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Cubic Mesoporous Aluminosilicate with Primary Structure Units of Zeolite Beta in the Pore Wall

Gong LI[1,2], Qiu Bin KAN[1]*, Tong Hao WU[1], Jia Hui HUANG[1]

[1]Department of Chemistry, Jilin University, Changchun 130023,
[2]Liaoning University of Petroleum & Chemical Technology, Fushun 113001

Abstract: Mesoporous aluminosilicate with cubic ordered structure was synthesized by two-step crystallization, which showed stronger acid sites and more effective activity for catalytic alkylation of 2, 4-*ditert*-butylphenol with *tert*-butanol than conventional H-AlMCM-48 materials.

Keywords: Cubic mesostructure, two-step crystallization, primary structure units, zeolite beta, catalysis.

Aluminosilicate M41s (MCM-41 and MCM-48) as acid catalysts have been intensively studied and shown attractive activity for the reaction catalyzed by acidic centers, especially for the catalytic conversion of large hydrocarbons or other organic molecules[1-2]. However, the acid strength of AlMCM-41 and AlMCM-48 is weak owing to the amorphous character of their pores wall. This characteristic limited their applications. For improving the acidic properties of MCMs, much effort has been made to synthesize new type of materials, which combine the advantages of mesoporous and microporous molecular sieves[3-7]**.** However, the synthesized mesoporous materials are in all hexagonal mesostructure. Here we report the primary structure units of zeolite Beta and lower concentration of cetyltrimethylammonium bromide to form a cubic mesoporous alumino- silicate AlMB48 with enhanced acidity in the mesoporous wall and improved catalytic activity for the reaction of larger molecules.

The design of AlMB48 is based on two-step crystallization procedure. The complete structure of zeolite phase had not formed in the stage of synthesis of zeolite precursor, but the primary structure units of zeolite possessed stronger acid strength than amorphous aluminosilicate. The primary structure units of zeolite were constructed at the second crystallization stage in the presence of organic surfactant cetyltrimethylammonium bromide. The crystallization kinetics of zeolite Beta was studied and found that the Beta precursor with Si/Al = 25 could be formed under our conditions for certain period of time. The typical procedure is as follows: 0.1906 g sodium aluminate was dissolved in 2.9 mL water and then 13.9 mL 25% aqueous solution of tetraethylammonium hydroxide (TEAOH) and 2.25 mL of 3.70 molL^{-1} HCl were added,

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

respectively, followed by addition of 2.5 g fumed silica under vigorous agitation. The mixture was stirred for 1 h at room temperature to form the homogeneous gel with the composition of SiO_2: 0.02 Al_2O_3:0.028 Na_2O:0.6 TEAOH:0.2 HCl:20 H_2O. The gel mixture was loaded into a teflon-lined stainless steel autoclave and heated at 140°C for 22 h. The products did not contain the zeolite phases verified by XRD, but embodied the primary structure units of zeolite. The products were cooled to room temperature, stirred for 25 min and kept on for second crystallization stage. The above precursor was combined with 9 mL of 19.28% aqueous solution of cetyltrimethylammonium bromide(CTMAB) and 1.12 mL of 3.70 mol L^{-1} HCl and stirred for 1 h to form homogeneous composition of SiO_2:0.02 Al_2O_3:0.028 Na_2O:0.6 TEAOH:0.14 CTMAB:0.3 HCl:33 H_2O. This mixture was heated under static condition at 140°C for 24 h. After cooling to room temperature, the solid products was obtained by filtration, washed with deioned water, dried in air at ambient temperature and calcined in nitrogen and in air stream at 540°C for 1 h and 8 h, respectively. The obtained mesoporous sample is designated as AlMB48(25), in which the Si/Al ratio=25. For comparison, AlMCM-48(25) was prepared according to procedures reported in literature[8].

XRD patterns of AlMB48(25) in **Figure 1** showed the characteristic cubic ($Ia\bar{3}d$) structure of mesoporous materials[9] without observing any diffraction peaks in 2θ $=10\text{-}50^{o}$. Calcination of the sample led the unit cell to contract from 97.24 to 87.20 Å. The TMAB/ SiO_2 ratio of reactant mixture in the second crystallization stage is lower than that in the conventional mesoporous MCM-48[8]. The two-step crystallization procedure also can synthesize cubic mesoporous AlMB48 with Si/Al ratios in range 15 – 200.

^{27}Al MAS NMR spectroscopy showed that more than 90% of the aluminum centers in AlMB48(25) are in tetrahedrally coordinate sites. FTIR spectra(not shown) of AlMB48(25) indicated a vibrational peak at 550-600 cm^{-1} region, which is characteristic of five-membered rings[10] and verified the presence of the primary structure units of zeolite. AlMCM-48(25), possessing amorphous pore wall, only showed very weak absorption at this wavelength. TEM measurements(not shown) further confirmed the absence of zeolite Beta phase in AlMB48(25).

Figure 1 XRD pattern of (a) as-synthesized and (b) calcined AlMB48(25)

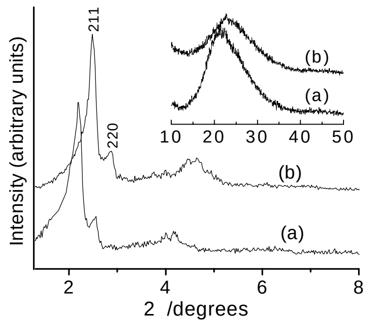
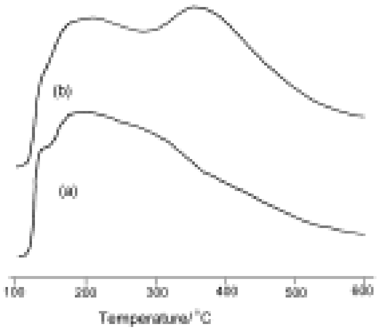


Figure 2 NH_3-TPD profiles of (a) H-AlMCM-48(25) and (b) H-AlMB48(25)



The nitrogen adsorption-desorption isotherms of calcined AlMB48(25) showed(not shown) a typical type IV curves of mesoporous materials. The sharpe steps between p/p_o=0.3 and 0.4 indicated the distribution of mesopore is narrow and the pore diameter (D_{BJH}), cumulative pore volume (V_{BJH}) and BET surface area (A_{BET}) of AlMB48(25) are 28.48 Å, 0.75 cm^3g^{-1} and 881 m^2g^{-1}, respectively.

The calcined AlMB48(25) was treated with 2 $molL^{-1}$ NH_4NO_3 at 40°C for three times to displace exchangeable sodium ions, followed by washing, drying and calcining at 540°C to convert NH_4 at exchange sites to protons(designated H-AlMB48(25)). The XRD and nitrogen adsorption-desorption isotherms measurements of H-AlMB48(25) were similar to the calcined AlMB48(25) in cubic mesostructure properties.

Temperature -programed desorption of ammonia(NH_3-TPD) profiles on H-AlMB48 (25) in **Figure 2** showed that besides the peak at 185°C there is another peak at 360°C and these imply the presence of stronger acid centers on the primary structure units of zeolite Beta in the framework walls of the cubic mesostructure. H-AlMCM-48(25) which does not give any peak at higher temperature. The acidic amounts of the studied H-AlMB48(25) and H-AlMCM-48(25) are 0.80 and 0.72 $mmolg^{-1}$, respectively.

For the standard reaction of cumene cracking, the conversion of cumene over H-AlMB48(25) is 89.7% which is much higher than that over H-AlMCM-48(25) (52.9%) under the same conditions (the flow rate of the carrier gas hydrogen 50 mL /min, the amount of cumene was 1 μL for each test at 350°C and the amount of catalyst is 50 mg). For alkylation of larger molecules, *e.g.*, 2, 4-*ditert*-butylphenol with *tert*-butanol, the results are shown in **Table 1** and the orders of activity and selectivity are: H-AlMB48(25) >H-AlMCM-48(25)>H-Beta (25).

In conclusion, a mesoporous material H-AlMB48(25) with cubic ordered structure has been synthesized,which possessed stronger acid sites and showed higher activity for the reactions catalyzed by acid centers than the mesoporous H-AlMCM-48(25). This new material may be useful for the treatment of heavier feeds and the production of fine chemicals.

Table 1 The Alkylation of 2,4-*ditert*-Butylphenol with *tert*-Butanol[a]

sample	conversion of 2,4-*ditert*-butylphenol (%)	selectivity of 2,4,6-*tritert*-butylphenol (%)
H-AlMB48(25)	22.7	45.6
H-AlMCM-48(25)	15.7	35.9
H-Beta(25)[b]	14.2	14.7

a. Reaction condition: continuous flow fixed bed reaction; 500 mg catalyst; molar ratio of 2,4-*ditert*-butylphenol / *tert*-butanol = 0.5; reactant flow rate 1.5 mL h^{-1}; N_2 carrier gas 15 cm^3 min^{-1}; average conversion reported in 10 h at 120°C.

b. Supplied by Fushun Petrochemical No.3 factory in China.

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