

Synthesis of Meso-/Macroporous Zeolite (Fe,Al)-ZSM-5 Microspheres from Diatomite

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Microspheres of (Fe,Al)-ZSM-5 crystallite aggregates with abundant meso-/macropores have been synthesized by hydrothermal treatment of natural diatomite in a NaCl-containing solution. It was found that the addition of NaCl would lead to the formation of spherical product as well as promoting the incorporation of the Fe originally existed in diatomite into zeolitic framework.

Morphology, size and pore structure of zeolitic materials would determine the diffusion of reactant/product molecules on- and off active sites, which may greatly influence their adsorption and catalytic efficiency.¹ Therefore, deliberately controlling the morphology and pore structure of zeolites has been attached increasing importance in the last decades. In recent years, zeolites with spherical morphology prepared no matter by direct synthesis² or through templating approach³ have attracted special attention because of their facile manipulability and homogeneous packing density during catalysis and adsorption processes. Moreover, some researchers have also attempted to further introduce macro-⁴ and/or mesopores⁵ into the zeolitic materials to form hierarchical pore structures, which were expected to further facilitate the diffusion of reactants/products.

Diatomite is a kind of siliceous biologic sedimentary rock, which has been used as the raw material to prepare zeolites LTA,^{6,7} SOD,⁷ and MOR⁸ due to its relatively low cost and large reserves. However, because of the high silica content (e.g., >90 wt %) in high-quality diatomite, it also seems to be a suitable precursor to synthesize high-silica zeolites, such as zeolite MFI, which has been widely used in catalysis due to its shape-selective property.⁹ More notably, the iron species contained in the natural diatomite may be utilized to prepare Fe-containing zeolites which could be applied as an environment-conservative catalyst dealing with NO_x.¹⁰ In this study, with natural diatomite as the sole nutrition source, zeolite (Fe,Al)-ZSM-5 crystallite aggregates with microspherical morphology and enriched meso-/macropores have been successfully fabricated in a NaCl-containing solution without any pre-activation processes such as calcination or melting in caustic soda, which were usually necessary in the zeolitization of natural minerals. The spherical morphology and intercrystalline meso-/macropores of such materials may endow them with easy manipulability and fast diffusion rate during their application in catalysis and adsorption.

Diatomite (Figure 1a) was obtained from Jilin Province of China with main components by weight as follows: SiO₂ 86.7%, Al₂O₃ 4.5%, Fe₂O₃ 1.23%, and K₂O + Na₂O 0.9–1.1%. Its X-ray powder diffraction (XRD) pattern (Figure 2a) indicates that the silica within uncalcined diatomite is basically amorphous except for extremely small amount of quartz. The typical synthetic method was as follows: 0.06 g of sodium hydroxide (NaOH), 0.20 g of tetrapropylammonium bromide

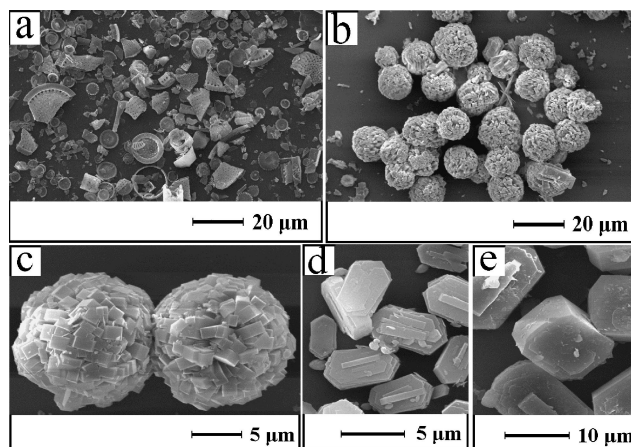


Figure 1. SEM images of natural diatomite (a), NaCl-added product (b, c), salt-absent product (d), and KCl-added product (e).

(TPABr) and 1.0 g of sodium chloride (NaCl) were dissolved in 15-mL distilled water. Then 0.5 g of diatomite was slowly added to the stirring solution and the synthetic mixture was kept stirring for about 3.5 h. Afterwards, the mixture was transferred to a Teflon-lined autoclave for hydrothermal synthesis at 180 °C for 6 days. The product was rinsed, filtered, dried at 100 °C overnight, and finally calcined at 550 °C in air for 6 h to remove the template TPABr.

Figures 1b and 2b are the scanning electron microscopy (SEM) image and XRD pattern of product, respectively. It is clear that the product presented as porous microspheres, which were composed of highly crystallized submicron-sized zeolite MFI crystallites (see Figure 1c also). The diameters of the spherical aggregated crystals are about 10 μm, and the energy dispersive spectrum (EDS) analysis indicated that the SiO₂/Al₂O₃ and SiO₂/Fe₂O₃ ratios of product were 82.3 and 284.5, respectively.

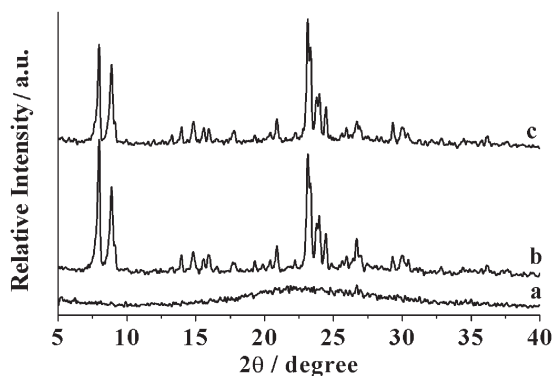


Figure 2. XRD patterns of diatomite (a), NaCl-added product (b), and KCl-added product (c).

The electron spin resonance (ESR) spectrum (Figure 3A-a) further proves the incorporation of certain quantity of Fe into the zeolitic framework due to the signal at $g = 4.3$, which was assigned to Fe^{3+} ions of tetrahedral coordination (i.e., framework iron).¹¹ The signal at $g = 2.0$ in ESR spectrum indicates that the product contains some extra-framework iron, which was also considered as active site of zeolite Fe-ZSM-5 in some catalytic reactions.¹² The BET surface area of the product was $312 \text{ m}^2 \text{ g}^{-1}$ and N_2 adsorption/desorption isotherm (Figure 3B-a) indicates that the product possesses mesopores with wide distribution, which can be attributed to the intercrystalline pores between crystallites. The relatively small size of crystallite and the abundant intercrystalline mesopores may facilitate the diffusion of reactants/products and improve the catalytic performance of such materials.

It was found that the amounts of NaOH and NaCl in the synthetic mixture were two crucial factors that affected the crystallinity and morphology of products, as shown in Table 1. When $W_{\text{NaCl}}/W_{\text{diatomite}}$ was maintained at 2.0, the percentage of spherical aggregated crystals and crystallinity of products initially increased with the alkalinity (i.e., the NaOH amount) of synthetic mixture, and reached an optimal level at $W_{\text{NaOH}}/W_{\text{diatomite}} = 0.12$. However, when the $W_{\text{NaOH}}/W_{\text{diatomite}}$ ratio further increased, the crystallinity of zeolites decreased while certain amount of quartz appeared in the products, and over $W_{\text{NaOH}}/W_{\text{diatomite}} = 0.20$, only quartz was obtained. On the other hand, with the increasing amount of NaCl added to the synthetic mixture at a constant alkalinity (e.g., $W_{\text{NaOH}}/W_{\text{diatomite}} = 0.12$), the ratio of product with spherical morphology gradually increased and totally became spherical crystallite aggregates when $W_{\text{NaCl}}/W_{\text{diatomite}}$ was over 2.0. However, if no NaCl was added, the product (Figure 1d) exhibited the typical coffin-like morphology of MFI-type zeolite, and possessed the typical N_2 adsorption/desorption isotherm (Figure 3B-b) of normal microporous zeolite ZSM-5. Moreover, its Fe content is much lower than that of NaCl-added product. Its $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio is 412.8 by EDS ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 75.2$), and its signals at $g = 4.3$ and $g = 2.0$ in ESR spectrum (Figure 3A-b) are much weaker than those of the NaCl-added product, indicating that the adding of NaCl can both facilitate the incorporation of Fe into the zeolitic framework and increase the content of extra-framework iron besides the promotion of spherical product formation. More interestingly, when NaCl was replaced with equal mole of KCl, only highly crystallized

Table 1. Relative crystallinity of zeolite and morphology of product synthesized with different amount of NaOH and NaCl^a

| $W_{\text{NaOH}}/W_{\text{diatomite}}$ /g g ⁻¹ | $W_{\text{NaCl}}/W_{\text{diatomite}}$ /g g ⁻¹ | Relative Crystallinity /% | Product ^b |
|--|--|---------------------------------|----------------------|
| 0.04 | 2.0 | 12 | D + C |
| 0.08 | 2.0 | 93 | C + S |
| 0.12 | 0 | 100 | C |
| | 1.0 | 93 | C + S |
| | 2.0 | 90 | S |
| | 3.0 | 83 | S |
| 0.16 | 2.0 | 73 | S + Q |
| 0.20 | 2.0 | 0 | Q |

^aDiatomite, TPABr and H_2O in the synthetic mixture were 0.5, 0.20, and 15.0 g, respectively.

^bSymbols D, C, S and Q denote diatomite, coffin-like ZSM-5, spherical ZSM-5 and quartz, respectively.

coffin-like product with large size (Figures 2c and 1e) was obtained, which may be explained by the different influence of Na^+ (decrease) and K^+ (increase) on the crystal size of zeolites.¹³ The smaller zeolite crystals generated in NaCl-containing system tended to intergrow at high hydrothermal temperature and form spherical crystallite aggregates.

In conclusion, zeolite (Fe,Al)-ZSM-5 crystallite microspheres with enriched meso- and macropores have been prepared by utilizing silicon, aluminum and iron species in natural diatomite. It was found that the amounts of additive NaCl in the synthetic mixture played an important role in the formation of the zeolite microspheres. Such materials are expected to be ideal catalysts and adsorbents due to their homogeneous microspheric morphology, relatively small size of crystallites and abundant meso-/macropores.

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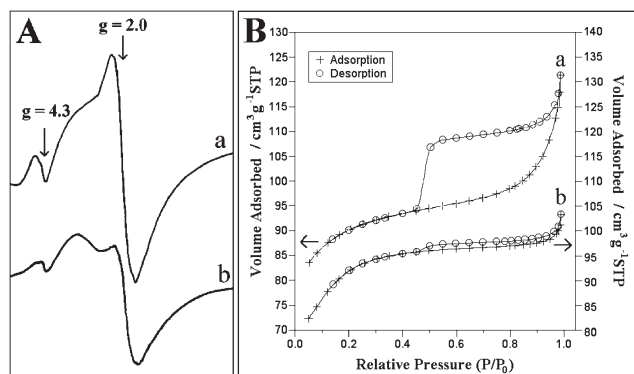


Figure 3. ESR spectra of NaCl-added product (A-a) and salt-absent product (A-b); N_2 adsorption/desorption isotherms of NaCl-added product (B-a) and salt-absent product (B-b).