

BENTONITE PILLARED BY MESOPOROUS SILICA AND ITS APPLICATION FOR GASOLINE TREATMENT

**Vo Thi My Nga^{1*}, Bui Xuan Vuong², Do Trung Hieu³, Nguyen Thanh Binh³,
Tran Tan Nhat⁴**

¹*Tuy Hoa Industrial College, 261 Nguyen Tat Thanh Road, Tuy Hoa City*

²*Sai Gon University, 273 An Duong Vuong Road, District 5, Ho Chi Minh City*

³*Faculty of Chemistry, VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Ha Noi City*

⁴*HCM City University of Food Industry, 140 Le Trong Tan, Tan Phu District, Ho Chi Minh City*

*Email: *vothimynga.pc@gmail.com*

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ABSTRACT

Di Linh bentonite was successfully pillared by mesoporous silica and this result had been published in previous reports. The acidity of this material was estimated by modern physico-chemical methods such as IR, TPD-NH₃ and the material was applied in the field of petrochemical catalysis. The acidity of the material has also been demonstrated by Cumen cracking at low temperatures about 350 °C with benzene conversion of 36.46 % and benzene selectivity of 73.98 %. In addition, the gasoline yield of silica mesoporous material pillared bentonite had got more twice higher than the one when using a mixture of bentonite powder and MCM-41 powder in the cracking Wax. This result confirms that the bond formation between bentonite and mesoporous silica when using one-step method, which increase acidity of the synthesized material.

Keywords: bentonite, MCM-41, mesoporous material, cracking catalyst, pillared-clay.

1. INTRODUCTION

Fossil fuels are being used very much in the world as well as in Vietnam. Therefore, to save resources, currently, oil refining industry has paid attention to thorough exploiting and effective using heavy oil (residue oil) as a feedstock for producing the high-value products such as gasoline, light olefins, transportation fuels, etc., or as an important raw material to create necessary initial-feedstock products for petrochemical industry and chemical industry. The raw materials are processed in the catalytic cracking units, in which the C-C bonds of long chain molecules have been broken and formed into shorter chain molecules having more useful and higher economic value, for example: C₃ to C₁₀. The quality of product segmentations in this process depends on the properties of every catalyst type used. They are the solid acidic catalysts having combined micro – and meso-pores with their high activities in catalytic cracking process

to break the C-C bonds through primary-treatment as well as secondary-treatment and be able to withstand heavy metal poisoning such as Ni, V, etc.

In the previous reports [1 - 2], the structural properties and the ability to react in cracking reaction of these materials were characterized by modern physical methods such as SEM, TEM, BET, XRD, TGA-DTA and was also evaluated by Wax cracking reactions at different temperatures. These obtained results confirmed that bentonite pillared by mesoporous silica material has stability structure. The major components of bentonite are mainly montmorillonite clay. Bentonite has been widely used in the industrial sector, adsorption material and catalytic field due to its characteristics such as swelling, ion exchange capacity. Bentonites are also named as "activated clay" because of their affinity in certain chemical reactions that are caused by excessive negative charge [3 - 4]. In this report, the textural properties and acidic properties of raw bentonite material and the bentonite pillared by mesoporous silica material were further investigated by modern physical methods such as TPD-NH₃ and IR. In this report, the textural properties and acidic properties of raw bentonite material and the bentonite -mesoporous were further investigated by modern physical methods such as TPD-NH₃ and IR. Besides, the catalytic activity of Cumen model molecule cracking reaction and meso-catalysts Wax cracking reaction ($d_{15\text{Wax}} = 0.8431 \text{ g/cm}^3$) were confirmed the synthesized catalysts using as the acid catalysts to break the C - C bonds in the hydrocarbon molecules of large molecular weight.

2. EXPERIMENTAL

Bent.Na had been exchanged by ion H⁺ and but not changed the pristine-state layer structure of bentonite [1, 2]. This obtained solid was denoted as Bent.H.

Bentonite acid materials (Bent.H) pillared by mesoporous silica was synthesized by one pot method in the optimal conditions as following: aging temperature 100 °C; aging time 20 - 40 hours; ratio of Si/Bent.H of around 1.2 [1, 2]. This synthesized sample was called BHSMC.

For comparison, the mixture of Bent.H and MCM-41 with ratio of Si/BentH of around 1.2 was used as reference. This sample was called BHSMC-mix.

Temperature-Programmed Desorption (TPD) of ammonia for characterizing the acid sites on BHSMC was practiced on Autochem II 2920 at the laboratory of School of Chemical Engineering, Hanoi University of Science and Technology.

The FT-IR spectra of the samples were obtained at Department of Chemistry, Hanoi University of Science, VNU.

The catalytic activity of BHSMC was evaluated by Cumen cracking reaction at atmospheric pressure, temperature of 350 °C in a gas phase reactor with weight hourly space velocity (WHSV) of 1.72 h⁻¹. Liquid products were analyzed on GC-MS HP 6840 with mass spectrometry detector MSHP 5684 (U.S.) and capillary column HP-5 at Department of Chemistry, Hanoi University of Science, VNU.

The catalytic activity of the acid solids such as BHSMC, Bent.H and BHSMC-mix was evaluated by the Wax cracking reaction on the FCC-SCT-MAT system. The components in products were analyzed by GC-SIMDIS, GC-GAS, GC-RON in Petrovietnam Research and Development Center for Petroleum Processing (PVPro) of Vietnam Petroleum Institute.

(Wax is a product of pyrolysis reaction of waste plastics in the Dung Quat refinery. This product has an average molecular weight: 528.5; density at 15 °C: 0.8431 (g/ml) and kinematic viscosity at 70 °C is 21.51 (cSt)).

3. RESULTS AND DISCUSSION

3.1. IR results

Figure 1 shows the FT-IR spectrum of the obtained materials in the range of 4000 – 600 cm^{-1} . Spectral band at 1630 cm^{-1} is assigned to $\delta\text{SiO-H}$. The strong and wide bands around 1200 – 1000 cm^{-1} correspond to the asymmetric Si–O stretching modes of bentonite layers. The bentonite also has the wide band around 1200 – 1000 cm^{-1} . However, BHSMC has sharper band at 1050 cm^{-1} . This suggests that the crystallinity of the particles increased and the particles became more compact. Moreover, these results indicate that the mesoporous silica structure have been intercalated into the interlayer of bentonite [3 - 7].

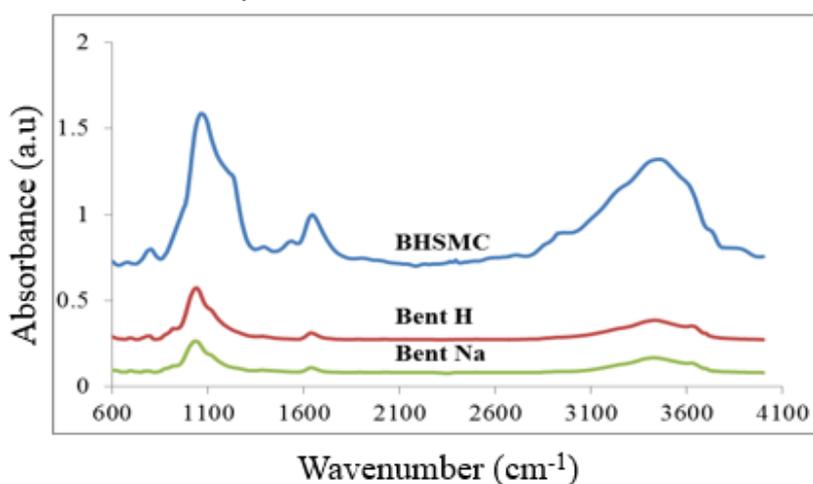


Figure 1. FT-IR spectrum of BHSMC, Bent H and Bent Na.

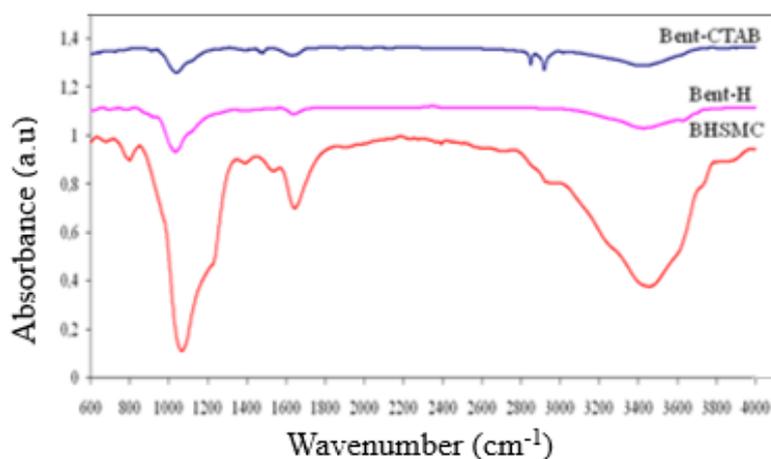


Figure 2. FT-IR spectrum of BHSMC, Bent.H and Bent.CTAB.

During BHSMC synthesis process, the surfactant cetyltrimethylammonium bromide (CTAB) had been added into gel - silica and after that removed by heating at 550 °C. Figure 2 shows the FT-IR spectrum of the samples, includes: Bent CTAB, BHSMC and Bent H in the

4000 - 400 cm^{-1} area. Bands at 3050 cm^{-1} and at 1630 cm^{-1} attribute to the $\delta\text{SiO-H}$ bond. The adsorption bands at 3622 cm^{-1} can be attached to the vibration of Si-OH-Al group which characterizes the covalent bonding of the OH (δOH) bonds of the water adsorbed molecules. They are also the Bronsted acid sites, being necessary for the conversion of hydrocarbons. Broad and strong bands at 1200 – 1000 cm^{-1} correspond to the Si-O asymmetric bonds in the silicate layers of bentonite. However, the BHSMC solid sample has sharper bands, especially at 1050 cm^{-1} . This is the oscillating band of the O-Si-O bond in the silica (SiO_2) network of mesoporous material. In addition, peaks of N-H or C-H only appeared on the IR spectrum of the Bent.CTAB but those peaks were not visible on the IR spectrum of BHSMC. This result indicated that CTAB was removed after calcination.

The 1445, 1546 and 1490 cm^{-1} bands are featured for Lewis and Bronsted acid sites. These results indicated that BHSMC, Bent.H, Bent.CTAB solid samples are acidic solids. Furthermore, the results also indicated that the synthesized silica structures were intercalated into the layers of bentonite.

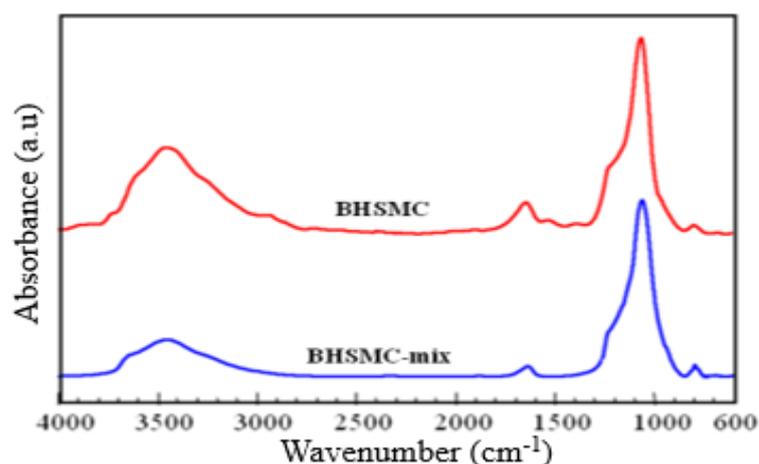


Figure 3. FT-IR spectrum of BHSMC and BHSMC-mix.

It is interesting to analyze the FT-IR spectrum of BHSMC and BHSMC-mix on Figure 3. The absorption area of 3625 – 3000 cm^{-1} of BHSMC is stronger than that of BHSMC – mix. Addition, it can be seen that the absorbing bands specified acidity of BHSMC (as described of the above paraphrase) has higher intensity and wider feet of peaks than their bands of BHSMC-mix.

3.2. TPD-NH₃ result

Among the methods for determining the amount and strength of acidity of acid catalyst, the adsorption-adsorption method of ammonia with the temperature program is very popular. The TPD-NH₃ results of the Bentonit-silica mesoporous samples are shown in Figures 4 and Table 1.

Before being pillared by mesoporous silica, volume adsorption of NH₃ was only about 0.07 ml/g [1]. However, pillaring by mesoporous silica made increasing significantly volume adsorption of NH₃, $V_{\text{NH}_3} = 30.37$ ml/g equivalent to 1.355 mmol/g. So, the acidity of BHSMC was greatly improved. This opens the possibility for applications of materials BHSMC as catalysts for cracking reactions of hydrocarbon with large molecular weight. Specially, due to

spatial structure too big of BHSMC, hydrocarbon with large molecular easily diffused through the pores of BHSMC.



Figure 4. TPD-NH₃ of BHSMC.

Table 1. Results of TPD-NH₃ for BHSMC.

Peak number	Temperature for NH ₃ desorption, °C	Volume of NH ₃ released, ml/g	Acid quantity, mmol/g	Acidic force
1	175.5	3.88	0.173	Weak
2	300.7	9.68	0.432	Medium
3	454.1	16.06	0.717	Strong
4	543.4	0.75	0.033	Very strong

3.3. Catalytic activity of BHSMC in Cumen cracking reaction

Cracking Cumen (isopropylbenzene) has long been viewed as a model reaction for evaluating cracking catalysts in the scale of laboratory.

Table 2. Results of liquid product analysis of cumene cracking reaction at 350°C on BHSMC catalyst and WHSV mass = 1.72 h⁻¹.

Catalysts	Composition of total liquid product, % wt		Conversion of Cumene, % wt	Selectivity of benzene, % wt
	Benzene	Other product		
BHSMC	26.985	9.483	36.46	73.98

Other products: α -methylstyren is ~ 42 - 53 %.

From the obtained results in Table 2, it can be concluded that BHSMC material has a good catalytic activity for Cumen molecular cracking and opens the direction in studying BHSMC catalysts for cracking reaction of hydrocarbon with large molecules.

3.4. Catalytic activity of BHSMC in Wax cracking reaction

Table 3. Analytic results of the total products in WAX cracking reaction at 460 °C with ratio C/F = 1.

Catalysts	Composition of total product, %wt					Standard MAT conversion, %
	Total gas	Coke	Total Gasoline	LCO	HCO	
No - cat	0.31	0.00	3.35	4.67	91.67	3.66
Bent.H	7.55	0.99	66.25	20.55	4.65	74.80
BHSMC	11.61	0.56	72.69	11.68	3.46	84.86
BHSMC-mix	4.22	0.79	25.78	15.34	53.87	30.78

Here in, No-cat: No use catalysts.

In order to compare the catalytic activity between BHSMC and Bent.H, the Wax cracking reaction was conducted at 460 °C and ratio catalyst/feed (C/F) was of 1. The products were analyzed by the GC-MS method. Results are given in Table 3 and Figures 5 - 6.

At 460 °C, in the absence of catalyst (only a glassbead amount used) with short time on stream 12 s, almost no reaction occurred, including even thermal cracking reactions, and conversion increased to 84.86 %, which was larger than Bent.H conversion of 74.80 % for BHSMC. At the same time, the main gas product was also higher than the one of Bent.H.

Comparing the activity of BHSMC and BHSMC-mix catalysts at a reaction temperature of 460°C, the results showed that the conversion, when using BHSMC-mix, was 2.75 times less than that of BHSMC. Obtained results highlight that BHSMC material obtained by the one-step method formed the bonds between bentonite layer and Si and thus generated Bronsted acid sites on the surface of BHSMC or in the walls of pores.

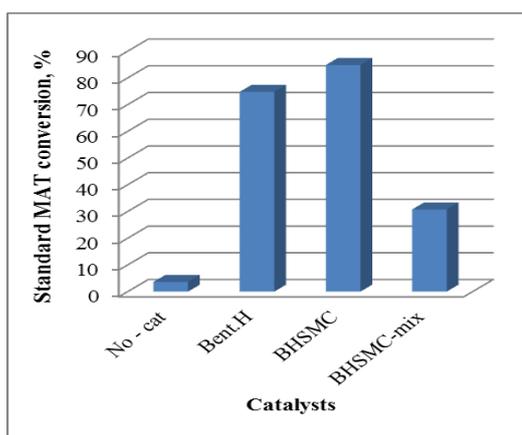


Figure 5. Descriptive graph of standard MAT conversion, %.

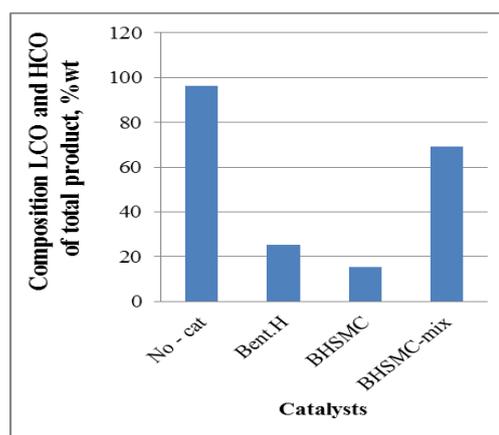


Figure 6. Descriptive graph of Composition LCO and HCO of total product, %wt.

4. CONCLUSIONS

BHSMC can be able to join in Cumen cracking reaction with conversion 36.46 % at 350 °C, in the bed-flow system, WHSV = 1.72 h⁻¹ and the selectivity of benzene is 73.98 %.

Conversion, efficiency of gasoline and of LPG in Wax cracking reaction at 460 °C on BHSMC were the highest in comparison with other catalysts: BHSMC got conversion of 84.86 % and higher 2.75 times than that of BHSMC-mix.

Acidities of BHSMC materials are completely different from mix of Bent.H and MCM-41 separately and results showed acidity of BHSMC in Wax cracking reaction in accordance with the TPD-NH₃ results of BHSMC.

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