



RESEARCH ARTICLE

CALCINATION OF MOLECULAR SIEVES BY SIMPLE TECHNIQUE ENHANCING THERMAL STABILITY OF NOVEL NANOPOROUS MATERIAL

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ABSTRACT

Calcination is an important process to remove the template to open the pores of molecular sieves. The calcination process is difficult when the interaction of the template with the framework of molecular sieves is too strong. In some cases, it breaks the framework and reduces the thermal stability and crystalline nature of materials. During this investigation, the template molecules swift out from the pores when calcination at lower temperatures without breaking the framework. The synthesized catalyst is characterized by various spectroscopic techniques as XRD, FT-IR, BET surface area, TGA, SEM and TEM. The catalyst showed high thermal stability and also has good catalytic activity for the esterification of n-butanol and acetic acid.

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INTRODUCTION

Porous materials are solid forms of matter permeated by interconnected or non-interconnected pores (voids) of different kinds: channels, cavities or interstices. Porous materials are of great interest in various applications, ranging from catalysis, adsorption, sensing, energy storage and electronics owing to their high surface area, tunable pore size, adjustable framework and surface properties (Sayari and Liu, 1997). The discovery of nanoporous materials has opened a wide range of opportunities in fundamental researches and applications in various fields of technology. Through this intense research, new families of mesoporous materials such as AlPO₄, SBA, MSU and FSM were developed with characteristic porosities and particle shapes (Limin Wang *et al.*, 2004). Templating is one of the extensively used methods to synthesize materials with structural units ranging from nano to micrometers. The template self-assemblies provide unlimited opportunities to design the porous frameworks of the materials (Nataša Zabukovec Logar, 2006).

Most of the porous materials are not survive in high-temperature calcination (Seong-Su Kim, 2000; Filip Ciesielczyk *et al.*, 2014; Ji Man Kim *et al.*, 2000). The key to successful calcination is to select the right template. In the conventional synthesis method, the templates are soluble in the synthesis medium and the framework chemically interacts with the template molecules. So calcination of the material synthesized by conventional methods is extremely intricate. Since it requires high temperature and long time, it collapses the framework of the material and leads to the formation of amorphous substances. This problem has overcome by this effortless calcination technique. In this method, the template molecule swift out from the pores at lower temperature.

Experimental

Synthesis

Hydrocarbon of alkyl chain length C₁₂ is used as a template in the molecular sieve synthesis. The molar composition of the gel is 0.05 Na₂SiO₃: 4 H₂O: 0.01 C₁₂H₂₆. Sodium silicate (14.21g) was dissolved in deionized water (75ml) under stirring. Then 0.01 mole of C₁₂ hydrocarbon is added into the solution. The resulting mixture was stirred for 2 hour at room temperature and the pH of the mixture is adjusted to 10 by the drop wise addition of concentrated sulphuric acid.

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Table 1. Selectivity of ester and conversion of n-butanol

Molar Ratio (alcohol : acid)	Conversion (%)	Product Selectivity (%)
1:1	98.00	97
1:2	99.95	99
1:3	99.00	98

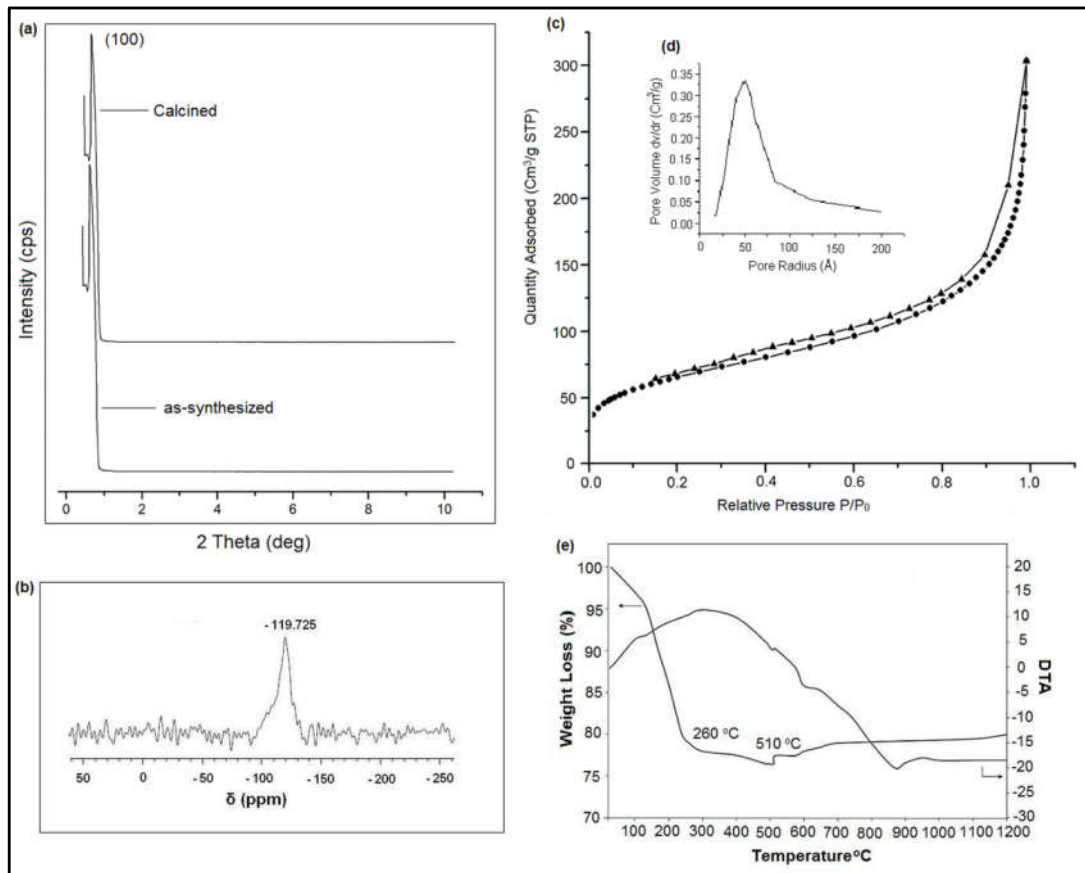


Figure 1. Characterization results for the mesoporous hexagonal molecular sieves

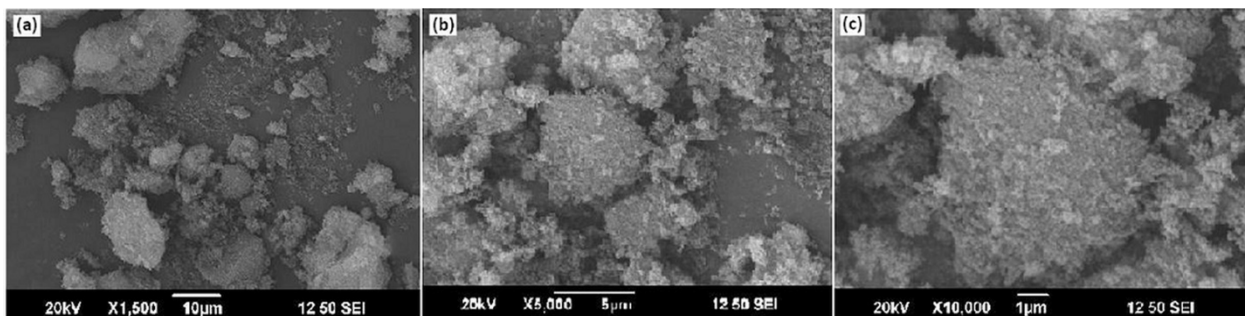


Figure 2. SEM micrograph of thermally treated (1200 °C) molecular sieves

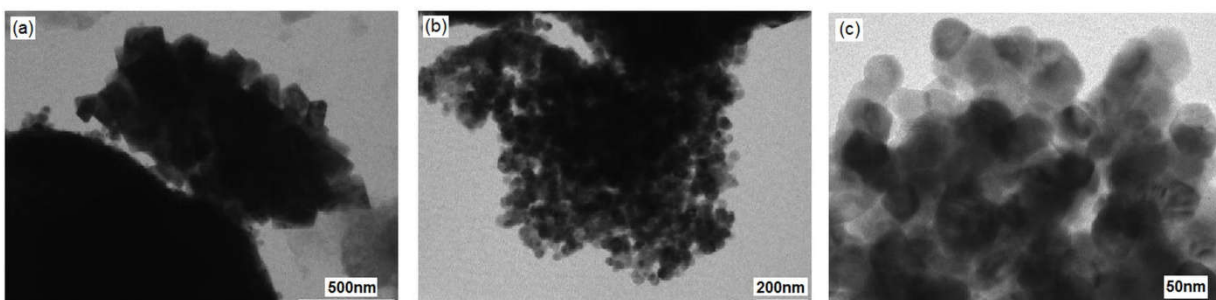


Figure 3. TEM images showing the typical hexagonal morphology of the thermally treated (1200 °C) material

The gel is aged at room temperature for 48 h and heated on hot plate to evaporate water and to attain complete crystallization of the molecular sieves. The sample is washed thoroughly using distilled water and dried at 110°C for 2hr in a hot air oven. The sample is calcinated at 260°C in the presence of air until all impurities and template are completely removed from the pores of the molecular sieves.

Characterization

The synthesized sample is characterized by XRD, IR, Nitrogen adsorption, SEM and TGA/DTA for verifying the structure, framework vibration, surface area and pore size, morphology and thermal stability respectively. X-ray powder diffraction pattern is recorded on a Shimadzu 6000 diffractometer using Cu-K α radiation ($\lambda = 1.5418\text{\AA}$) at room temperature with the scanning rate of 5 degrees per minute. The BET surface area and pore size are measured on Micromeritics, ASAP 2020 V3.00H. ^{29}Si NMR spectra recorded by using JEOL-LA400WB 400 MHz spectrometer at 79.4 MHz and a sample spinning frequency of 10 KHz. TGA and DTA analyses are carried out on Thermal analyst STA 409PC. The SEM analysis is performed on a JEOL JSM 6360 scanning electron microscope. Transmission electron micrograph (TEM) image is recorded by JEOL 2011 microscope operated at 200 kV.

RESULTS AND DISCUSSION

Characterization of material

The as-synthesized and calcinated sample (heated up to 1200°C) are characterized by the powder XRD (Figure – 1a). Both XRD patterns of the samples are almost similar. It proved that the catalyst is stable upto 1200°C. The XRD pattern shows one strong diffraction peak appeared at around 0.8° and 0.9° for as-synthesized and calcinated samples respectively which is usually associated to the 100 plane and it also proved the high ordering and thermal stability of mesoporous (as-synthesized and calcinated) materials. Apart from this intense peak, we also observed two distinct weak peak at 1.1° and 1.3°, which are related to the characteristic of hexagonal ordering of the mesophase. The d spacing value 9.81 nm and $a_0 = 11.33$ nm indicated the large pores of the mesoporous catalyst. The unit cell parameter a_0 and d spacing values are calculated from the equation $a_0 = (2/\sqrt{3})d_{100}$. The shifting of the peak to lower 2θ values is associated with well grown unit cell and large mesopores of the materials (Chellapandian Kannan et.al., 2013).

Nitrogen - adsorption and desorption isotherm of the thermally treated (1200°C) mesoporous hexagonal molecular sieve is shown in Figure – 1(c). The isotherm of type IV is as typical of mesoporous materials. Nitrogen adsorption at lower relative pressure ($P/P_0 < 0.3$) is accounted for monolayer adsorption of N_2 on the walls of the mesopores. The P/P_0 of 0.4 to 0.97 is corresponds to capillary condensation within the framework of textural porosity (Chellapandian Kannan et.al., 2013). The pore size distribution curve shown in Figure – 1 (d) indicates a mesopore with the pore diameter 9.1 nm at maximum of the distribution. The specific pore volume, BET surface area and

estimated pore wall thickness of thermally treated material are 0.22cm³/g, 100 m²/g and 1.33 nm respectively.

Figure - 1(e) gives an idea about the TGA/DTA profile of the material which indicated two stages of weight loss. The observed weight loss from 130°C to 260°C is nearly 20% which confirms desorption of adsorbed water and organic template molecules. We understand that the template is completely removed around 260°C within 15 minutes. The weight loss of 2.5% is recognized between 260°C – 530°C, which corresponds to the condensation of adjacent OH group of the molecular sieves (Hui, K.S., Chao, C.Y.H. 2006, Junqiang Xu et.al., 2006). The additional increase of temperature reveals that there is no weight loss in the material. The result proved that our synthesized material is stable up to 1200°C, whereas the previous reported mesoporous materials are stable up to 800°C only.

The ^{29}Si -MAS-NMR of mesoporous materials is used to investigate the surface information of the material and the same has been illustrated in Figure - 1(b). The spectrum of thermally treated sample at 1200°C is shown a sharp single line with chemical shift of -119 ppm, characteristic of Q4(40Si)-Si units, in which the central Si atom is interconnected via four oxygen bridges with other Si atoms characteristic of the unique tetrahedral frame work (Elangovan, S.P et.al., 1998, Rebecca Faulkner et.al., 2013). It confirms the existence of tetrahedral phase of the material. SEM image of thermally treated material is shown in Figure - 2. As seen from the image, the sample is composed of nano particles. The average dimension of the particles ranging from 100 to 200 nm is confirmed the crystalline nature of the material (Grosso Boissière et.al., 2004).

The crystalline morphology is further confirmed by the TEM image of the sample. The morphological outlook of Figure – 3 (b) is shown that the nano particles are appear as uniform sphere with lacking of interlinked pore system. The result gives evidence that the mesoporous networks can be crystallized in the assigned condition. Figure – 3 (a & c), indicates the hexagonal shape or elongated hexagonal structure of the novel large pore mesoporous molecular sieve.

Esterification of alcohol

The synthesized material is used as a catalyst for esterification reaction of n-butanol and acetic acid to test the catalytic activity. Esterification reactions are carried out in a batch reactor fitted with a reflux condenser and a thermometer. Table 1 presents the conversion and product selectivity of esterification reaction over this silica catalyst.

In a typical reaction, the desired amount of n-butanol, acetic acid and 0.1g of calcined catalyst are added and kept in stirring for 2 hrs. Temperature of the reaction mixture is slowly raised up to 200°C and reflex for 6hr. Reaction products are separated from the catalyst and analyzed by gas chromatography. It is observed that the product selectivity and conversion of the reaction is 99% which is an evidence for the high catalytic activity of the material.

Conclusion

This study reveals that the template is easily removed from the pores. The HRTEM image proved that the hexagonal Mesopore units cannot interconnect among them to form a large extended network.

Hence, template molecules are swift out from the pores easily during calcination. The lower temperature calcination (130-260°C) indicates that the template molecules physically fitted inside the pores, but not chemically interacted with the framework of the material. So the removal of the template is not causing the crystalline nature of the material. Hence the material has a large mesoporous nature, high thermal stability and good catalytic activity.

REFERENCES

- Chellapandian Kannan, Kumarasamy Muthuraja, Murugan R Devi. 2013. Hazardous dyes removal from aqueous solution over mesoporous aluminophosphate with textural porosity by adsorption. *J Hazard Mater.* 10: 244–245.
- Chellapandian Kannan, Sivakami K., Ilavarasi Jeyamalar J. 2013. A simple method for the synthesis of thermally stable large pore mesoporous aluminophosphate molecular sieves *Mater Lett.* 113: 93-95.
- Elangovan, S.P., Kannan, C., Banumathi Arabindoo, V. Murugesan. 1998. Aniline methylation over AFI and AEL type molecular sieves. *Appl Catal A Gen.*, 174: 213-219.
- Filip Ciesielczyk, Przemyslaw Bartczak, Lukasz Klapiszewski, Dominik Paukszta, Adam Piasecki, Teofil Jesionowski. 2014. Influence of calcination parameters on physicochemical and structural properties of co-precipitated magnesium sulphate. *Physicochem. Probl. Miner. Process.* 50: 119-129.
- Grosso Boissière, C., Smarsly, B., Brezesinski, T., Pinna, N., Albouy, P.A. Amenitsch, H., Antonietti, M., and Sanchez, C. 2004. Periodically ordered nanoscale islands and mesoporous films composed of nanocrystalline multimetallic oxides. *Nature Mater.* 3: 787-792.
- Hui, K.S., Chao, C.Y.H. 2006. Synthesis of MCM-41 from coal fly ash by a green approach: Influence of synthesis pH. *J Hazard Mater.*, B137: 1135-1148.
- Ji Man Kim, D., Galen Stucky. 2000. Synthesis of highly ordered mesoporous silica materials using sodium silicate and amphiphilic block copolymers. *Chem Commun.* DOI: 10.1039/b002362k: 1159-1160.
- Junqiang Xu, Wei Chu, Shizhong Luo. 2006. Synthesis and characterization of mesoporous V-MCM-41 molecular sieves with good hydrothermal and thermal stability. *J Mol Catal A Chem.* 256: 48-56.
- Limin Wang, Jie Fan, Bozhi Tian, Haifeng Yang, Chengzhong Yu, Bo Tu, Dongyuan Zhao, 2004. Synthesis and characterization of small pore thick-walled SBA-16 templated by oligomeric surfactant with ultra-long hydrophilic chains. *Micro. Meso. Mater.*, 67: 135–141.
- Nataša Zabukovec Logar, Venčeslav Kaučič, 2006. Nanoporous Materials: From Catalysis and Hydrogen Storage to Wastewater Treatment. *Acta Chim Slov.* 53:117-135.
- Rebecca Faulkner, A., Joseph Di Verdi, A., Yuan Yang, Takeshi Kobayashi, E., Gary Maciel. 2013. The Surface of Nanoparticle Silicon as Studied by Solid-State NMR. *Materials.* 6: 18-46.
- Sayari, A. and Liu, P. 1997. Characterization of Large-Pore MCM-41 Molecular Sieves Obtained via Hydrothermal Restructuring. *Chem Mater.*, 9: 2499–2506.
- Seong-Su Kim, R. and Thomas Pauly, J. 2000. Thomas Pinnavaia. 2000. Non-ionic surfactant assembly of ordered, very large pore molecular sieve silicas from water soluble silicates. *Chem Commun.* DOI: 10.1039/b002856h: 1661-1662.
