

Preparation and catalytic activity of mesoporous Al-SBA-16 solid acid catalysts

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Abstract : Mesoporous aluminosilicates with Si/Al ratio = 50 have been synthesized from SBA-16 by post synthetic aluminum incorporation into the silica framework. The aluminum sources used for Al incorporation were aluminum isopropoxide and sodium aluminate. Characterization by low angle XRD and N₂ adsorption has been carried out for the confirmation of 3D cubic pore structure of mesoporous aluminosilicates. The obtained mesoporous aluminosilicates and H-ZSM-5 zeolites were used as catalysts for liquid phase esterification of benzyl alcohol with hexanoic acid. The liquid-phase esterification reaction is used as a tool to probe the interdependence of mesoporosity, acidity and method of aluminium incorporation. The catalytic activity results suggest that apart from acidity, mesoporosity is required for catalyzing the reaction.

Keywords : Al-SBA-16, mesoporosity, benzyl hexanoate, esterification.

Introduction

Benzyl hexanoate is widely used as flavoring agent in food industries¹. It is obtained by esterification reaction between benzyl alcohol and hexanoic acid. Conventionally, the esterification reaction is catalysed either by an acid or a base. Solid acids like zeolites have been found to be eco-friendly alternatives to liquid acids. The superior catalytic performance of zeolites is due to the presence of well-defined micropores. However, the presence of micropores affects mass transfer of bulky reactants/products to and from the active sites located within the zeolite crystal. In order to process bulky organic molecules, ordered mesoporous materials with proper acidity are desired. Mesoporous materials such as mesoporous zeolite^{2,3} and mesoporous Al-MCM-41⁴ were used as catalysts for reactions involving bulky molecules. Among mesoporous silicas, SBA-16 is considered to be a very interesting mesostructure, as it contains a 3D cubic arrangement of mesopores (body centered, wrapped package) corresponding to Im3m space group⁵. It is expected that 3D structure can provide favourable mass transfer kinetics. Moreover, SBA-16 possesses high surface area, large pore volume, and high thermal and hydrothermal stabilities. In the present study, Al incorporated SBA-16

has been synthesized by post synthetic modification of siliceous SBA-16 with two different Al precursors namely aluminium isopropoxide and sodium aluminate. The catalytic activity of these mesoporous aluminosilicates and H-ZSM-5 zeolite was studied in the liquid-phase esterification of benzyl alcohol with hexanoic acid. Since hexanoic acid and the product benzyl hexanoate are bulky molecules, microporous H-ZSM-5 zeolite cannot catalyze the reaction efficiently. However, mesoporous aluminosilicates can catalyze the same reaction more efficiently. Hence, the reaction was employed as a tool to understand the role of ordered mesopores for catalyzing reactions involving bulky molecules.

Experimental

Materials and methods :

SBA-16 was synthesised using tetraethylorthosilicate (TEOS) (>99.9% Sigma-Aldrich) as silica source and amphiphilic triblock copolymer, Pluronic F-127 (Sigma-Aldrich) as structure directing agent as per the verified synthesis procedures reported elsewhere⁶. Mesoporous aluminosilicates with Si/Al ratio of 50 were prepared by post synthetic modification of the mesoporous silica SBA-16 as reported in the literature⁷. The aluminum sources

were aluminum isopropoxide (Sigma-Aldrich) and sodium aluminate (Sigma-Aldrich).

Characterization of materials :

Low angle X-ray diffraction patterns were obtained using Bruker, D8 Advance X-ray diffractometer. Nitrogen adsorption measurements were carried out using a Quantachrome Autosorb-1 instrument at 77 K. Samples were out gassed at 300 °C for 4 h prior to adsorption.

Catalytic activity :

Liquid phase esterification on mesoporous aluminosilicate was carried out using a batch reactor (round bottom flask) equipped with reflux condenser and a magnetic stirrer. Benzyl alcohol (1.08 g, 10 mmol), hexanoic acid (1.16 g, 10 mmol), and toluene (15 ml) were mixed and 100 mg of catalyst was added. The reaction was carried out at 388 K for 5 h. A silicon oil bath fitted with a PID temperature controller was used to maintain the reaction temperature. After the completion of the reaction, the reaction mixture was cooled down to room temperature and aliquots were analyzed using a gas chromatograph (Shimadzu GC-2010 plus; Rtx-1 capillary column (30.0 m, 0.32 mm ID, 0.5 μ m df); FID detector). The products were identified and confirmed by gas chromatograph coupled with mass spectrometer (Perkin-Elmer, Clarus 680 GC; Clarus 600EI MS; Elite-5MS capillary column (30.0 m, 0.25 mm ID, 0.25 μ m df)).

Results and discussion

The Al incorporated SBA-16 materials prepared using aluminium isopropoxide and sodium aluminate were denoted as Al-SBA-16(G) and Al-SBA-16 respectively. Fig. 1(A) shows low angle XRD patterns of SBA-16 and mesoporous aluminosilicates. The 3D cubic cage type mesostructure of the parent SBA-16 and mesoporous alumi-

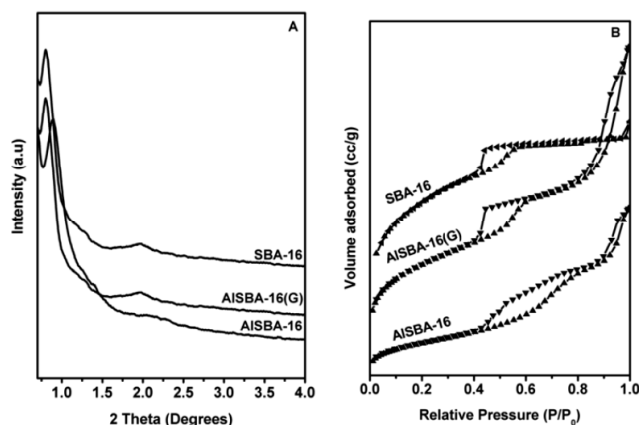


Fig. 1. (A) Low angle XRD patterns and (B) N_2 adsorption isotherms of the prepared materials.

nosilicates prepared from it is confirmed from the XRD patterns⁸. The results clearly indicate that 3D cubic mesostructure is retained even after Al incorporation into silica framework of SBA-16. Fig. 1(B) represents N_2 adsorption isotherms for parent SBA-16 and Al incorporated SBA-16 samples. The N_2 adsorption results are quite similar to the already reported results⁷. The isotherms are type IV with H2-type hysteresis loop indicating the presence of a mesostructure with ink bottle type pores⁹. This kind of pore structure is a characteristic of materials with 3D cubic mesopores. The results indicate that Al incorporated samples retain 3D cubic mesostructure of the parent SBA-16. However, the isotherm of Al-SBA-16 slightly differs from others. This difference may be due to desilication caused by OH^- ions present in sodium aluminate solution resulting in the partial collapse of pore network of parent SBA-16. So apart from aluminum incorporation, partial collapse of pore network could reduce the surface area of Al-SBA-16 as found in Table 1. The decrease in pore diameter of Al-SBA-16 may be due

Table 1. Textural characteristics and catalytic activity of catalysts

Sr. No.	Catalyst	Total surface area (m ² /g)	BJH pore diameter (From adsorption branch) (nm)	BA Conversion (%)	% Selectivity		
					BH	BMP	DBE
1.	Al-SBA-16	299	6.2	43	87	–	13
2.	Al-SBA-16(G)	419	4.6	75	15	44	41
3.	SBA-16	620	8.4	–	–	–	–
4.	H-ZSM-5	–	–	17	100	–	–

BA – Benzyl alcohol, BH – benzyl hexanoate, BMP – 1-methyl-4-(phenylmethyl)benzene, DBE – dibenzyl ether.

to introduction of Al in the mesopore walls of SBA-16. In the case of Al-SBA-16(G), the decrease in surface area and pore diameter may be due to the fact that the Al is grafted on the mesopore walls (Table 1).

The catalytic activity of mesoporous aluminosilicates was tested in the liquid phase esterification of benzyl alcohol (BA) with hexanoic acid and the results are presented in Table 1. Over H-ZSM-5 (Si/Al ratio = 54), BA conversion (17%) is low due to the absence of mesopores, however, BH selectivity was 100%. The conversion and product selectivity of the two mesoporous aluminosilicates are significantly different. It is worthy to note that Al-SBA-16(G) is more active than Al-SBA-16 in terms of BA conversion. Comparison of N₂ adsorption data and catalytic activity results indicates that mesoporosity and surface area play crucial roles in converting BA. As far as BH selectively is concerned, Al-SBA-16 is more selective than Al-SBA-16(G). The decrease in selectivity of the ester product on Al-SBA-16 and Al-SBA-16(G) compared to H-ZSM-5 is due to the formation of side products such as dibenzyl ether (DBE) and 1-methyl-4-(phenylmethyl) benzene (BMP). It seems that formation of the bulky ether and alkylated products are favoured by mesopores. Between the two mesoporous aluminosilicates, on Al-SBA-16, BMP is not at all formed. This absence of BMP indicates the active site responsible for alkylation of toluene by benzyl alcohol to give BMP is not present in Al-SBA-16. It has been observed that esterification of BA with hexanoic acid requires mesopores with strong acid sites³. Further the requirement of mesoporosity and Lewis acid sites for the formation of DBE and BMP has been also established^{3,7,10,11}. So the difference in catalytic activity observed in the present study indicates the interdependence between mesoporosity, acidity and method of Al incorporation. To understand this interdependence more clearly further studies such as ²⁷Al-MAS-NMR and NH₃-TPD are underway.

Conclusion

Mesoporous aluminosilicate solid acid catalysts have been prepared from SBA-16 by post synthetic Al incorporation. Al-SBA-16 prepared by using aluminium isopropoxide as aluminum source completely retain the mesoporosity where as Al-SBA-16 prepared using sodium

aluminate shows partial collapse of mesopores. The conversion of benzyl alcohol and product selectivity of the two mesoporous aluminosilicates and H-ZSM-5 are significantly different. Mesoporosity and surface area play crucial roles in converting benzyl alcohol. The lower selectivity of the ester product on the two mesoporous aluminosilicates compared to H-ZSM-5 is due to the formation of side products such as dibenzyl ether and 1-methyl-4-(phenylmethyl)benzene. It seems that formation of the bulky ether and alkylated products are favoured by mesopores. The difference in catalytic activity observed indicates the interdependence between mesoporosity, acidity and method of Al incorporation.

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