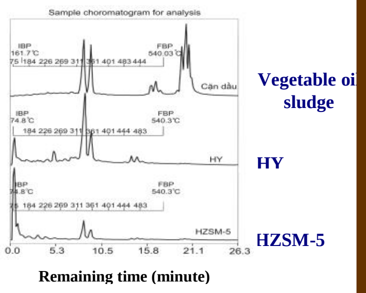


Figure 11: ***The distribution of liquid product by the boiling point***

CONCLUSION

HY and HZSM-5 catalysts were successfully synthesized from rice husk silica. The characterization results show that the synthesized materials have the crystallinity is equivalent to that of standard samples. **The liquid product of cracking reaction using HZSM-5 has the octane number much higher than that using HY due to the higher content of aromatic hydrocarbon (from the result of GCMS).** Besides the conventional pores system exits in zeolite structure, there is another pores system which has diameter in range of 10-50nm (mesoporous system) due to the burning of organic compounds remain in material during the calcination process. This mesopours system might increase the catalytic activity of synthesized matyerials.

HZSM-5 proved that it is a good catalyst in the cracking reaction of vegetable oil sludge with not only high conversion but also high selectivity for LPG and gasoline products in comparison to HY. The obtained results have found a new way in the salvage of agricultural waste to produce the promising catalysts which apply not only to catalysis and adsorption fields but also to produce biodiesel from vegetable oil sludge replacing the exhausted natural petroleum oil resource.

Acknowledgment: The authors thank the Vietnamese Ministry of Science and Technology and the Begian federal science policy office for financial support.