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Highly dispersed zinc phosphate microdomains in mesoporous silica

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Abstract

In situ immobilization of crystalline zinc phosphate nuclei in the mesoporous silica material resulted in a highly ordered 2D-hexagonal mesoporous material with evenly dispersed crystalline $NaZnPO_4$ microdomains in its matrix using the self-assembly of cationic surfactant under hydrothermal synthesis condition. Four samples with different Si:Zn:P:Na mole ratios have been prepared. X-ray diffraction (XRD) patterns of the as-synthesized as well as template-free samples indicated the presence of mesophase in each case. N_2 adsorption data indicated mesoporosity in the samples together with the existence of crystalline $NaZnPO_4$ phase for the materials synthesized with Si/Zn mole ratio 5-12. ^{29}Si MAS NMR results showed high value of the Q^4/Q^3 ratio in these materials suggesting highly crosslinked structure.

Keywords: Immobilization; Mesoporous silica; Microstructure; Zeolites; Zinc phosphate

1. Introduction

Mesoporous materials (Kresge et al., 1992)with exceptionally high surface area, tunable nanopore openings and versatility their chemical compositions are found to have huge potential in adsorption, ion-exchanger, catalysis, etc. However, amorphous nature of the mesoporous silica has restricted their catalytic applications causing high surface hydrophilicity, relatively poor thermal and hydrolytic stability, and a broad distribution of acid sites. A combination of large pore dimensions of mesoporous materials together with strong acid sites like that of zeolites (Holland et al., 1999) would be highly desirable for a useful catalytic material. However, the macroporous and mesoporous zeolites (Huang et al., 2000; Lee et al., 2001; Sawant and Lobo, 2002) synthesized in recent times using the seed of zeolite crystals or other nanostructured materials through the self-assembly and cooperative organization of inorganic and organic species in aqueous media consisted of a too thick pore wall together with low surface area, which limits their practical utility. Hence, the mesoporous composite material having crystalline microdomains/clusters within the mesostructure is highly desirable for their good catalytic activity. Open framework zinc phosphate (Gier and Stucky, 1991; Harrison et al., 1996; Yang and Sevov, 1999) is one of the most studied inorganic materials. However, because of very high charge density of the inorganic shell vis-á-vis self-assembly of the surfactants, attempted the synthesis of mesoporous zinc phosphate which resulted in only microporous and lamellar meso-phases (Sing and Dutta, 2000; Echavarria and Saldarriaga, 2001). Thus, an alternative synthesis method for the mesoporous material containing zinc phosphate nuclei is required to exploit its potential utility. Moreover, the immobilization of different metal complexes in mesoporous silica was found to enhance the catalytic activity of the resulting solid (Lau et al., 1999). Here we report, the hydrothermal synthesis of mesoporous silica having zinc phosphate microdomains or clusters using self-assembly of cationic surfactants. $Si(OH)_4$, Zn^{2+} and PO_4^{3-}

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present in the synthesis medium serves as the inorganic precursor for the synthesis of this novel composite material.

2. Experimental

In a typical synthesis of this composite material, 9.2 g cetyl trimethylammonium bromide (CTAB, Loba Chemie) was dissolved in 60 g water and 20.9 g of tetraethyl orthosilicate (TEOS, E-Merck) was added to it and the mixture was homogenized by stirring vigorously. Then 3.75 g H_3PO_4 (E-Merck) followed by 4 g NaOH each mixed in 10 g water was added into the solution with constant stirring to hydrolyze the silica. Finally after 1 h, 7.35 g zinc acetate (E-Merck) dissolved in 30 g water was added slowly to the mixture. pH of the starting gels were 3.5–4.0 for different synthesis batches. Then the resultant solution was autoclaved in a polypropylene bottle at 353 K for 1 day under static condition. The molar ratio of the constituents in different gels were

(20–120)TEOS:10 Zn^{2+}:(5–30)CTAB:10H_3PO_4:
(20–120)NaOH: (1200–7200)H_2O.

Surfactants were removed from the solid products by HCl/EtOH extraction at 353 K for 4 h. Removal of the templates were confirmed from the disappearance of the C–H bands in the FT IR spectra of these extracted samples using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. Bulk chemical analyses of various samples were performed using a Perkin Elmer AAS 3310 atomic absorption spectroscopy. XRD patterns were obtained with a Shimadzu 5000 diffractometer using Cu $K_\alpha(\lambda = 1.5406\,\text{Å})$. The thermal stability and cyclohexylamine adsorption capacity of the immobilized catalyst was determined using a Mettler Toledo TGA/SDTA 851. Nitrogen adsorption isotherms were obtained using a Belsorb 28 at 77 K. Prior to N_2 adsorption, samples were degassed for 2 h at 323 K. Transmission electron micrographs were recorded in a Hitachi H9000NA at an accelerating voltage of 300 kV. Philips Xl-30/FEG, XL-serial scanning electron microscopy with an EDX (New XL-30) attachment was used for the determination of morphology and chemical composition. NMR experiments were carried out on a Bruker DSX500 machine equipped with a wide-bore super conducting magnet operating in a field-strength of 11.744 T. ^{29}Si NMR was referenced with respect to TMS.

3. Results and discussion

The low-angle powder XRD patterns for different samples (1–4) are shown in Fig. 1. 2D-hexagonal mesophase structure of MCM-41 was retained in these mesoporous samples on loading of zinc phosphate in the silica matrix with the unit cell size ranging from 3.8 to 4.9 nm. The high-angle XRD pattern for sample 1 (inset, Fig. 1e) related to the characteristic peaks for $Na_6(ZnPO_4)_6 8H_2O$ (powder diffraction file PDF 45-0122, (JCPDS, 1981) P43n symmetry) with cubic

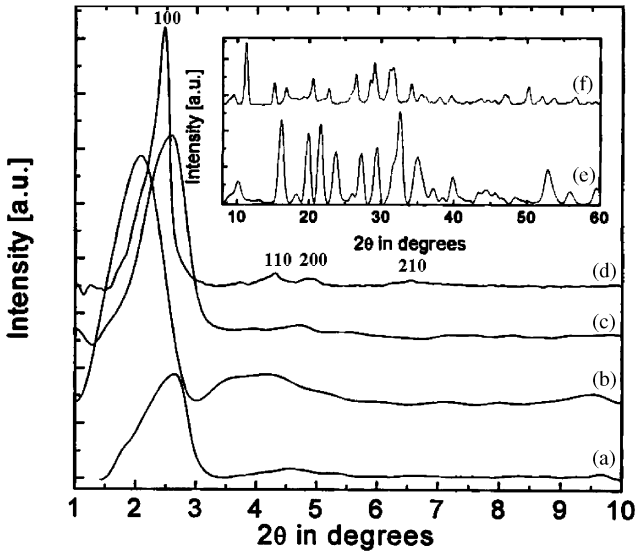

Fig. 1. XRD patterns of mesoporous materials. a, b, c and d corresponds to samples 1, 2, 3 and 4, respectively. High angle patterns for samples 1 and 2 are in the inset (e and f, respectively).

framework structure. The change in unit cell is more drastic in sample 2 leading to an unknown $NaZnPO_4$ phase (Fig. 1f). Samples prepared with low Zn^{2+} and PO_4^{3-} concentration with respect to SiO_2 show little (sample 3) to no (sample 4) high-angle reflections. However, sample 4 show very good long-range ordering for the 2D-hexagonal mesophase characterized by the presence of sharp 100, 110, 200 and 210 reflections (Fig. 1d) corresponding to the 2θ angles of 2.48°, 4.30°, 4.96°and 6.56°, respectively, following the equation for 2D-hexagonal lattice indices $d_{hk0} = [(4/3a^2)(h^2 + k^2 + hk)]^{-1/2}$. With the increase in loading of zinc phosphate nuclei, peaks became broader. FWHM also increase with the increase in diffraction angle in the range 1–7°of 2θ. Thus, the observed peak broadening is due to the imperfections and strain in the pore wall created as a result of the loading of zinc phosphate nuclei. Similar peak broadening was also observed in other mesoporous silica materials (Solovyov et al., 2001).

SEM images of sample 1 (Fig. 2a) showed uniform small spherical crystallites of 0.3–0.4 μm size, whereas, for sample 2 (Fig. 2b) they showed plate like crystals of 0.5–0.8 μm size. Thus, with a change in the concentration of Zn^{2+} and PO_4^{3-} in the synthesis gel, both the morphology as well as the crystal size change. In Fig. 3, the N_2 adsorption/desorption isotherms for mesoporous material is shown. Mesoporous materials with other chemical compositions follow identical type IV isotherms (Kresge et al., 1992; Bhaumik et al., 2003; Jun et al., 2000). Corresponding pore size distributions is shown in the inset of Fig. 3. Physico-chemical properties of different samples are shown in Table 1. The pore diameters of these mesoporous materials estimated using BJH model on the respective adsorption isotherms were 21.4–31.3 Å, which is comparable to the ones with mesoporous silicas