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Synthesis of Hierarchical Porous Structures in Zeolites using Rubber Latex as Macromolecular Templates

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Abstract. Recently, there has been a great deal of interest in the synthesis of hierarchical porous materials with zeolite structures. The introduction of mesopores or macropores into zeolites has been achieved using macrotemplates. Construction of zeolite materials with hierarchical porous structures can improve reaction efficiencies and minimize channel blocking. In this paper, we compare the fabrication of zeolite structures having three generations, micro-, meso-, and macro porosities using silicalite-1 nanocrystals with Styrene Butadiene Rubber (SBR) or Natural Rubber (NR) latex particles as macropore templates. The method is general, which means that the conditions are applicable to the fabrication of hierarchical zeolite materials of all zeolite systems.

Keywords: Nano zeolite, Macro template, Hierarchical zeolite

1. Introduction

Zeolites are used in several industrial applications as catalysts, ion-exchangers and molecular sieves. The superior performance is related to the presence of well-defined micropores in the zeolite structure. However, in many cases the presence of micropores causes some limitations on their applicability.According to IUPAC classification, porous solids can be arranged in to three domains, depending on their pore size, micro (<2nm) meso (2-50 nm) and macroporous (>50nm) materials [1]. Hierarchical porous material contains more than one type of the above mentioned pore system. Silica based porous systems have long been interested involving adsorption, separation and catalytic process [2]. Well known members of the macroporous materials include zeolites, which posses excellent catalytic properties by virtue of their crystalline aluminosilicate network and ordered pore system. Pore enlargement is the prominent target of zeolitic chemistry of research [3].

A variety of approaches for preparing hierarchical zeolites have been earlier reported, direct synthesis, different post synthesis treatments and finally, novel dual templating method [2, 4-6]. Crystallization of zeolite inside the porous template leads to zeolite template composite. Upon calcination, the template composite is transferred to zeolitic material. The current work was undertaken to compare the fabrication of zeolite structures having three generations, micro-, meso-, and macro porosities using silicalite-1 with Styrene Butadiene Rubber (SBR) or Natural Rubber (NR) latex particles as macropore templates.

2. Experimental

2.1. Chemical

Tetraethoxysilane (TEOS), tetrapropylammonium hydroxide (TPAOH, 40%aq), were commercial samples from Merck and were used without further purification. Styrene Butadiene Rubber latex (POWERENE L 2000) having zeta potential +74.7 mV and particle size around 350nm was purchased from

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Apar Industries, India. Natural Rubber (NR) latex having zeta potential +24.8 mV and particle size around 450nm.

2.2. Preparation of Hierarchical Nanozeolite

In the present work we demonstrate the fabrication of hierarchical zeolite materials using dual template approach under controlled steaming at 150˚C. Tetrapropylammoniumhydroxide (TPAOH) was used as a structure directing agent and styrene butadiene rubber (SBR) latex and Natural Rubber (NR) latex particles were used as macro pore templates. At first, a clear solution of zeolite was prepared by mixing 6.34g of tetrapropyl ammonium hydroxide (TPAOH), 10.4 g of tetraethylorthosilicate (TEOS), and 15 g of water with stirring for 2 hrs. The above solution was divided to two portions; to one portion Natural Rubber (NR) latex of 0.3g of solid content was added and dried at room temperature. To the other portion, 0.3 g of SBR latex solid content was added and dried at room temperature. The above two samples were steamed at 150˚C for 6 hrs and calcined at 550˚C for 6 hrs. The obtained hierarchical zeolite material was subjected to the following analysis.

2.3. Characterization

X-ray diffraction patterns were recorded on a Regaku 2000 diffractometer using Cu-Kα radiation from $2\theta = 5$ to 30° at a scan rate of 2°/min with a step size of 0.04°. Morphology and particle size of the zeolite nanocrystals were examined with SEM (JEOL SM-6500f) analysis. FT-IR spectra were recorded using the KBr wafer technique (1.2% w/w) on a Jasco-410 FT-IR instrument. The spectra were recorded with a resolution of 2 cm^{-1} from 400 to 4000 cm^{-1} and corrected for background.

2.4. XRD Analysis

The XRD patterns of the samples are shown in Fig.1. The peaks are characteristic of MFI and the peaks are broadened indicating the smaller crystal size.

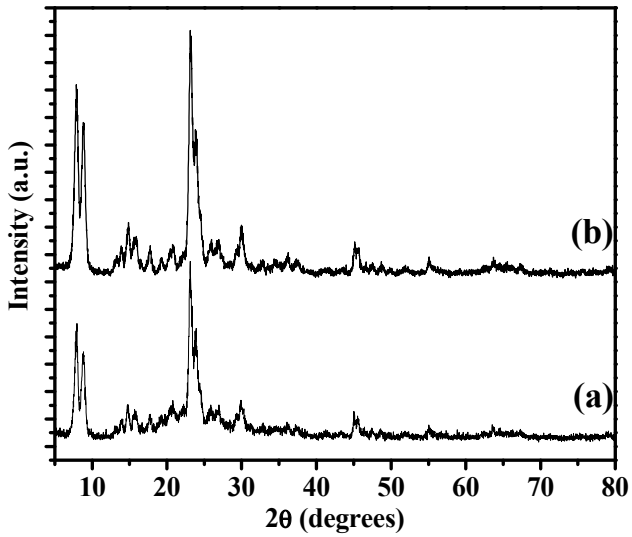

Fig. 1: XRD patterns of hierarchical nanozeolite: (a) SBR added to zeolite; (b) NR added to zeolite.

2.5. FT IR Analysis

The hierarchical zeolite structures after calcinations were compared through FTIR spectroscopy (Figure 2). The band at 950 cm^{-1} can be attributed to localized Si–OH stretching mode. The regions 750-850 cm^{-1} and 500-650 cm^{-1} can be attributed to the ring structure of silica. The band observed at ~540 cm^{-1} is assigned to the double 5–rings of crystalline MFI. (For nano-sized MFI, a doublet at 542 and 556 cm^{-1} is observed). The broad band around 550 cm^{-1} could be due to the small ring structure of silica, although its intensity is not strong. (In fully crystalline MFI, the 550 cm^{-1} band is about 70% of the Si–O bending region at 450 cm^{-1}). The FT-IR pattern reveals a structure characteristic of MFI (strong 550 cm^{-1}).

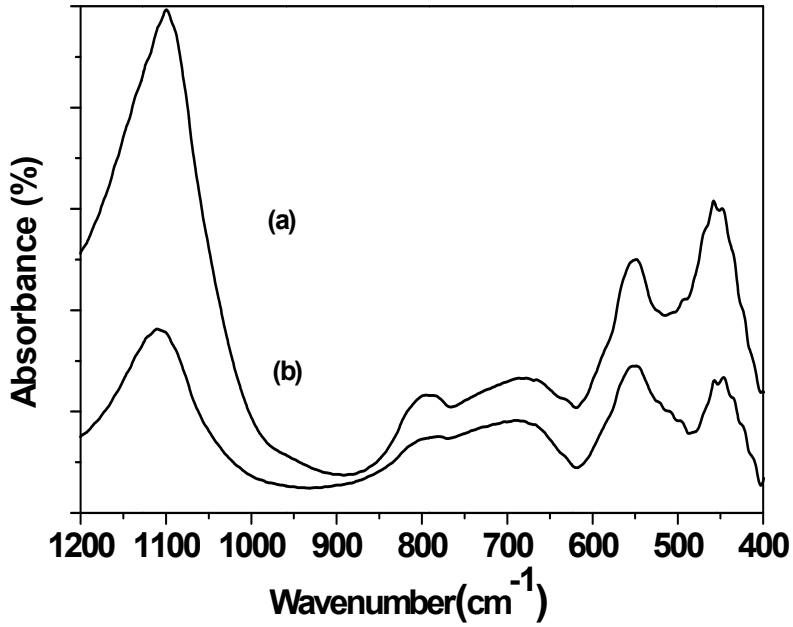

Fig. 2: FTIR spectra of hierarchical nanozeolite: (a) SBR added to zeolite; (b) NR added to zeolite.

2.6. SEM Analysis

The hierarchical zeolite material after calcination was analyzed through Scanning Electron Microscopy and obtained the following images. It is very clear from the picture that, the zeolite mixed with SBR (Figure 3a) produced better ordered porous material than that mixed NR (Figure 3b).

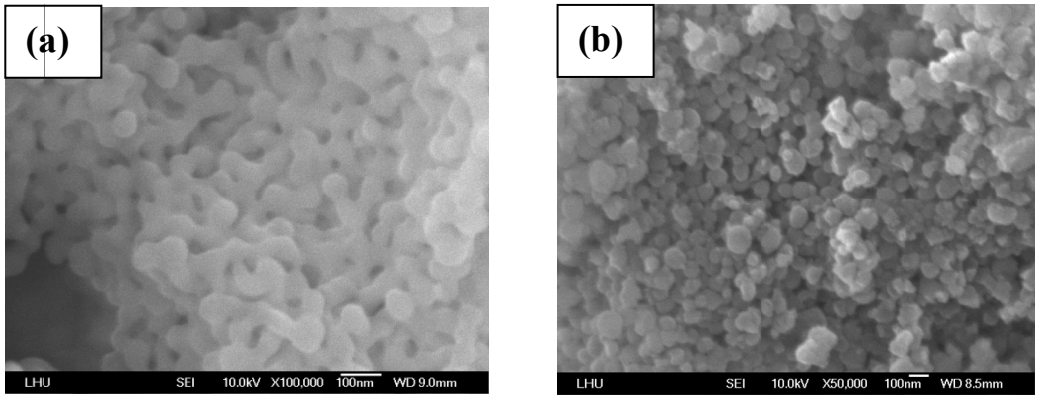

Fig. 3: SEM images of hierarchical nanozeolite: (a) SBR mixed with zeolite; (b) NR mixed with zeolite.

2.7. Conclusions

We have established a procedure for the fabrication of nanocrystalline silicalite-1 with hierarchical pore systems. The sample consists of well-defined nanosized crystals aggregated in such a way that macropores, mesopores, and micropores are formed. We compared the two macrotemplates, SBR latex particles and NR latex particles, and we optimized SBR latex is the better macrotemplate than NR latex, it produces well ordered porous structure.

3. Acknowledgements

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