Facile Synthesis of Small MgO Nanoparticles / Metal-Organic Framework Hybrid Material

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【Introduction】Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have emerged as attractive materials for the applications such as gas storage, molecule separation and catalysis. Recently, the composites of metal nanoparticles (NPs) and MOFs have been studied due to synergistic effects. A wide variety of metal NPs/MOF composites including Pt, Pd, Ag or Au have been reported. However there are few reports on metal oxides NPs/MOF composites thus far.

Nanostructured MgO materials are important heterogeneous catalysts in Henry and Michael reactions and also play important roles in biological and medical applications for cancer therapy.

MgO NPs are usually obtained by calcination of Mg(OH)₂ NPs. Although synthesis by calcination is simple, size control at less than 5 nm has not been reported. Here, we report a novel facile synthesis of MgO NPs (ca. 2.5 nm) hybridized with Mg-MOF-74 from a partial decomposition of Mg-MOF-74.

Figure 1. XRPD patterns for samples of (a) Mg-MOF-74 (b) 420-24 h (c) 530-12 h (d) simulated pattern for MgO.
【Experiments】Mg-MOF-74 was prepared by Mg(NO$_3$)$_2$·6H$_2$O and 2,5-dihydroxyterephthalic acid dissolved in solvent consisting of DMF : EtOH : H$_2$O = 15:1:1 (v/v/v) and heated at 125 °C for 20 hours. Mg-MOF-74 was confirmed by X-ray powder pattern (XRPD), thermogravimetric analysis (TGA) and N$_2$ sorption.

The thermal decompositions of activated Mg-MOF-74 were carried out in a Schlenk tube filled with H$_2$ gas and we obtained two samples, 420-24h at 420 °C for 24 h and 530-12h at 530 °C for 12 h, respectively. The products were investigated by X-ray powder pattern (XRPD), transmission electron microscopy (TEM) and infrared spectroscopy (IR).

【Results】Figure 1 shows the XRPD patterns from Mg-MOF-74 heated at various temperatures of 420 and 530 °C under H$_2$ gas, respectively. For the sample heated at 420 °C, in addition to the diffraction pattern from the Mg-MOF-74 lattice, a new diffraction pattern appeared, which is assigned to the MgO lattice. A higher-temperature heat treatment at 530 °C provided MgO as a main component.

As shown in Figure 2, for sample 420-24h, small NPs with a mean diameter of 2.5 ± 0.7 nm were present and distributed throughout the MOF (Figure 2b). For sample 530-12h, highly dispersed NPs were also found, and the mean diameter was estimated to be 4.4 ± 0.9 nm.

From these results, it was found that the heat treatment at 420 °C with H$_2$ atmosphere provides the hybrid material composed of MgO NPs and Mg-MOF-74, and the heat treatment at 530 °C with H$_2$ atmosphere provides MgO NPs as a main component. In addition, the mean diameter of the MgO NPs is changed by the heating conditions.