Fabrication of Hollow Zeolite Fibers through Layer-by-Layer Adsorption Method

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Hollow fibers with nanozeolite walls are firstly fabricated through layer-by-layer (LbL) technique, using carbon fibers as templates, coupled with removal of the templates by calcination. The thickness and the composition of the walls can be readily controlled by varying the number of the deposition cycles and the zeolite types used, respectively.

Zeolites have been widely used as catalysts, adsorbents and other advanced materials for their uniform micropores, molecular sieving behavior and high hydrothermal stability. To offer faster diffusion and lower pressure drop in the practical application, zeolite coated fibers and hollow zeolite fibers have attracted considerable research enthusiasm.[1–5] These materials have generally been prepared using in situ soft solution process,[1,2] in situ zeolite deposition[3,4] and seed film method.[5] However, these methods are usually uneasy to control the film thickness and the zeolite particle size. In addition, the last two methods are often difficult to avoid the zeolites crystallizing concurrently in the synthesis solution.[5] Recently, the layer-by-layer (LbL) technique, which provides a procedure that readily allows control over the film composition, structure and thickness, has been widely adopted to fabricate flat and spherical materials using the electrostatic attraction between the charged species deposited and oppositely charged polyions.[6] It is reported that colloidal zeolites are negatively charged at base condition and can readily form aggregations due to the high concentration and reactivity of external surface silanol groups among nanozeolite particles under certain conditions.[7,8] By a combination of these properties of nanozeolites and the LbL technique, here, we propose a convenient and versatile approach that is capable of producing hollow fibers with zeolite walls (labeled as HFZ). Compared with the present method,[5] the novel approach may have advantages in below aspects. First, the wall thickness of the HFZ is convenient to control. Second, the novel materials are expected to have even more favorable conditions for mass transfer since their walls are solely composed of nanozeolites. Furthermore, fabrication of hybrid hollow nanozeolite fibers should be possible in principle through alternately deposited different kinds of nanozeolites.

Colloidal crystals of silicalite-1, TS-1 and ZSM-5 were prepared according to methods given in the literature.[9–11] The produced colloidal zeolites were purified and then dispersed in 0.1 mol dm^{-3} NaCl solution at pH 9.5 (adjusted with NH_4OH) with a concentration of approximately 1.0 wt%. In order to provide a smooth and positively charged surface to aid subsequent adsorption of zeolites, the carbon fibers (with diameters of 8–12 μm) were pre-coated with a five-layer polyelectrolyte film of the cationic poly(diallyldimethylammonium chloride) (PDDA) and the anionic poly(styrene-sulfonate, sodium salt) (PSS) in the order of PDDA/PSS/PDDA/PSS/PDDA.[12] Then, the nanozeolites and PDDA were alternately deposited on the above modified carbon fiber surface to form homogeneous nanozeolite/PDDA multilayer films (20 min each adsorption step). After every adsorption step was finished, the fibers were rinsed four times with 0.1 mol dm^{-3} NH_4OH solution to remove the excess nanozeolites or PDDA. When every layer of zeolite nanocrystals was deposited, the fibers were dried at 393 K for 2 h. After certain deposition cycles had attained, the nanozeolites coated carbon fibers were calcined at 873 K (heating rate 5 K min^{-1}) for 8 h in air to yield hollow fibers. The hollow fibers of silicalite-1, TS-1 and ZSM-5 are labeled as HFS-1, HFTS-1 and HFZSM-5, respectively.

The uniform and compact degree of the nanozeolite layers deposited on the carbon fibers determines the morphology of the HFZ samples. To obtain intact HFZ, two key factors should be considered. First is the pH value of the nanozeolite suspension used. Near neutral conditions, the nanozeolites were readily to form aggregations for they have an isoelectric point at about 7[13,14] and the fibers shrank and broke dramatically after calcination. When pH value shifts to about 9.5, the negatively charged nanozeolites adsorbed onto the positively charged carbon fibers at a proper speed and formed a uniform and compact film on them. It is also found that drying after every layer of zeolite nanocrystal deposition is also necessary. As water evaporates, the nanozeolites are linked together more compactly by capillary forces and eventually the hydrogen bonds and/or chemical bonds formed between the nanoparticles.[7] Hence, dropping of the adsorbed nanoparticles is largely lessened in the subsequently steps. The scanning electron micrograph (SEM) images of HFZ (Figure 1), formed by calcining carbon fibers coated with more than eight nanozeolites/PDDA multilayers, show that the HFZ have a cylindrical morphology. The HFZ high-fidelity replicated the superstructures of the carbon fibers used and was proved to be hollow with homogeneous wall thickness when observed from the end or cross-section of the fibers. The wall thickness (measured by SEM from the open-ended or broken fibers) is directly related to the number of nanozeolites/PDDA deposition cycles. For example, the wall thickness composed of eight and sixteen layers of nanosilicalite-1 was ~500 and ~1100 nm, respectively. With the deposition cycles increasing, the uniformity of the HFZ surface seems decreased. This is probably because the dropping of the adsorbed nanoparticles is not completely avoidable in the following rising steps. At high magnifications, we can clearly observe that the walls of the HFZ are made up of densely packed nanoparticles. Some of the nanoparticals are coalesced, due to the condensation reaction of the surface hydroxyl bond between the nanozeolite particles during the period of calcination. Hence, the walls of the HFS-1 were further reinforced by the condensation reaction.

The X-ray diffraction (XRD) patterns of as-synthesized and calcined HFZ (Figure 2) are well matched with those of

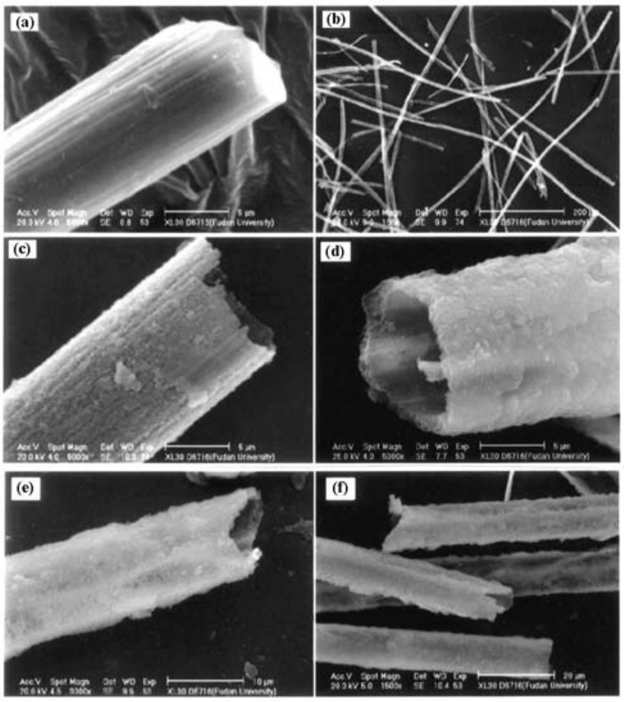

Figure 1. SEM images of the carbon fibers (a), HFS-1 prepared with eight nanosilicalite-1/PDDA deposition cycles (b, c) sixteen cycles (d), HFTS-1 prepared with twelve TS-1/PDDA deposition cycles (e) and HFZSM-5 prepared with twelve ZSM-5/PDDA deposition cycles (f).

zeolites with MFI-type structure, except that the diffraction lines are broadened as a result of the small crystal size. After calcination, the base line of the XRD spectra is straightened, because the amorphous carbon fiber substrate is removed. The IR spectra further confirmed that the walls of the samples are composed of MFI-type zeolites.[9] Being different from those of micrometer-sized zeolites, there is a shoulder peak at 960 cm^{-1} for the as-synthesized HFS-1 (Figure 3a), which is ascribed to silanol groups associated with the Q^3 silicon species. This band disappears after calcination (Figure 3b), implying that the condensation of surface Si–OH groups on nanozeolites happened upon the heat treatment process.[9] The condensation reaction was further demonstrated by the ^{29}Si MAS NMR results. The intensity of the peak at –104 ppm, assigned to Q^3 silicons from surface hydroxy groups or to an amorphous component,[15] decreased from 19.8% for the as-synthesized nanophase silicalite-1 to 4.5% for the calcined HFS-1.

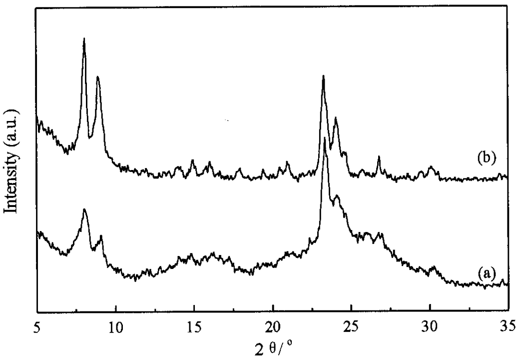

Figure 2. XRD spectra of the as-synthesized (a) and calcined (b) HFS-1 samples prepared with sixteen nanosilicalite-1/PDDA deposition cycles.

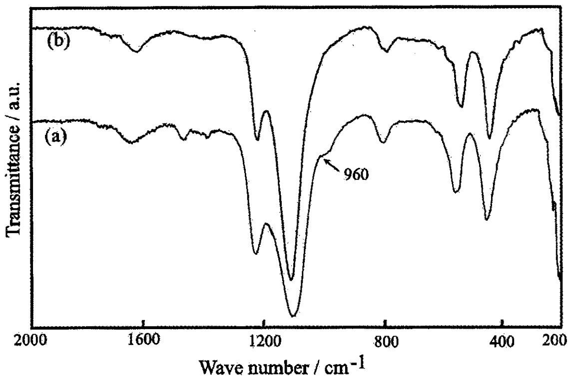

Figure 3. IR spectra of the as-synthesized (a) and calcined (b) HFS-1 samples prepared with sixteen nanosilicalite-1/PDDA deposition cycles.

This study has demonstrated that HFZ can be fabricated using nanozeolites as "building blocks" through LbL technique, coupled with removal of the templates by calcination. Varying the number of the deposition cycles and the nanozeolite types used the thickness and composition of the walls can be readily controlled. Although not yet investigated, fabricating of hybrid hollow zeolite fibers with bi- and/or multifunction should also be possible through alternately deposited various kinds of nanozeolites. Currently, detailed studies are in progress to determine the sorption and catalysis property of the novel materials.

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