1P032

微小な MgO ナノ粒子/多孔性金属錯体ハイブリッド材料の簡便な合成

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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.

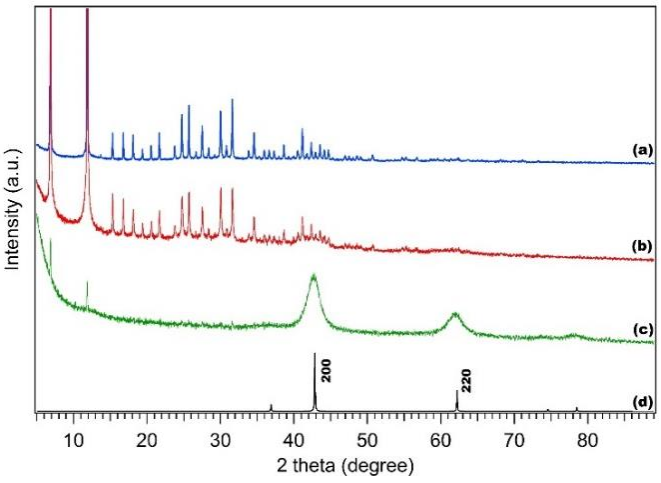

Figure 1. XRPD patterns for samples of (a) Mg-MOF-74 (b) **420-24 h** (c) **530-12 h** (d) simulated pattern for MgO.

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.

【**Experiments**】Mg-MOF-74 was prepared by $Mg(NO_3)_2 \cdot 6H_2O$ and 2,5-dihydroxy-terephthalic acid dissolved in solvent consisting of DMF : EtOH : H_2O = 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.

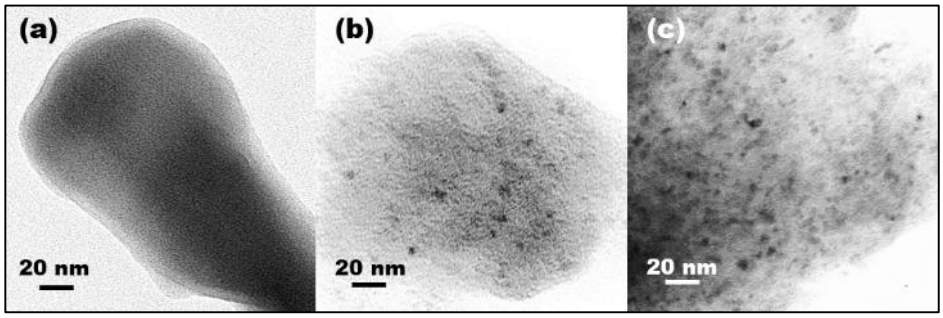

Figure 2. TEM images for samples of (a) Mg-MOF-74 (b) **420-24 h** (c) **530-12 h**.

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.