

Mesoporosity derived by nonionic silylated-surfactant in the synthesis of siliceous MFI zeolite

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Introduction

Biomimetic materials with hierarchical architecture have been mimicked and served as a model for the synthesis of novel inorganic-derived materials. This motivation has been used in these days with a purpose to enhance performance of the available crystalline microporous materials (e.g. zeolites) that have been widely used as catalysts in the chemical and petrochemical industries. By introducing mesoporosity to the pore characteristics of zeolite, diffusivity of bulky reactant molecules in the heterogeneous catalysis would be enhanced, resulting in further possible reactions. The key to the formation of zeolite with hierarchical porous structures is to incorporate the surfactant molecule that has capability of introducing mesoporosity during the synthesis of zeolite framework. For this occasion, cationic surfactants consisting of quaternary ammonium, hydrolysable alkoxyethyl moiety, and a hydrophobic alkyl chain were used and applied to the synthesis of mesoporous ZSM-5, an MFI type of aluminosilicate framework zeolite [1]. However, this method cannot be further applied to the synthesis of mesoporous silicalite-1, an MFI type of siliceous framework zeolite since amorphous mesoporous silica and bulk zeolite crystal (without mesoporosity) were formed separately [2]. This phase separation indicates that the surfactants are expelled from the neutrally-charged siliceous domain during zeolite crystallization process; therefore, they were unable to modulate the zeolite crystallites performing the mesoporosity. In order to solve this problem, our strategy is to implement nonionic surfactant for the synthesis of mesoporous silicalite-1. The alkyl polyoxyethylene ether was used as nonionic surfactant, which was modified with hydrolysable alkoxyethyl moiety. This nonionic organosilane surfactant provides weaker interaction than that by cationic surfactants, while it is suitable to be employed for synthesizing mesoporous siliceous zeolites that do not require any charge compensation by counter ions in the framework.

Experimental

An alkyl polyoxyethylene ether, in which the hydrophobic alkyl group consists of 16 carbon units and the hydrophilic head group contains 10 units of ethylene oxide, abbreviated as C₁₆EO₁₀, was used as nonionic surfactant after being functionalized with triethoxysilylpropyl (TESP) group. TESP-C₁₆EO₁₀ was then added into clear solution of silicalite-1 and aged at 353 K for 6 h under vigorous stirring. Further hydrothermal synthesis was employed in a Teflon-lined stainless steel autoclave at 393 K for 2 days. The resulting precipitates was washed with distilled water, separated by centrifugation and dried in an oven at 373 K. The organic structure-directing agents were removed by calcination in air at 823 K for 8 h with ramp of 1 K/min. The final products were then characterized by powder X-ray diffraction (XRD), N₂ sorption isotherm, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Results and Discussion

The formation of hierarchical porous zeolite was initially confirmed by X-ray diffraction pattern, showing typical ones due to mesoporous and zeolite structures at low and high angle regions, respectively (Figure 1a). The formation of mesoporosity exhibiting a single broad peak at 1.05 degree of 2θ angle can be attributed to uniform mesoporous structure with d -spacing of 8.36 nm; however, the structure was confirmed to be disordered. Subsequently, TEM image shows crystalline lattice fringe of zeolite nanoparticles, confirming that the mesoporosity is generated after organization of zeolite crystallites, resulting in wormhole-like arrangement (Figure 1b).

Significance

Mesoporous silicalite-1 having more hydrophobic properties compared to mesoporous ZSM-5 was synthesized under nonionic surfactant pathway [3]. It might work as catalyst for converting larger molecules into fine chemicals as well as adsorbent with higher diffusivity.

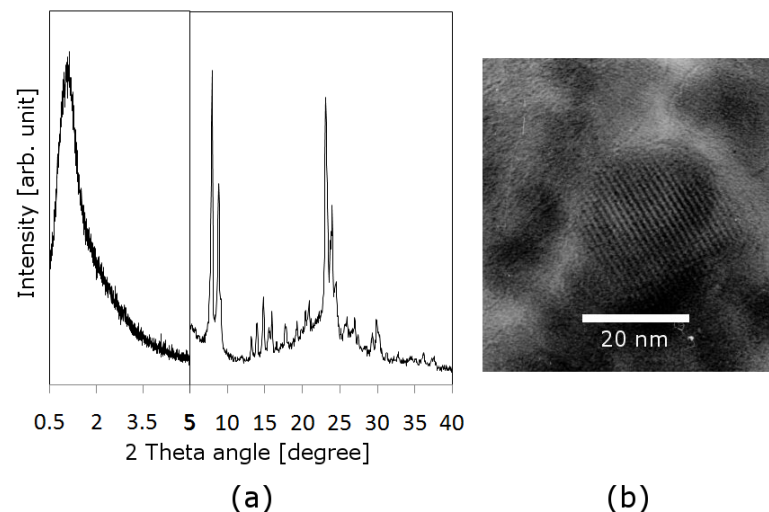


Figure 1. XRD pattern (a) and TEM image (b) of mesoporous silicalite-1.

References

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3. Hirahara, H., Mukti, R. R., Sugawara, A., Shimojima, A., Okubo, T., unpublished data.