

SYNTHESIS AND PROPERTIES OF MATERIAL BASED ON ORGANIC SILICA AND ZEOLITE MORDENITE

Nguyen Thi Huong^{1,*}, Le Thanh Son², Tran Hong Con²

¹*Institute for Chemistry and Material, Vietnam Academy of Military Science and Technology*

²*Faculty of Chemistry, Hanoi University of Natural Science, VNU*

Received 25 November 2014; Accepted for Publication 20 April 2015

Abstract

The materials based on organic silica and zeolite mordenite were synthesized from self-assembly of polymethylhydrosiloxane, tetraethoxysilane and zeolite mordenite using sodium hydroxide as catalyst. The structure characteristic and the porosity of the resultant mesoporous material were studied by SEM, XRD and the nitrogen adsorption isotherm techniques. Chemical bondings were characterized by using Fourier transform infrared spectroscopy. Results indicate that the obtained materials exhibit the large surface area and porosity.

Keywords. Polymethylhydrosiloxane, Tetraethoxysilane, Zeolite mordenite, Mesoporous, Silica-based.

1. INTRODUCTION

Materials based on organic-inorganic silica such as: mesoporous nanocomposites, membrane zeolite, zeolite-polymer hybrid materials, are increasingly interested because of their ability of heat resistance, chemical resistance, high catalytic activity and effective application in environmental treatment. These materials have been studied, fabricated and classified according to micro- and mesoporous, in correlation of their structure and properties [1].

The results of the recent research show that the membrane combined of polymer and zeolite has ability of selecting and infiltrating gases [2-9]. Kloetstra and his coworkers synthesized composite of zeolite faujasite (FAU) and MCM-41 by developing a thin membrane of MCM-41 on FAU and achieving some good results from this materials' application in vacuum oil cracking [10]. Furthermore, Y. Zang synthesized MCM-41/b composite with dual acid and porous structure by double crystallization [11]. Recently, some mesoporous materials based on methylate, have been synthesized by using non-ion surface-active agent and bimodal material with micro/mesopore without using surface-active agent [1]. This article shows the synthesis method and properties of the material based on organic silica and zeolite mordenite with application orienting in treatment of volatile organic gases.

2. EXPERIMENTAL

Chemicals producing the materials include: zeolite mordenite (MOR) (as synthesized in [12]), polymethylhydrosiloxane (PMHS) (Mn 1,700-3,200, Aldrich), tetraethoxysilane (TEOS, 98 %, Aldrich), ethyl alcohol (anhydrous) and sodium hydroxide. The materials were prepared by: weighing 0.06 g NaOH and 60 ml ethanol in a glass cup, adding 3 ml PMHS and stirring well for 120 minutes. Adding 2 ml TEOS and 1 ml deionizing water and stirring for 180 minutes. A compound gel (sample G1) was obtained. Weighing 1 g zeolite mordenite in a glass cup, and doing the same experiment as sample G1; the compound gel (sample G2) was produced. Samples G1, G2 was dried at 75 °C for 72 hours. After-drying samples were powdered. Such powder was washed twice with the deionizing water; and then dried at room temperature for 12 hours, then at 75 °C for 24 hours. Finally, samples were produced, respectively marked as Z1 and Z2.

The materials' surface structure was identified by scanning electron microscope (SEM) (Jeol 6610LA machine, Japan). Chemical bondings were determined by infrared (IR) spectroscopy (GX-Perkin Elmer machine (USA), thermal properties - (STA 409PC Netzsch differential thermal analyzer, Germany), surface area-(Tristar 3000-Micromeritics, USA).

3. RESULTS AND DISCUSSION

The characteristic bonding of the materials was determined by analyzing infrared spectrum of samples Z1 and Z2 (figure 1).

Sample Z1's spectrum shows that a broad peak at 3434.12 cm^{-1} may be caused by stretching vibration of O-H bonding of water as moisture and water crystallized in the sample. The C-H stretching vibration of CH_3 group is observed at 2933.86 cm^{-1} . The bands appeared at 1108.77 and 1029.61 cm^{-1} with strong to medium intensity are the results of the coupling of the Si-O-Si and Si-O-C stretching; the band of the Si-C stretching vibration appeared at 1276.55 cm^{-1} in variable weak intensity. For sample Z2, its spectrum is similar to the sample Z1: the O-H

stretching vibration of water crystallized in the sample is observed at 3513.44 and 1629.38 cm^{-1} , the C-H stretching vibration of CH_3 group is observed at 2983.95 cm^{-1} . The Si-O stretching vibration of MOR, Si-O-Si structure, Si-O-C in organic part after hydrolysis occur in the region of 1034.57 - 1124.45 cm^{-1} . Moreover, the band appeared at 1277.78 cm^{-1} with weak intensity is symmetric bending vibration of Si- CH_3 bonding. Noticeably, there is no presence of peaks at 2200 and 800 to 950 cm^{-1} in both samples Z1 and Z2. This proves that Si-H bonding of PMHS no longer survived, and the bonding was removed by the hydrolysis.

Morphology and chemical composition of surfaces of samples Z1 and Z2 were determined by analyzing SEM-EDX (figure 2).

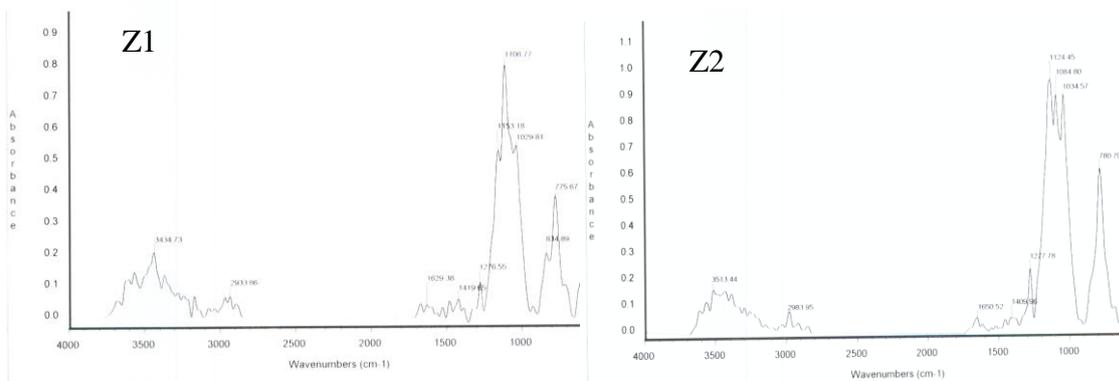


Figure 1: Infrared spectra of samples Z1 and Z2

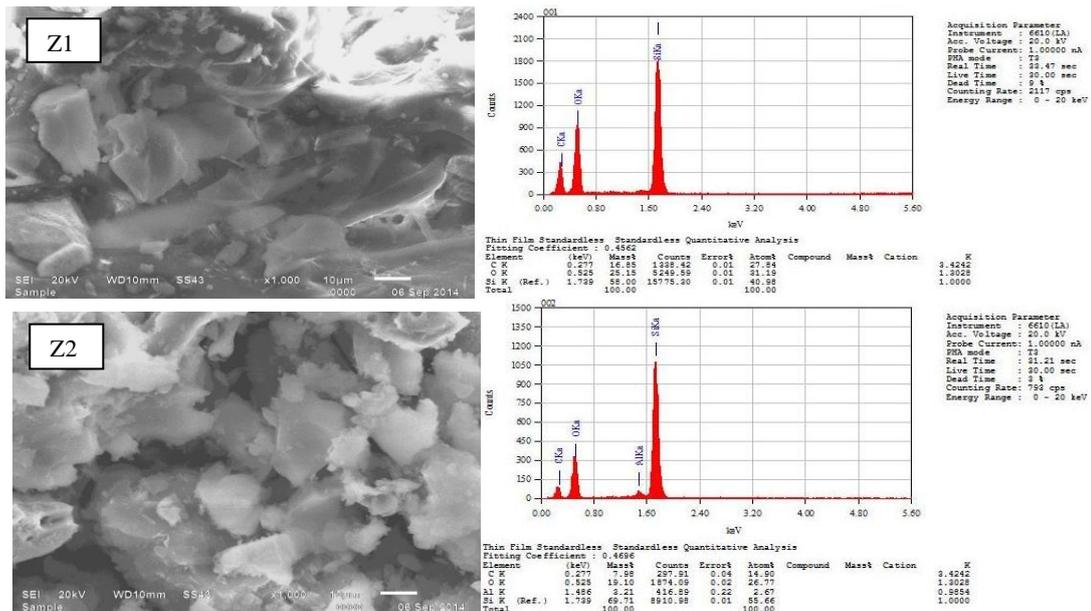


Figure 2: SEM image and chemical composition of the surface of samples Z1 and Z2

Figure 2 indicates that sample Z1 does not contain MOR. Its surface structure is smooth, and creates a mass form (figure 2 Z1) respectively chemical composition of the sample surface includes main elements: Si (58 %), O (25.15 %) and C (16.85 %). With the sample containing MOR, its surface changed a lot (figure 2 Z2); it is a group of porous particles in different size; its surface structure is composed by elements: Si (69.71 %), O (19.10 %) and C (7.98 %) and Al (3.21 %). Comparing

composition with sample Z1 indicated that element Si increased significantly from 58.00 % (sample Z1) to 69.71 % (sample Z2). This increases in chemical composition resulted from MOR's elements existing in the sample. SEM results also showed that the materials distributed irregularly; separation between phases was not found. This proves that MOR disperses well and binds to the synthetic materials. Figure 3 is XRD diagram of materials Z1 and Z2.

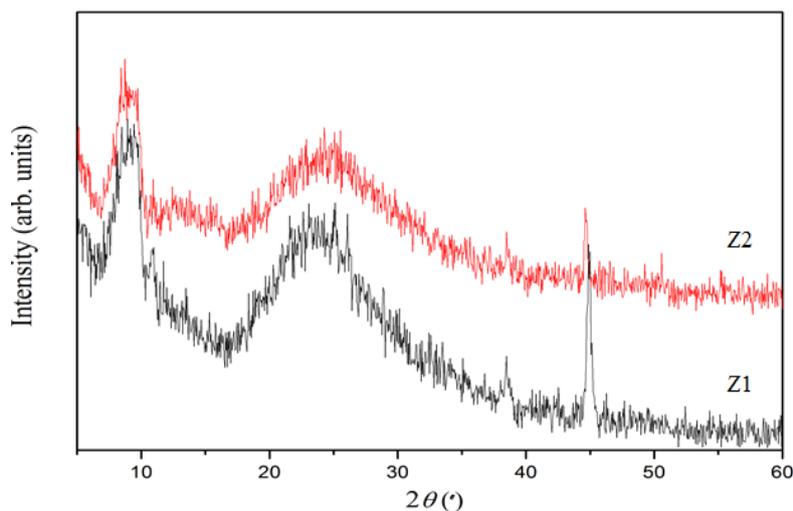


Figure 3: XRD diagram of samples Z1 and Z2

Spectra showed that diffraction spectral diagram of samples Z1 and Z2 covered a wide diffraction peak (reflex 100).

According to Dongjiang Yang [1], this diffraction was corresponding to distance $d=6.8$ nm, resulted in overlapping reflexes 110 and 200. These spectra are similar to those described in the report on materials based on meso-structured silica. Maybe, adding CH_3 groups led to formation of wide peaks [1]. Moreover, on the chart, many single peaks at value $2\theta = 25^\circ$ (figure 3 Z1), $2\theta = 24^\circ$ (figure 3 Z2) appear, this indicates that silicon frame has amorphous structure. Noticeably, diagram in figure 3 Z2 has not characteristic peak of MOR, that is may be caused by enclosing compounds of amorphous silicon frame which confined the MOR.

To have better understanding about these materials structure, porous structure and surface area of the samples were determined by nitrogen isothermal adsorption. Diagram results were represented in figure 4.

Figure 4 is diagram of nitrogen adsorption and desorption of samples Z1 and Z2.

Studying on surface features of synthesized materials Z1 and Z2 was based on adsorption and de-adsorption method (BET). Nitrogen adsorption and de-adsorption isotherm belongs to type IV and

has hysteresis loop type H2 (as sorted by IUPAC). The properties belongs to materials have medium capillary with cylinder in both ends, and corresponding to distribution of Barret-Joyner-Halenda (BJH) pores, and corresponding to distribution of Barret-Joyner-Halenda (BJH) pores. In figure 4, it can be seen that desorption curves of samples Z1 and Z2 is very smooth, of which sample Z2 (figure a-Z2) has adsorption and de-adsorption isotherm curve beginning to condensate at relative pressure P/P_0 about 0.6-0.7. This prove that the materials' capillary diameter is fairly large, and larger than that of sample Z1. Moreover, sample Z2's capillary diameter distribution curve is type of narrow peak, high intensity. This proves that the synthesized materials has relatively uniform dimension, the capillary diameter is about 15.5 nm on average. Correspondingly, the sample Z2 has surface area of $297.85 \text{ m}^2/\text{g}$ higher than sample Z1 ($238.00 \text{ m}^2/\text{g}$). Results show that synthesized sample Z2 has extra MOR and thus its surface area increased significantly and range of pore dimension distribution also was larger than the non-MOR containing sample.

After surveying on the materials' structure, its thermal properties were studied. Figure 5 illustrates the differential thermoanalysis diagrams of samples

Z1 and Z2.

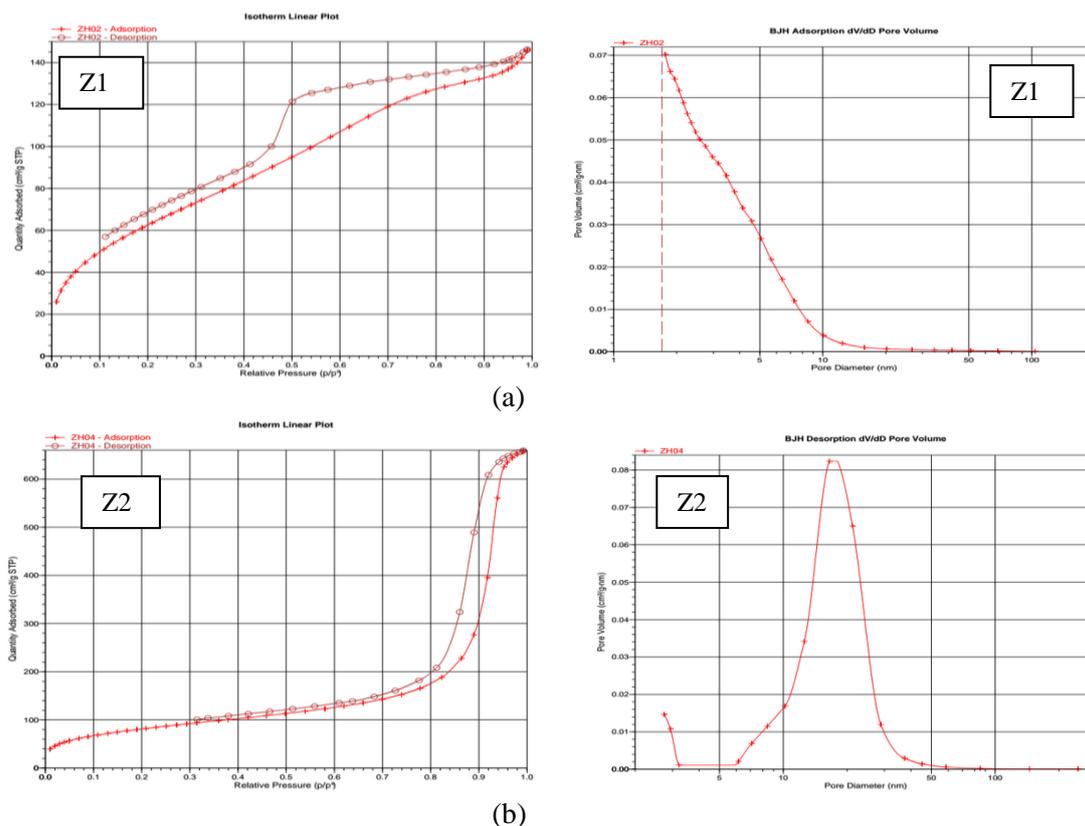


Figure 4: Diagram of nitrogen adsorption and desorption (a) and distribution of pore size (b) of samples Z1 and Z2

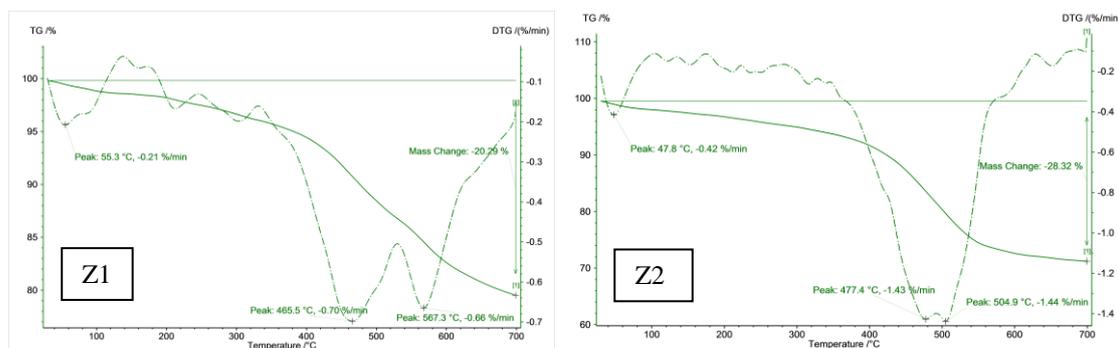


Figure 5: Differential thermoanalysis diagrams of samples Z1 and Z2

Differential thermoanalysis diagrams show that at higher temperature, the samples' mass was reduced and stabilized, of which sample Z2 was more stable than sample Z1. At 300 °C, the sample's weight was reduced insignificantly, about 5 % for sample Z1 and 6 % for sample Z2. Thermal effects on DTA curve were stable. At higher temperature, the mass reduction happened rapidly with strong thermal decomposition and this phenomenon was represented on DTG line with great endothermic effect, respectively at 465.5 and 567.3 °C for Z1 and

477.4 and 504.9 °C for Z2. These results show that the material based on silica has very good thermal resistance, that is an advantage of this material.

4. CONCLUSION

Properties of materials based on organic silica and zeolite mordenite were prepared and studied. The study on silica-based materials containing MOR (Z2) shows that there is the presence of characteristic peaks for OH bonding, CH bonding in

CH₃, Si-O-Si in the structure of MOR and Si-O-Si, Si-O-C in the post-hydrolysis organic part. MOR dispersed and bound well in the materials. Sample Z2 has more porosity and creates more uniform particles than the non-MOR sample (Z1). These samples have micro/mesoporous structure with pore diameters distributed from 10-200 nm, surface area of 238.00 m²/g (Z1) and 297.85 m²/g (Z2). Both samples have good ability of thermal resistance and these are decomposed at > 450 °C, but Z2 has thermal stability better than Z1.

REFERENCES

1. Dongjiang Yang, Jungping Li, Yao Xu, Dong Wu, Yuhan Sun, Huaiyong Zhu and Feng Deng. *Micropor. Mesopor. Mater.*, **95**, 180 (2006).
2. Fei Zhang, Longnv Xu, Na Hu, Rongfei Zhou and Xiangshu Chen. *Separation and Purification technology*, **129**, 9 (2014).
3. A. J. Maira, W.N. Lau, C. Y. Lee, P. L. Yue, C. K. Chan and K. L. Yeung. *Chemical Engineering Science* **58** 959 (2003).
4. M. P. Bernal, J. Coronas, M. Menéndez and J. Santamaría. *AIChE Journal*, **5**, 127 (2014).
5. Najib Tijani, Khalid Yamni, SaidLamsiah and Abdelhadiel Krouk. *Toxicology and Food technology (IOSR-JESTFT), Journal of Enviromental Science*, **8** 90 (2014).
6. Ahmad Fausi Ismail, Norida Ridzuan and Sunarti Abdul Rahman. *Membrane Sci&Tech*, **24**, 1025 (2002).
7. Kyung Byung Yoon. *Acc. Chem. Res.*, **40** 29 (2007).
8. Dariush Bastani, Nazila Esmaeili and Mahdieh Asaddollahi. *Journal of industrial and engineering chemistry*, **19**, 375 (2013).
9. Nikolay Kosinov, Venkata G. P. Sripathi and Emiel J. M. Hense. *Microporous and mesoporous materials*, **194**, 24 (2014).
10. K. R. Kloetstra, H. W. Zandbergen, J. C. Jansen, H. Van Bekkum. *Micropor. Mesopor. Mater.*, **6** 287 (1996).
11. Y. Zang, J. M. Kim, D. Wu, Y. H. Sun, D. Y. Zhao and S. Y. Peng. *J. Non-Cryst. Solids*, **351**, 777 (2005).
12. Manh Huy Do, Fengqiu Chen, Xiaoli Zhan. *Materials Letters*, **141**, 231-234 (2015).

Corresponding author: **Nguyen Thi Huong**

Institute for Chemistry and Material
 Vietnam Academy of Military Science and Technology
 17 Hoang Sam, Cau Giay, Hanoi, Vietnam
 E-mail: nguyenuong0916@gmail.com
 Mobile: (+84) 0916026627.