Preparation and Characterization of 3DOM $H_3PMo_{12}O_{40}$–SiO_2 with Keggin Structure

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(Received April 2, 2007; CL-070352)

$H_3PMo_{12}O_{40}$ with Keggin structure was supported on three-dimensionally ordered macroporous (3DOM) SiO_2 to synthesize a new-type 3DOM composite material of $H_3PMo_{12}O_{40}$–SiO_2. Through comparative analysis of $H_3PMo_{12}O_{40}$ and 3DOM $H_3PMo_{12}O_{40}$–SiO_2, it could be found that the thermal stability of $H_3PMo_{12}O_{40}$ was increased after supporting and that Keggin structure was remained also in 3DOM $H_3PMo_{12}O_{40}$–SiO_2, but the crystalline form was changed. Moreover, $H_3PMo_{12}O_{40}$ combined with SiO_2 tightly and the synthesized $H_3PMo_{12}O_{40}$–SiO_2 had unique porous structure like crown and interconnected through small windows.

In recent years, various three-dimensionally ordered macroporous (3DOM) materials including polymers, metals, and oxides have been a hot research topic because of their potential applications as photonic crystals, sensors, catalyst supports, and so on.[1–10] So far, it should be noted that the research for 3DOM materials mainly centered on the process of preparation but that the functional research of these 3DOM materials is very few.[11,12] The structural modification of 3DOM materials with special function will be one of research emphases in the future. Porous SiO_2 material is a kind of common support and it is expected that 3DOM SiO_2 also can be used as a new-type support because of their uniform pore size, narrow distribution and ordered array of macropores. In this paper, $H_3PMo_{12}O_{40}$ with Keggin structure was supported on 3DOM SiO_2 to synthesize a new-type composite material of $H_3PMo_{12}O_{40}$–SiO_2. After supporting, 3DOM SiO_2 had the properties of heteropolyacids and the Keggin structure of $H_3PMo_{12}O_{40}$ was not destroyed. Moreover, the thermal stability of $H_3PMo_{12}O_{40}$ could be enhanced, and a novel and unique macroporous structure like crown was formed.

3DOM SiO_2 was first prepared according to the previous report.[10] $H_3PMo_{12}O_{40}\cdot xH_2O$ which was purchased from China National Medicines Corporation Ltd. was supported on the prepared 3DOM SiO_2 by isovolume impregnation method. $H_3PMo_{12}O_{40}\cdot xH_2O$ solution with concentration of 25 wt % were impregnated with 3DOM SiO_2 under isovolume condition and the coated 3DOM SiO_2 was dried at 110 °C for 48 h. After that, the $H_3PMo_{12}O_{40}$–SiO_2 composites were obtained through sintering at 500 °C in the air for 6 h. The synthesized $H_3PMo_{12}O_{40}$–SiO_2 composites were analyzed by various analytic approaches of FT-IR, TG–DTA, XRD, and SEM.

The structures of $H_3PMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$–SiO_2 composites were first determined by FT-IR and the FT-IR spectra shown in Figure 1. From FT-IR spectra, it could be seen that there were four absorption peaks, which indicated the Keggin structure of $H_3PMo_{12}O_{40}$, at the positions of 1064, 963, 869, and 809 cm^{-1}, which were caused by stretching vibration of PO_4 tetrahedron, stretching vibration between MoO_6 and terminal oxygen, stretching vibrations of Mo–O_c (corner-sharping oxygen) and Mo–O_e (edge-sharping oxygen), respectively.[13] Simultaneously, it could be found that the peaks disappeared when the $H_3PMo_{12}O_{40}$ was calcined for 2 h at 500 °C, which indicated the decomposition of Keggin structure. However, after supporting on 3DOM SiO_2, the $H_3PMo_{12}O_{40}$–SiO_2 remained in the Keggin structure. The positions of absorption peaks of $H_3PMo_{12}O_{40}$–SiO_2 had deviations to some degree, and the wave numbers of stretching vibration were 1095, 960, 878, and 805 cm^{-1}, respectively. Moreover, the intensity of each peak decreased to a certain extent. From these changes of peaks, it could be seen that $H_3PMo_{12}O_{40}$ interacted with 3DOM SiO_2 intensively and that the microstructure of $H_3PMo_{12}O_{40}$ had small distortions, but that Keggin structure of $H_3PMo_{12}O_{40}$–SiO_2 was not destroyed.

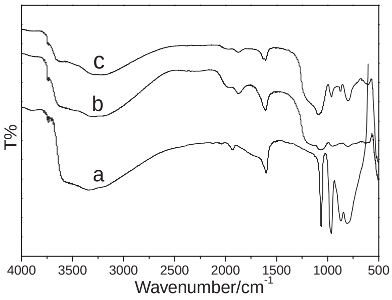

Figure 1. The FT-IR spectra of $H_3PMo_{12}O_{40}$ (a), $H_3PMo_{12}O_{40}$ after sintering at 500 °C (b), and $H_3PMo_{12}O_{40}$–SiO_2 (c).

The thermal stabilities of $H_3PMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$–SiO_2 composites were analysed by TG–DTA and the curves were shown in Figure 2. From Figure 2a, it could be seen that there were two endothermic peaks which were caused by the loss of crystal water before 150 °C and the maximum weight loss appeared in TG curve. In addition, there was a single exothermic peak which indicated the decomposition of Keggin structure of $H_3PMo_{12}O_{40}$ near to 420 °C, and some weight loss were accompanyed from TG curve. However, after supporting on the 3DOM SiO_2, the Keggin structure of $H_3PMo_{12}O_{40}$ was not decomposed at 420 °C because there was no exothermic peak and no loss of weight over a large range of temperature from 150 to 650 °C from Figure 2b. In this regard, the thermal stability of supported $H_3PMo_{12}O_{40}$ increased, which indicated the compact combina-

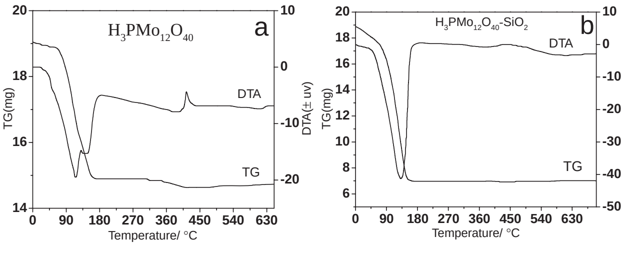

Figure 2. TG–DTA profile of $H_3PMo_{12}O_{40}$ (a) and TG–DTA profile of $H_3PMo_{12}O_{40}$–SiO_2 (b).

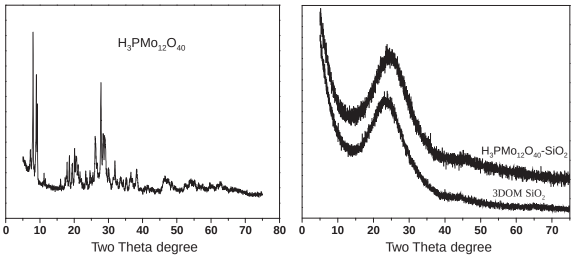

Figure 3. XRD patterns of $H_3PMo_{12}O_{40}$, 3DOM SiO_2, and $H_3PMo_{12}O_{40}$–SiO_2.

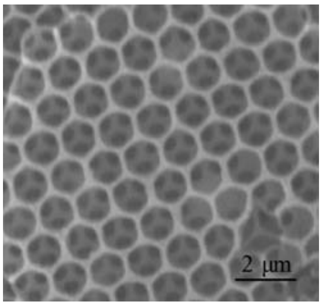

Figure 4. The SEM image of 3DOM SiO_2.

tion $H_3PMo_{12}O_{40}$ with 3DOM SiO_2. The possible reason was that the –OH on SiO_2 surface reacted with hydrogen ion of heteropolyacid resulting in condensation dehydration and that anion of heteroployacid were fixed to the 3DOM SiO_2 after dehydration and led to the improvement of thermal stability.[14] The mechanism can be summarized as follows:

$$SiO_2\text{–}OH(s) + nH^+(aq) = SiO_2OH_2{}^{n+}(s) \qquad (1)$$

$$SiO_2OH_2{}^{n+}(s) + [H_{3-n}PMo_{12}O_{40}]^{n-}(aq)$$
$$= SiO_2(H_{3-n}PMo_{12}O_{40})(s) + nH_2O(l) \qquad (2)$$

The crystalline forms of $H_3PMo_{12}O_{40}$, 3DOM SiO_2, and $H_3PMo_{12}O_{40}$–SiO_2 were characterized by XRD. From their XRD patterns shown in Figure 3, it could be found that 3DOM SiO_2 was amorphous and that the XRD curve of $H_3PMo_{12}O_{40}$–SiO_2 had not peaks expected for crystalline phase. The process of impregnation could induce amorphization of supported substance on SiO_2.[15] The Keggin structure of $H_3PMo_{12}O_{40}$–SiO_2 has been confirmed by FT-IR, so the expected existence form of $H_3PMo_{12}O_{40}$ on 3DOM SiO_2 was microcrystal which could not be found by diffraction profiles of XRD.

The surface morphologies of the resulted SiO_2 and $H_3PMo_{12}O_{40}$–SiO_2 composites were observed through SEM images. As shown in Figure 4, the resulted SiO_2 had good three-dimensionally ordered structure, regular hexagonal array and no obvious caves in pore walls. The macropores had an average diameter of 380 nm, and the thickness of pore wall was approximate 60 nm. Macropores were interconnected with three round holes which appeared as black dots in the wall to form three-dimensional integral structure, which was also in favor of the infiltration of $H_3PMo_{12}O_{40}$ solution. The SEM images of $H_3PMo_{12}O_{40}$–SiO_2 composites were shown in Figure 5, and the unique pore structure like crown could be found. At the same time, the interconnected structure through small holes was not destroyed and had smooth pore wall without any sediments. This result was from the very small size of $H_3PMo_{12}O_4$ and even distribution of $H_3PMo_{12}O_4$ in the form of microcrystal throughout the pore structure. The formation of crown-like macroporous structure mainly depended on the concentration of $H_3PMo_{12}O_{40}$ solution. If the concentration was lower, the surface of 3DOM SiO_2 had no obvious variation. On the other hand, if the concentration was higher, the projecting parts like crown would collapse. The concentration between 20 and 30% was the most favorable to fabricate the crown-like macroporous structure. This kind of $H_3PMo_{12}O_{40}$–SiO_2 with unique crown-like macroporous structure may have important effects on catalysis of macromolecule and some catalytic reaction at higher temperature.

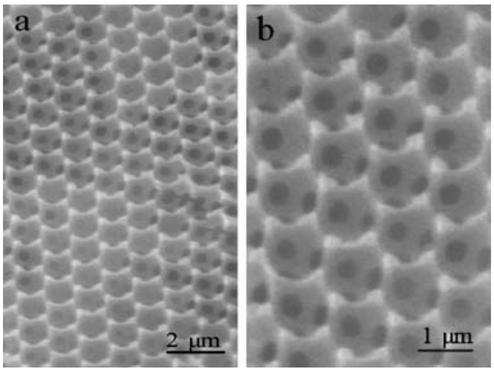

Figure 5. The SEM images of low magnification (a) and high magnification (b) 3DOM $H_3PMo_{12}O_4$–SiO_2.

In summary, it was a new attempt that heteroployacids with Keggin structure were supported on 3DOM mterials. Through supporting $H_3PMo_{12}O_4$ on 3DOM, the thermal ability of $H_3PMo_{12}O_4$ with Keggin structure was increased and $H_3PMo_{12}O_4$ were distributed evenly on the 3DOM SiO_2. Moreover, obtained $H_3PMo_{12}O_{40}$–SiO_2 composites had interconnected pore structure and formed unique projecting parts like crown. The merits both $H_3PMo_{12}O_{40}$ and 3DOM SiO_2 were combined together and these factors made this kind of composites possiblely produce special effects in the fields of catalyst, adsorption, separation and the like.

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Published on the web (Advance View) May 19, 2007; doi:10.1246/cl.2007.758