A Facile Route to Mesoporous Carbon Catalyst Support Modified with Magnetic Nanoparticles

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Magnetically separable ordered mesoporous carbon with Fe_3O_4 nanoparticles, which were grafted on the outer surface of the mesoporous carbon material CMK-3, was prepared through a facile route. The catalytic performance for hydrogenation of cyclohexene to cyclohexane validates the mesoporous nanocomposite material as a promising magnetically separable catalyst support.

Recently, highly ordered mesoporous carbons (OMCs) obtained through using appropriate mesoporous silicas as templates have been attracting increasing interest because these materials find promising applications as catalyst supports, adsorbents, hydrogen storage media, and as materials for electronic device manufacture.[1] However, small carbon particles are generally difficult to separate from liquid phases and some of their applications, such as in the fields of catalysis and adsorption involving liquids, are restricted to a considerable extent. In the past, active carbon was often chosen as catalyst support for liquid-phase hydrogenation, and the catalyst-supporting carbon was separated by filtration or centrifugation after catalytic reactions.[2] Obviously, the separation procedure is inconvenient and noneconomical. To overcome this shortcoming, magnetic particles may be introduced to porous carbons, and it is possible to separate the composite support material from the liquid catalytic reaction system using magnets. Lu and co-workers fabricated a magnetically separable mesoporous carbon material through depositing cobalt nanoparticles on the outer surface of a mesoporous carbon with the help of carbonization of furfuryl alchohol to fasten cobalt nanoparticles and to protect the main channels from blocking.[3] Nevertheless, this preparation route is rather complicated, and this may restrict its application to a certain degree. Although Hyeon and co-workers reported a simpler route for the formation of mesoporous carbon with magnetic nanoparticles, the preparation steps involved should be precisely controlled to obtain good quality (such as high surface area) product.[4]

Here, we report a low-cost and convenient route for the preparation of magnetically separable mesoporous carbon material with high surface area. The composite material (designated Fe@CMK-3), consists of CMK-3 and superparamagnetic Fe_3O_4 particles. The preparation of the SBA-15 template and the mesoporous carbon CMK-3 was conducted by following the procedures described elsewhere,[5,9] whereas the Fe@CMK-3 material was prepared as follows. 100 mg of CMK-3 and 40 mg of $FeCl_2 \cdot 4H_2O$ were added into the mixture solution of 12.5 mL water and 12.5 mL of ethanol. Under N_2 atmosphere, 14 mg of NaOH was further added into the mixture followed by stirring for 1 h. The product was dried by rotating vaporization, heated for 1 h at 200 °C under vacuum, washed by a mixture of water and ethanol, and finally dried under N_2 atmosphere.

The transmission electron microscopic (TEM) images of the Fe@CMK-3 materials (Figure 1) show the typical hexagonal structure of CMK-3. Nevertheless, the dispersion of the magnetic nanoparticles on the surface of the CMK-3 material differs depending on preparation temperature. When NaOH is added into the reaction mixture at room temperature, the magnetic nanoparticles are homogeneously deposited on the mesoporous carbon, and most of the magnetic particles have a size of 20–30 nm (Figures 1a and 1b). Whereas if the reaction temperature is increased to about 80 °C (Figures 1c and 1d), the magnetic nanoparticles are not well dispersed on CMK-3, and most of the magnetic nanoparticles agglomerate together. In this case, the magnetic nanoparticles are not tightly bound to the surface of CMK-3, and as a result, they are easy to fall off from CMK-3. Therefore, the room-temperature reaction is more favorable for the formation of magnetically separable material.

The wide-angle powder X-ray diffraction (XRD) pattern of the Fe@CMK-3 material (Figure 2a) shows distinct peaks typically associated with Fe_3O_4 particles,[6] whereas the broadness of the peaks is indicative of the presence of nanocrystals in the Fe@CMK-3 material. An X-ray diffraction line profile analysis technique[7] has been employed to evaluate the average Fe_3O_4 nanocrystal size. On the basis of the (311), (511), and (440) peak profiles, the average sizes of the Fe_3O_4 nanocrystals are 24.5, 22.6, and 24.6 nm, respectively, and, therefore, the final average size of the nanocrystals is estimated to be about 23 nm. This nanocrystal size is much larger than the pore diameter of the mesoporous carbon material CMK-3, and, hence, the nanocrystals must be located on the external surface of the porous material. Moreover, the microenvironments of the iron species in Fe@CMK-3 were detected through Mössbauer spectroscopy (Figure S1 and Table S1),[9] and the result indicates that the main component of the magnetic nanocrystals is Fe_3O_4. The

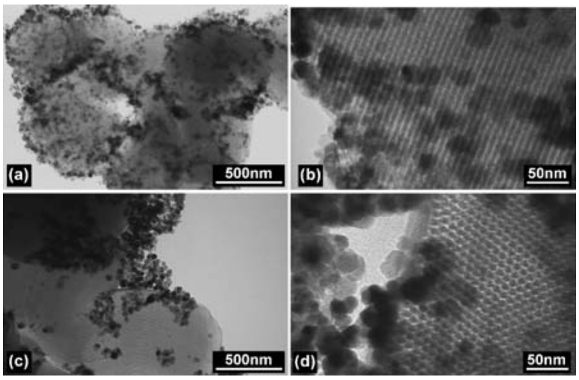

Figure 1. TEM images of Fe@CMK-3 samples prepared at (a), (b) room temperature and (c), (d) 80 °C.

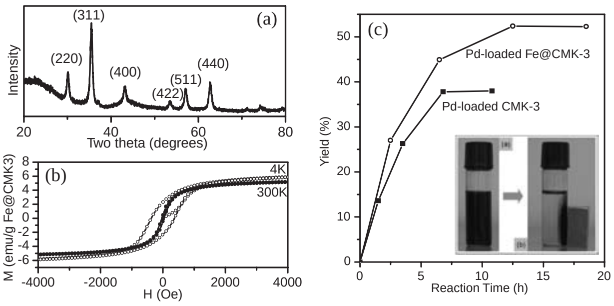

Figure 2. (a) The wide-angle XRD pattern of Fe@CMK-3 (Cu Kα X-ray radiation, $\lambda = 1.5418$ Å). (b) Magnetization curves at 4 and 300 K for Fe@CMK-3. (c) Plots of yield versus reaction time for hydrogenation of cyclohexene to cyclohexane over Pd-loaded Fe@CMK-3 and Pd-loaded CMK-3. The inset shows the Pd-loaded Fe@CMK-3 catalyst in cyclohexene before and after magnetization.

small-angle XRD pattern (Figure S2)[9] indicates the presence of ordered mesostructure of the CMK-3 material.

In the current preparation system, the reaction proceeded with the protection by nitrogen gas so that the Fe^{2+} ions could hardly get oxidized by the oxygen from air. Therefore, the formation of the Fe_3O_4 nanoparticles may have followed alternative routes[6] as represented by eq 1:

$$3Fe^{2+} + 6OH^- \rightarrow Fe_3O_4 + H_2 + 2H_2O \qquad (1)$$

Under the protection by N_2 gas, the majority of the magnetic nanoparticles in Fe@CMK-3 are Fe_3O_4, as observed by the Mössbauer spectroscopy. Even there exists a small amount of oxygen, which could convert a small part of the Fe^{2+} ions to Fe^{3+} ions, the formation of Fe_3O_4 nanoparticles in the reaction system would not be affected as long as the majority of the Fe^{2+} ions are not oxidized.[6] Therefore, the reaction condition for our system is not restrictive, and there is no need to control the synthetic steps very carefully.

The N_2 adsorption/desorption isotherm and the corresponding BJH pore size distribution curve of the Fe@CMK-3 sample (Figure S3)[9] suggest that the material has a mesoporous structure, and the pores are relatively uniform with a pore diameter of about 3.3 nm. Although a considerable amount of magnetic nanoparticles are dispersed on the outer surface of the mesoporous carbon, a high surface area (793 m^2/g) and a large pore volume (0.82 cm^3/g) are still observed for the material.

The magnetic property of the Fe@CMK-3 sample is demonstrated by the magnetization curves at 4 and 300 K, respectively (Figure 2b). At 4 K, a large hysteresis loop is observed for the curve, whereas at 300 K the loop disappears almost completely, indicating that Fe@CMK-3 exhibits superparamagnetism at room temperature. The saturation magnetization of Fe@CMK-3 at 300 K is 5.6 emu/g, a value high enough for magnetic separation.

To evaluate the catalytic performance of the magnetically separable carbon catalyst support, we chose the hydrogenation of cyclohexene to cyclohexane as a model reaction.[9] The magnetically separable catalyst was prepared through loading Fe@CMK-3 with 1% palladium. For comparison, another catalyst sample was also prepared through loading CMK-3 with 1% palladium. The TEM images of the two samples are shown in Figure S4. The yield of cyclohexane was monitored as the reaction proceeded. Figure 2c shows the plots of cyclohexane yield versus reaction time for the Pd-loaded CMK-3 and the Fe@-CMK-3 catalyst samples. It is seen that the Pd-loaded Fe@CMK-3 catalyst has a higher catalytic activity and a longer catalytic life than Pd-loaded CMK-3. The catalytic result indicates that the Fe_3O_4 nanoparticles function as a cocatalyst, and they extend the lifetime of the catalyst.[8]

To demonstrate the magnetic separation of the Pd-loaded Fe@CMK-3 catalyst, the sample after hydrogenation reaction testing was added into a glass bottle containing cyclohexene, and the solution became black immediately after the sample was added. This indicates that the catalyst modified with superparamagnetic Fe_3O_4 nanoparticles are well dispersed in the solvent. The catalyst can be separated by placing a magnet near the glass bottle as shown in the inset of Figure 2c. A few minutes after the magnet was placed near the bottle, the catalyst particles were attracted to one side of the bottle by the magnet, and the solution in the bottle became clear again. This phenomenon demonstrates that magnetic separation is an easy and efficient way to separate the catalyst from the solution after catalytic reaction.

In summary, superparamagnetic Fe_3O_4 nanoparticles have been well dispersed on the external surface of mesoporous carbon CMK-3. The catalytic performance in combination with the magnetically separable property demonstrates that Fe@CMK-3 is a promising catalyst support with attractive application perspectives.

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