Alkylation of naphthalene with alcohols over mesoporous MCM-41

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Mesoporous MCM-41 is found to promote alkylation of naphthalene by alcohols. In addition to the preferred branched side chain products *n*-alkylated product is also observed in the case of propylation of naphthalene.

Keywords: MCM-41; naphthalene; alkylation; isomerization

1. Introduction

Catalytic alkylation of aromatics with various alkylating agents over zeolites has been the subject of extensive studies because of the shape selective features of the reaction [1–3]. However, the alkylation of polynuclear aromatics over zeolites is restricted primarily by its pore size. Alkylation of polynuclear aromatics with lower olefins, alcohols, and alkyl halides is carried out in presence of mineral acids or conventional Lewis acids, which yield non-selective product mixtures which are not environmentally acceptable [4].

Alkylation of naphthalene by zeolites, especially methylation, has been studied extensively [3,5–7]. Fraenkel et al. [5] have reported a higher conversion for methylation of naphthalene in vapour phase over large pore HM and HY zeolites in comparison to the medium pore HZSM-5. Katayama et al. [6] have reported liquid phase isopropylation of naphthalene over various zeolites. It has been observed that mordenite type zeolites show better selectivity towards alkylation by propylene and non-selective feature towards methylation, demonstrating the effectiveness of pore size in selective alkylation of polynuclear aromatics.

Recently, a family of mesoporous aluminosilicates designated as MCM-41 has been developed by Mobil [8,9]. These materials can be synthesized in a wide range of Si/Al ratios and the pore sizes can be tuned in the range of 20–100 Å. Although the catalytic activities of these materials are not well documented [10], MCM-41 can be envisaged a potential catalyst for polynuclear aromatic alkylations due to its acid characteristics and pore size distribution. Hence in this study the gas phase alkylation of naphthalene with *n*-propanol and *n*-butanol on HMCM-41 as catalyst is reported.

2. Experimental

Aluminosilicate MCM-41 was synthesized using Ludox AS40 (colloidal silica) and aluminium sulphate as the silicon and aluminium sources respectively. Cetyltrimethylammonium bromide was employed as the template. The procedure employed for synthesis was similar to that of Beck et al. [9]. The gel composition employed for the synthesis was: $59.78SiO_2 : 1.0Al_2O_3 : 15.59TEABr : 16.20CTABr : 5.25Na_2O : 2810H_2O$.

The HMCM-41 was obtained by ion exchange with 1 M ammonium chloride at 333 K for 6 h to achieve the maximum degree of exchange. The samples were then filtered and washed free of chloride and dried at 383 K. The H form of MCM-41 was then obtained by calcining the NH_4^+MCM-41 at 823 K for 6 h.

The Y zeolite ($SiO_2/Al_2O_3 = 4.9$) and ZSM-5 ($SiO_2/Al_2O_3 = 60$) were prepared using standard methods. The H forms of the Y and ZSM-5 were obtained by a method analogous to the method employed for MCM-41.

Surface area measurements were carried out by nitrogen adsorption at 77 K on a Carlo Erba sorptometer (1800). The XRD patterns were recorded with a Rigaku Miniflex powder diffractometer using Cu K_α radiation.

Catalytic reactions were carried out in a continuous flow reactor. The products were separated and analyzed using a GC MS (Shimadzu model QP1000EX) equipped

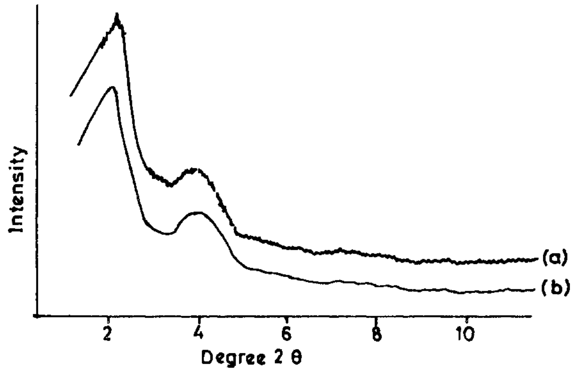


Fig. 1. XRD pattern of (a) calcined MCM-41, (b) HMCM-41.

Table 1
Catalytic propylation of naphthalene with *n*-propanol[a]

Catalyst	Temp. (K)	Time (min)	Conv. (%)	Product distribution (%)				Disubstituted product
				isopropyl-naphthalene		*n*-propyl-naphthalene		
				α	β	α	β	
HZSM-5	673	30	0.0	–	–	–	–	–
HY	673	30	7.4	–	99.5	–	–	traces
HMCM-41	673	30	23.2	–	86.7	–	13.3	–

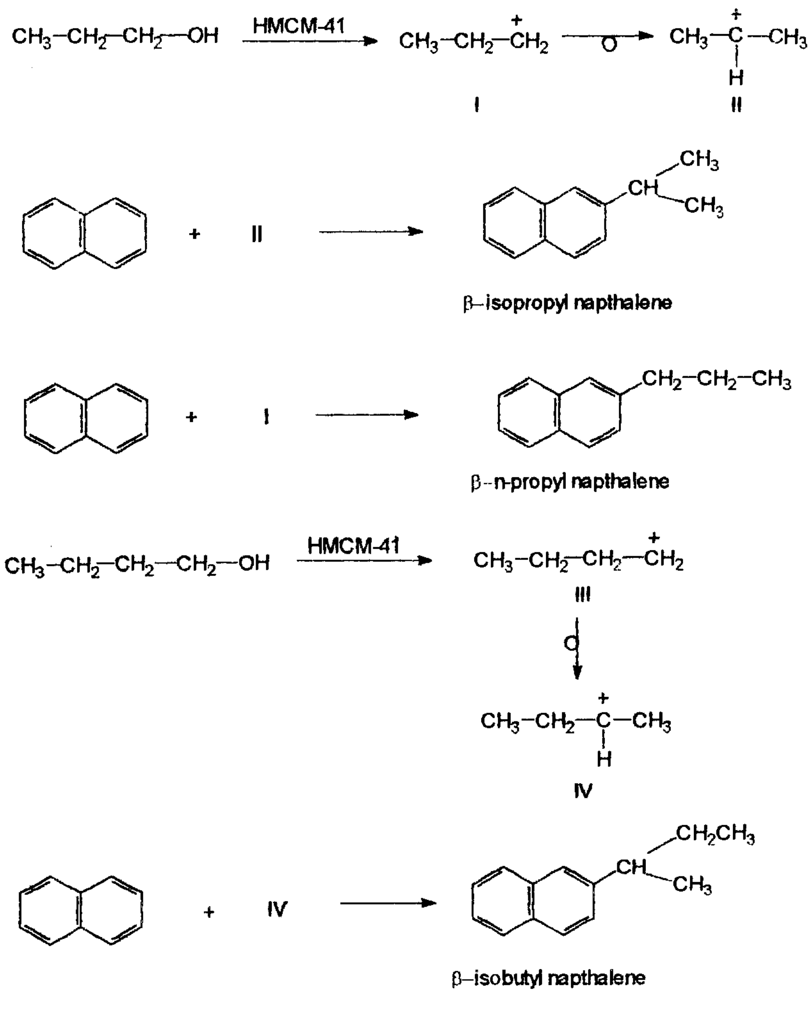
[a] Weight of the catalyst = 0.5 g; flow rate of reactants = 10 ml/h; naphthalene : *n*-propanol = 1 : 100 (molar ratio).

with a 20 m capillary column packed with phenyldimethyl silicone gum.

3. Results and discussion

The XRD patterns of MCM-41 exhibit low angle peaks typical of these mesoporous materials (fig. 1). The specific surface area determined by nitrogen adsorption measurements for MCM-41 is 760 m^2/g with pore size around 30 Å indicating a large void volume for the synthesized material.

The results of the catalytic activity for the alkylation of naphthalene by *n*-propanol on HMCM-41, HY zeolite and HZSM-5 are given in table 1. The mesoporous HMCM-41 gives a higher conversion as compared to the



Scheme 1.

HY and HZSM-5 zeolite propylation reaction. In the case of alkylation of naphthalene by *n*-butanol, β-isobutylnaphthalene was formed to an extent of 5% at 673 K at 10 ml/h flow rate with 1.4 : 100 molar ratio. Under the same reaction conditions HY and HZSM-5 zeolites do not show any activity.

The alkylation of polynuclear aromatics is governed simultaneously by several mechanisms. The selectivity is thereby determined by these routes as well as by the molecular sieving effects if the catalysts employed are porous in nature. In the case of alkylation of naphthalene both α and β positions are likely to be alkylated [4]. Kinetic factors favour alkylation at α position while β alkylation is preferred on thermodynamic consideration. The extent of α and β isomers formed due to the rearrangement of α to β isomers is governed by the catalysts and the reaction conditions employed.

Under the reaction conditions employed HY zeolite yields 100% β-isopropylnaphthalene whereas in the case of HMCM-41, although the same β isomer is observed, there seems to be also the formation of β substituted *n*-propylnaphthalene. It has been observed that isopropylation of naphthalene by propene over the H form of mordenite yields the least bulky 2,6/2,7-diisopropylnaphthalene (DIPN) isomer. However, the reaction rate yielding the isopropylnaphthalene (IPN) is higher compared to the disubstituted products [3]. At higher SiO_2/Al_2O_3, the ratio of β/α isomer formed in the initial stages of the reaction is higher [3]. The exclusive formation of mono-substituted alkylated product inspite of the large pores of HMCM-41 can be explained due to the presence of fewer acid centres and weak acidic nature of HMCM-41.

The formation of *n*-propyl substituted product in case of HMCM-41 is rather unusual as normally only the isopropyl alkylation takes place. The proximity of the active species generated from *n*-propanol and the adsorbed naphthalene could be responsible for the *n*-propyl alkylation of naphthalene. The envisaged reaction sequence is given in scheme 1.

In the case of butylation of naphthalene by *n*-butanol the percentage conversion over HMCM-41 is considerably lower due to the lower acidity whereas the size restrictions seem to control the reaction over HZSM-5 and HY zeolite. No alkylated product was formed under the same reaction conditions on HY and HZSM-5. As expected, isobutylnaphthalene was exclusively formed on HMCM-41.

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References

[1] S. Csicsery, Zeolites 4 (1984) 202.
[2] K.A. Becker, H.G. Karge and W.-D. Streubel, J. Catal. 29 (1973) 404.
[3] Y. Sugi and M. Toba, Catal. Today 19 (1994) 187.
[4] G.O. Olah, *Friedel Crafts and Related Reactions*, Part I, Vol II (Interscience, New York, 1964).
[5] N. Fraenkel, M. Cherniavsky, B. Ittah and M. Levy, J. Catal. 191 (1986) 273.
[6] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S. Niwa and S. Mitamura, Chem. Soc. Chem. Commun. (1991) 39.
[7] A.S. Loktev and P.S. Chekriy, Stud. Surf. Sci. Catal. 84 (1994) 1845.
[8] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.
[9] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[10] Z. Luan, C.F. Cheng, H. He and J. Klinowski, J. Phys. Chem. 99 (1995) 10590.