Chinese Chemical Letters Vol. 12, No. 9, pp 823 – 826, 2001
http://www.imm.ac.cn/journal/ccl.html

Esterification of Glycerol by Oleic Acid and Selective Hydrogenation of Oleic Acid Methylester Over Acid and Ru-Sn-B Supported Mesoporous AlMCM-41

Qiu Bin KAN[1]*, J. BARRAULT[2], Tong Hao WU[1]

[1]Department of Chemistry, Jilin University, Changchun 130023
[2]Laboratoire de Catalyse, CNRS URA 350-ESIP, 40, 86022 Poitiers, Cedex, France

Abstract: The AlMCM-41 molecular sieves with two different pore sizes are hydrothermally synthesized in the presence of surfactants with two different chain lengths. H-AlMCM-41 and Ru-Sn-B/H-AlMCM-41 which are prepared by the conventional ion-exchange and incipient wetness techniques of the AlMCM-41 show fair catalytic activity for esterification of glycerol by oleic acid and selective hydrogenation of oleic acid methylester, respectively.

Keywords: AlMCM-41, Ru-Sn-B/H-AlMCM-41, oleic acid, esterification, hydrogenation.

Demand for large pore size molecular sieves has given rise to great interests in a new family of silica-based mesoporous materials designated as M41s, which expand typical molecular sieves into an extra-large pore range and generate the potential for the applications of these materials in catalysis and sorption for very bulky molecules[1-6]. MCM-41 possesses a hexagonal arrangement of uniform mesopore ranging from 15 to 100 Å and can be prepared with varied Si/Al ratios. The investigations of the materials with very large uniform pore and acidic property have opened new possibilities for processing and producing large molecules. Esterification of glycerol by oleic acid and selective hydrogenation of unsaturated fatty ester for obtaining unsaturated alcohol are two important reactions of fine chemicals[7,8]. The acid AlMCM-41 with larger pore size is considered advantageous as catalyst or catalytic support for the two reactions. This note reports the preparations of acid AlMCM-41 and Pt-Sn-B supported AlMCM-41 catalysts and their catalytic performances for the two selected reactions.

Preparation of H-AlMCM-41 and Ru-Sn-B/H-AlMCM-41

AlMCM-41 material with Si/Al=40 is synthesized from a reaction mixture SiO_2-H_2O-TMAOH-C_nTMACl-NaOH-$NaAlO_2$ (or pseudoboehmite) (n=12 or 16)[1-3,9]. A typical example of preparation is as follows: solution A is obtained by addition of Cab-O-Sil M5 and NaOH to water. Mixing of another Cab-O-Sil M5 and TMAOH•$5H_2O$ with water forms solution B. Solution C contains C_{16}TMACl (25%) and water. At first the solution A is combined with the solution B, and then the solution C is dropped with

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* E-mail: qkan@mail.jlu.edu.cn

vigorous stirring into the mixture, followed by addition of a certain amount of Cab-O-Sil M5 and sodium aluminate or pseudoboehmite. Since sodium aluminate may introduce extraneous cations into the reaction mixture interfering the synthesis, sodium ions in solution A are quantitatively deducted on the basis of the amount of sodium aluminate, if it is used as aluminum source in the preparation. The resulting reaction mixture (pH≈11.5) is placed in Teflon-lined stainless steel autoclaves, sealed and shaken before heating to 110°C. After 24-72 hours, the autoclaves are cooled to room temperature and the solid products are filtered and washed with distilled water, and then dried at 100°C for 6 hours. The as-synthesized samples are calcined in a stream of nitrogen from room temperature to 550°C at a rate of 1°C /min, followed by calcination in air at 550°C for 6 hours. The calcined AlMCM-41 samples are ion-exchanged in 1.2 mol/L of NH_4NO_3 solution with liquid to solid ratio of 15 mL/g in order to form NH_4-AlMCM-41. The H-form of AlMCM-41 is obtained by heating the NH_4-AlMCM-41 at 600°C in air. The preparation procedure of Ru-Sn-B/MCM-41 is as follows: 0.1685 g of $RuCl_3{\cdot}xH_2O$ and 0.6239 g of $SnCl_2{\cdot}H_2O$ are firstly mixed in a flask, and then 3.0 g of H-AlMCM-41 is impregnated with the aqueous solution. This paste is left to stand for 20 hours. 0.3377 g of $NaBH_4$ is dissolved in 8.5 g of water and added to the above slurry of the impregnated H-AlMCM-41. After the reduction is completed, the solid is washed with distilled water and absolute alcohol, respectively, dried in the flow of N_2 at 120°C, and then treated by H_2 at 400°C for 12 hours before using as catalysts.

Characterization of mesoporous samples

XRD measurements reveal that the as-synthesized and calcined mesoporous samples have MCM-41 structures. When quaternary ammonium surfactant C_nTMACl with n=12 and 16 are respectively used as templates, the mesoporous AlMCM-41 materials exhibiting different d-spacing are obtained. The surfactant chain length has effect on the d-spacing (or pore size (2)) of the AlMCM-41: the longer the surfactant chain is, the larger the d-spacing is. The calcined AlMCM-41 is sensitive to treatment in water even at room temperature. Putting AlMCM-41C_{16} (synthesized using C_{16} TMACl as template) into water for 6 hours, the first peak intensity of its XRD patterns dramatically decreases. However, after calcination at 550°C, the peak intensity is almost recovered. Similar phenomenon is observed in the NH_4^+-exchange experiment of AlMCM-41C_{16}. The H-AlMCM-41 formed upon calcination of NH_4-MCM-41 has X-ray diffraction patterns similar to the calcined AlMCM-41. Chemical analysis shows that there is small difference of Si/Al ratio between reaction gels and the mesoporous products. The surface area of AlMCM-41C_{12} (synthesized using C_{12}TMACl as template) is similar to that of AlMCM-41C_{16} (~900m^2/g). For AlMCM-C_{12}, the H-form has somewhat larger surface area than the calcined sample. In contrast, for AlMCM-41C_{16}, aqueous solution can partly reduce its crystallinity causing a decrease in the surface area after NH_4^+ exchange to produce H-AlMCM-41C_{16} by calcination. The surface area of Ru-Sn-B/H-AlMCM-41C_{16} (~460m^2/g) is smaller than that of H-AlMCM-41C_{16} (~755m^2/g) because of introduction of guest atoms into the channel occupying the surface. The total amount of acid sites determined by NH_3-TPD and titration methods is 0.75 and 0.58 mmol/g for H-AlMCM-41C_{16} and H-AlMCM-41C_{12}, respectively.

Catalytic reactions

Esterification of glycerol by oleic acid over H-AlMCM-41

The catalytic reaction is carried out under normal pressure. The catalytic reaction results are listed in **Table 1**. H-AlMCM-41 catalysts are active for esterification of glycerol by oleic acid. However, H-AlMCM-41C_{16} and H-AlMCM-41C_{12} show different activity for producing ester of glycerol. Clearly H-AlMCM-41C_{16} which should have larger pore diameter than H-AlMCM41C_{12} is more active than H-AlMCM41C_{12}. On the other hand, H-AlMCM41C_{12} is more efficient in confining the larger volume of products, such as trioleate of glycerol and monooleate of diglycerol. Selectivity of product with smaller volume (monooleate of glycerol) obviously increases when using H-AlMCM41C_{12} instead of H-AlMCM41C_{16} as catalysts. In comparison with the size of the esterification products of glycerol by oleic acid, the pore size of H-AlMCM-41C_{12} may be still too large for an effective shape-selectivity of monooleate of glycerol. It is therefore expected that a further smaller pore of AlMCM-41 would be more selective for obtaining monooleate of glycerol.

Table 1 Esterification of glycerol by oleic acid

Catalyst	Yield (%) Ester of glycerol	Distribution of some ester products (%) MG	DG	TG	MD
H-MCM-41C_{16}	45	31	7	2	60
H-MCM-41C_{12}	22	61	10	1	28

MG=monooleate of glycerol, DG=dioleate of glycerol, TG=trioleate of glycerol, MD=monooleate of diglycerol

Selective hydrogenation of oleic acid methylester over Ru-B-Sn/H-AlMCM-41

The hydrogenation reaction is carried out under the pressure of 80 bar (H_2 50%, N_2 50%) at 270-280°C, using 1.1 g of catalyst and 50 mL of reactant oleic acid methylester. **Table 2** gives the results of catalytic hydrogenation reactions of oleic acid methylester over Ru-B-Sn/H-MCM-41C_{16} and shows that the supported mesoporous catalyst is effective for selective hydrogenation of unsaturated fatty ester to form unsaturated alcohol. It is observed that both conversion of hydrogenation and selectivity to unsaturated alcohol is increased with the reaction time. On the other hand, heavy ester decreases with the reaction time. At a longer reaction time, such as 21 hours, saturated alcohol and ester can be tested.

As a conclusion, H-AlMCM-41 and Ru-Sn-B/H-AlMCM-41 catalysts are potential for esterification of glycerol by oleic acid and selective hydrogenation of oleic acid methylester. Further investigations should be done in order to obtain optical reaction conditions and better catalytic performance and to fairly understand catalytic mechanism.

Table 2 Selective hydrogenation of oleic acid methylester over Ru-B-Sn/H-AlMCM-41C_{16}

Time	Conversion	Selectivity (%)				
(h)	(%)	Unsaturated Alcohol	Saturated Alcohol	Heavy Ester	Saturated Ester	Hydrogenolysis Products
1	19.5	3.0	--	76.5	–	20.5
3	30.5	9.5	--	54.5	–	36.0
4	47.5	21.5	--	63.0	–	15.5
6	62.5	46.0	--	42.0	–	12.0
8	74.5	47.5	--	41.0	–	11.5
21	90.5	53.5	3	20.5	6	17.0

Acknowledgment

This work is partly supported by NSFC (29973011).

References

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature*, **1992**, *359*, 710.
2. J. S. Beck, J. C. Vartuli, W. J. Roth, *et al.*, *J. Am. Chem. Soc.*, **1992**, *114*, 10834.
3. C. Y. Chen, H. X. Li, M. E. Davis, *Microporous Materials*, **1993**, *2*, 17.
4. M. Janicke, D. Kumar, G. D. Stucky, B. F. Chmelka, *Stud. Surf. Sci. Catal.*, **1994**, *84*, 243.
5. A. Sayari, *Chem. Mater.*, **1996**, *8*, 1840.
6. A. Corma, *Chem. Rev.*, **1997**, *97*, 2373.
7. J. A. Mira, A. Corma, *et al, Spain Pat 9202555*, **1992**.
8. P. Gallezot, A. Giroit-Fendler, D. Richard, *Catalysis Letter*, **1990**, *5*, 169.
9. M. Janicke, D. Kumar, G. D. Stucky, B. F. Chmelka, *Stud. Surf. Sci. Catal.*, **1994**, *84*, 243.

Received 1 February, 2001