

Fabrication of Hierarchical Structured Zeolitic Materials through Vapor-phase Transforming of the Seeded Diatomite

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Here, we report a new simple approach to the preparation of hierarchical structured zeolites through transforming the seeded diatomaceous silica into zeolite by vapor-phase transport (VPT) method. The morphology and macro-porosity of the diatomite are well preserved even in the samples with zeolite content higher than 50%. The products possess high mechanical strength and hydrothermal stability.

Hierarchical structured zeolites are attracting increasing interests because of their technological promise in a wide range of applications such as catalysis, adsorption and separation. The previous preparation processes generally relied on removable templates with the length scale from submicron to microns (e.g., latex spheres,^{1,2} carbon fibers,^{3,4} and bacterial superstructure⁵), around which zeolite walls were formed by in situ zeolite crystallization,¹ seed-film method³ or nanozeolite self-assembly technique.^{2,4,5} However, the final macroporous products would be very fragile after the removal of the templates, which would significantly limit their practical applications. To prepare multi-level porous materials with higher thermal and mechanical stabilities, an alternative route is the use of stable templates with intrinsic hierarchical structures. Diatomite is one of the perfect candidates for its unique pore structures, inexpensiveness, and easy availability. Recently, Anderson and co-workers⁶ have zeolitized diatomite hydrothermally treating the ultrasonic seeded diatomite in clear synthesis solutions including adsorptive silicon or aluminium sources. However the characteristic arrays of submicron pores, and even the larger internal voids of the barrel-like diatomite were lost with the overgrown zeolite crystals during the zeolitization process. To maintain the intact diatomaceous submicron pore arrays, we previously proposed a layer-by-layer assembly process to zeolitize diatomite.⁷ Although this method was easier to control both the thickness and composition of the zeolite coatings on diatomite, it seemed not appropriate for practical application owing to the low zeolite content in the final samples.

This paper is attempting to find a more economical and facile method to effectively zeolitize the diatomaceous silica while keeping the diatomite original morphology. A feasible process to attain this aim might be vapor phase transport (VPT) method, which has ever been used to prepare zeolites from the artificial dry-gel with pre-designed composition and morphology in an economic and environmental benign process.⁸ In this work, VPT method was successfully extended to the transformation of the diatomaceous silica into zeolite with the aid of nanosilicalite-1 seeds under a mixed vapor of amine and steam. The macro-porosity of the diatomite is well preserved even in the samples with high zeolite content (e.g. 50%).

The seeding process was necessary to induce diatomite into zeolite by VPT process because no zeolite phase was detected in the XRD pattern of the sample prepared from unseeded diatomite. A homogeneous layer of negatively charged nanosilicalite-1⁹ was seeded onto the positively modified diatomite¹⁰ through an electrostatic adsorption method⁷ described previously.¹¹ The VPT treatment was performed in a stainless steel autoclave. 0.2 g of the seeded diatomite was dispersed on a porous stainless steel board, which was placed horizontally in the middle of autoclave. 2 g of liquid mixture of ethylenediamine, triethylamine and H₂O with the molar ratio of 2 : 9 : 6 was injected into the bottom of the autoclave. Then the autoclave was heated in an oven at 453 K for different time. After the VPT treatment, the samples were collected and washed with distilled water. After drying at 393 K for 12 h, the samples were calcined at 823 K for 8 h in static air to remove the residual organic compounds.

Figure 1 shows the SEM images of the original diatomite and the samples after seeding and VPT treatment. The initial diatomites show a disc-like shape (ca. 1.2 μm in thickness and 20–40 μm in diameter) with a nearly regular array of submicron pores (about 300 to 500 nm in diameter). The diatomite surface was completely and homogeneously covered with one layer of silicalite-1 nanocrystals after the electrostatic deposition process. After the VPT treatment, the disk morphology and hierarchical pore structure of the diatomite were well preserved, and the zeolite nanocrystals were closely linked together and even converted to cross-grown cubic nanocrystals from the original spherical morphology. When the treatment period was prolonged, the surface of the disk plate was gradually plumped up, probably resulting from the interior stress caused by the conversion of the

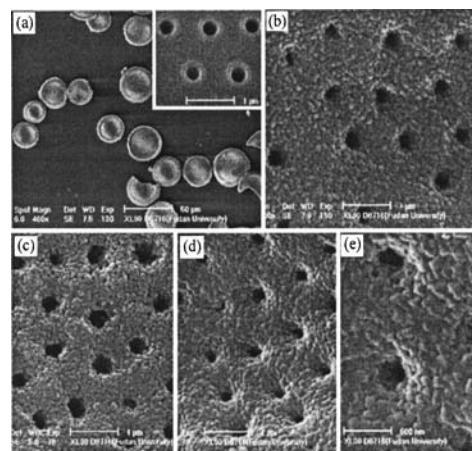


Figure 1. SEM images of the original diatomite (a), nanosilicalite-1 seeded diatomite (b), VPT treatment of the seeded diatomite for five days (c), ten days (d), and sample (d) after further sonication for 30 min (e).

dense diatomaceous silica to crystalline zeolites with microporous framework. No zeolite crystals were found to grow apart from the diatomite plates in all the SEM images. The well preserved hierarchical pore structure of the diatomite in our experiment might be explained by the fact that no adsorptive silica or alumina source was added and the emigration of diatomaceous silica was restrained in the VPT reaction system since the diatomite was separated from the alkaline solution.

XRD analysis was employed to ascertain the changes of the diatomite during VPT treatment (Figure 2). Only weak MFI-structure zeolite characteristic peaks¹² were observed in the seeded diatomite samples. After VPT treatment, however, the peak intensity obviously increased with the prolonging of the treatment time, indicating that zeolite content was gradually increased. The increase of the peak intensity at 550 cm^{-1} in their IR spectra also confirmed that a great portion of the amorphous silica in the diatomite had been converted into zeolite during the VPT process.

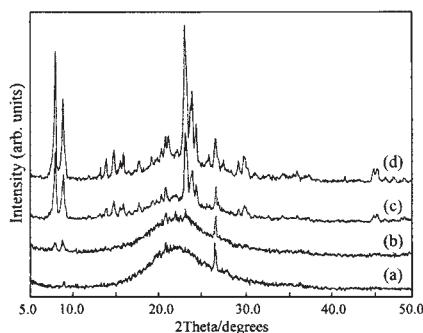


Figure 2. XRD patterns of the original diatomite (a), nanosilicalite-1 seeded diatomite (b), and VPT treatment of the seeded diatomite for five days (c) and ten days (d).

N_2 sorption/desorption data show that the initial diatomite had a surface area of $8\text{ m}^2\text{ g}^{-1}$ (BET). After seeding with one layer of nanosilicalite-1, the surface areas of the diatomite was increased to $22\text{ m}^2\text{ g}^{-1}$, corresponding to ca. 4% zeolite content. However, with the zeolitization of the diatomaceous silica, the surface area of the samples increased significantly. After 5 and 10 day treatments, the samples had the BET surface area of $120\text{ m}^2\text{ g}^{-1}$ (Langmuir surface area of $160\text{ m}^2\text{ g}^{-1}$) and $210\text{ m}^2\text{ g}^{-1}$ (Langmuir surface area of $268\text{ m}^2\text{ g}^{-1}$), respectively. About 50% of the diatomite was converted into zeolites after treatment for ten days (estimated according to the N_2 sorption data), and further, the zeolite composition was expected to be efficiently utilized in practice because the zeolitized thin layer was mainly formed on the surface of the hierarchical structured diatomite substrate.

The benzene adsorption experiment also proved the existence of well-crystallized zeolite in the samples. The benzene adsorption amounts of the samples after VPT treatment for 5 and 10 days were 2.6% and 4.6%, respectively. The adsorption amount per unit area was $2.8\text{ }\mu\text{mol m}^{-2}$ (BET), close to the value of ZSM-5 ($2.7\text{ }\mu\text{mol m}^{-2}$, supposing that the surface area is ca. $400\text{ m}^2\text{ g}^{-1}$ and adsorption amount of benzene is 8.4%¹³). However, benzene was scarcely adsorbed on the initial diatomite.

In order to determine the mechanical and hydrothermal stabilities of the products, the sample after VPT process for 5 days

was treated either by sonication for 30 min using a sonic bath (HF frequency = 50 kHz, 120 W) or hydrothermal treatment at 1073 K for 8 h under 100% steam. No desquamate and/or zeolite fragments were found (examined by SEM) in the samples under these treating conditions, meaning that the zeolites were really well bound to the diatomite substrates.

This study has demonstrated that hierarchical structured zeolite can be produced by an economical method, VPT treatment on seeded diatomite substrates. The method would be an environmental friendly process in which the amine solution of VPT process could be used repeatedly. The obtained materials possess a high zeolite content and intact diatomaceous hierarchical structure and are expected to be useful in catalysis, adsorption and separation. Moreover, the methods proposed here might also be extended to zeolitize other natural substrates containing abundant silicon.

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- 9 The nanocrystals of silicalite-1 ($80 \pm 10\text{ nm}$) were prepared by the method described in the literature and characterized by means of XRD, IR and SEM. The products were purified by repeated centrifugation (15 000 rpm) and washing, then resuspended in distilled water to form a stable colloidal suspension with a concentration of approximately 0.5 wt% at pH 9.5.
- 10 The diatomite was obtained from Jilin Province of China with components: SiO_2 86.7%, Al_2O_3 4.5%, Fe_2O_3 1.23%, CaO 0.44%, MgO 0.43%, TiO_2 0.4%, $\text{K}_2\text{O} + \text{Na}_2\text{O}$ 0.9–1.1%, and separated with sedimentary method in distilled water from the mixed scrappy minerals.
- 11 A homogeneous layer of nanozeolites was fixed onto the surface of the diatomite with the aid of cationic poly(diallyldimethyl ammonium chloride) (PDDA). The adsorption steps were done in a nanosilicalite-1 suspension with a liquid/solid volume ratio of 50 for a duration of 20 min, followed by rinsing the samples with 0.1 mol L^{-1} NH_4OH solution four times to remove the excess adsorbate.
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