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Coating Mesoporous Silica Remarkably Enhances the Stability of Highly Active Yet Fragile Flower-like MgO Catalyst for Dimethyl Carbonate Synthesis

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1. Experimental Details

1.1 Materials and Reagents:

Ethylene glycol (EG), $Mg(CH_3COO)_2 \cdot 4H_2O$, ethanol, Polyvinylpyrrolidone (PVP，K30), $NH_3 \cdot H_2O$ (25 wt%), Tetraethyl orthosilicate (TEOS), Ethanol, Methanol and Cetyltrimethylammonium bromide (CTAB) were purchased from Beijing Chemical Reagent Co. Ethylene carbonate (EC) and propylene carbonate (PC) were purchased form Alfa Aesar. All chemicals were used as received without further purification.

1.2 Preparation of flower-like MgO

Flower-like MgO was synthesized according to the method developed in our group with slight change. Typically, 0.856 g $Mg(CH_3COO)_2 \cdot 4H_2O$ and 0.664 g PVP were first dissolved in 20 mL EG. Then the clear solution was transferred into a 40-mL Telfon-lined stainless-steel autoclave, which was then kept in an oven at 180 °C for 4 h. The solid products were collected by centrifugation and then washed by ethanol for 3 times. Then the products were dried at 100 °C for 12 h and the MgO precursor was thus obtained. The MgO precursor was calcined at 500 °C for 2 h to obtain crystalline MgO.

1.3 Preparation of MgO@meso-SiO_2

In a typically procedure, 0.5 mL $NH_3 \cdot H_2O$ and 0.16 g CTAB were first added to the mixture 70 mL mixture of ethanol and water (EtOH: H_2O= 3: 4, V/V). After stirring for 0.5 h, a clear solution was obtained. Then 200 mg MgO precursor was dispersed in the solution, followed by the addition of 0.4 g TEOS. Then the mixture was stirred for another 5 h. The products were collected by centrifugation and then washed by water and ethanol for 3 times, respectively. After dring at 100 °C for 12 h, the solid powder was calcined at 500 °C for 2 h to remove all organic species and crystalline MgO@meso-SiO_2 was obtained. To obtain the content of the MgO@meso-SiO_2 composite, a certain amount of the composite was put in 2M HCl solution to remove the MgO core and then after washing and drying, the remaining SiO_2 coating was weighed. The mass ration of SiO_2 and MgO is calculated to be about 42:58. This value agrees with the starting materials (Note that in the coating process the starting flower-like MgO is MgO precursor not MgO crystal), indicating that mesoporous SiO_2 was fully coated on the surface of the MgO flower.

1.4 Characterization

The powder XRD pattern was recorded on Rigaku D/MAX-2500V (Cu Kα radiation). Scanning electron microscopy (SEM) images were obtained on JEOL-6701F scanning electron microscope at 10.0 kV. Transmission electron microscopy (TEM) was carried out on a JEOL 1011F electron microscope running at 100 kV while high resolution (HR) TEM image and energy dispersive absorption X-ray (EDAX) spectroscopy were acquired from JEOL 2010F electron microscope with an energy dispersive X-ray system operated at 200 kV.

1.5 Measurement of catalytic activity

The catalytic activity was measured by transesterification reaction process of EC with methanol, which was carried out in a flask with the molar ratio (methanol/EC) = 8.0. Typically, 30 mg solid catalyst was added into 5 mL methanol/EC mixture under vigorous stirring. Then the mixture was stirred at 140 °C for 6 h. The product was analysed by gas chromatography (GC) using an Agilent 6890N GC equipped with a flame-ionization detector and a CDWAX-10 capillary column. The catalyst was recovered by centrifugation and washed with methanol for 3 times for further usage.

2. Supporting Figures

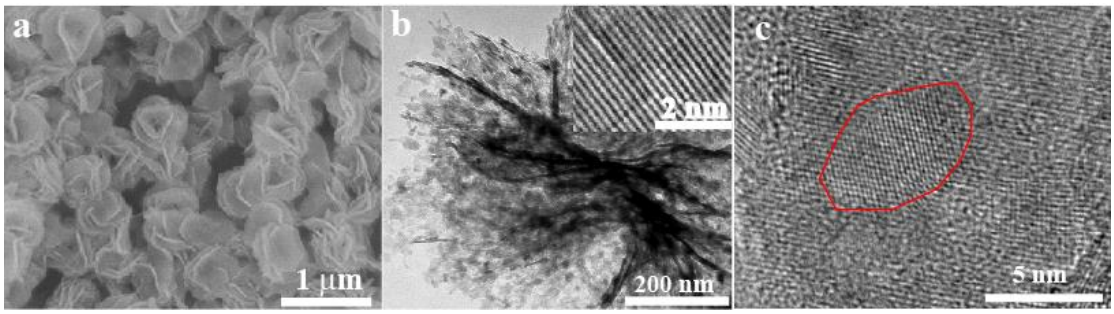

Figure S1. (a) SEM image of hierarchical flower-like MgO precursor produced from modified ethylene-glycol-mediated method; (b) TEM image of flower-like MgO [inset is the HRTEM image, crystal lattice plane with the lattice distance of 0.21 nm belongs to (200) plane of MgO]. (c) HRTEM image to MgO@meso-SiO_2 composite, it show that the size of MgO nanopartcle is about 5 nm, which is almost the same as that of flower-like MgO.

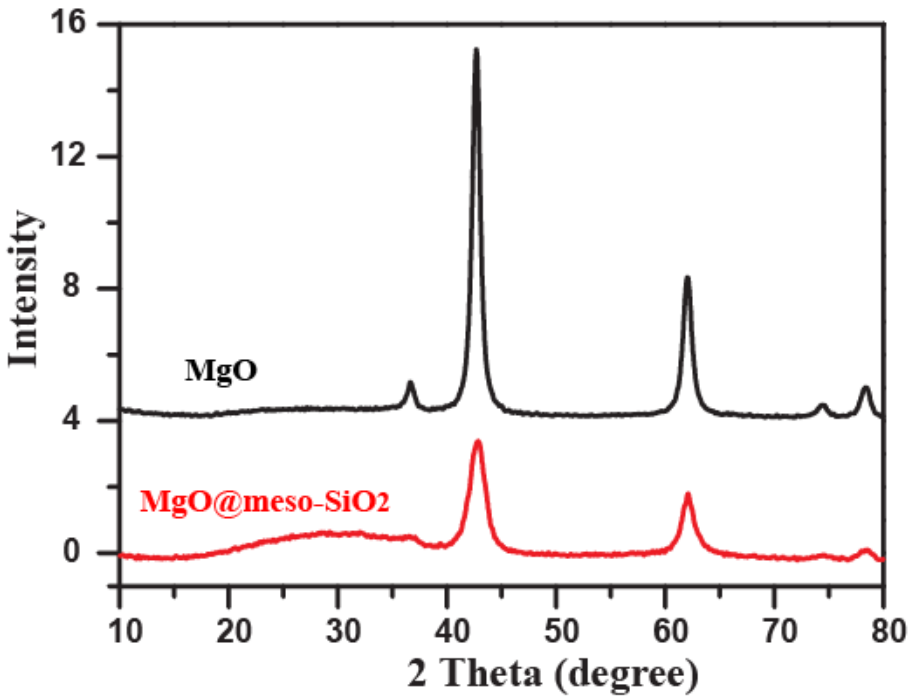

Figure S2. X-ray diffraction pattern of MgO and MgO@meso-SiO_2, respectively.

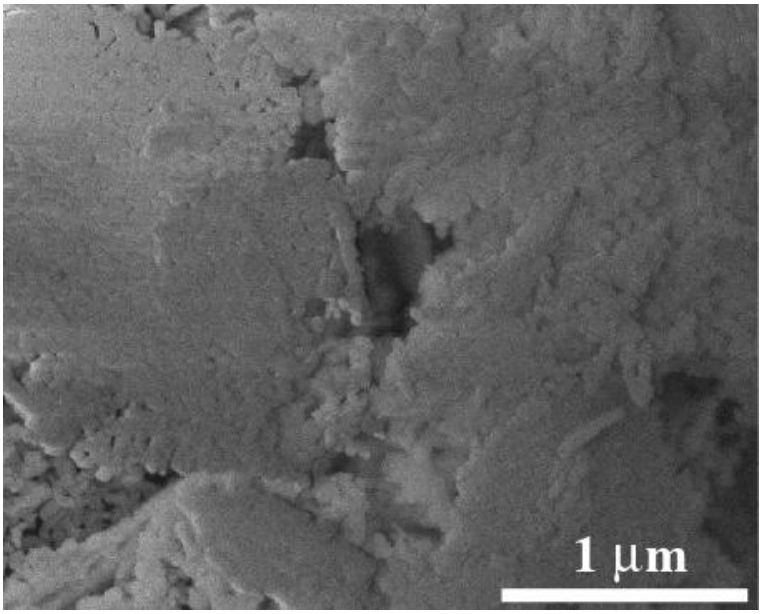

Figure S3 SEM image of commercial MgO. Commercial MgO is composed by sheets which are closely stacked by much bigger MgO nanoparticles than hierarchical flower-like MgO.

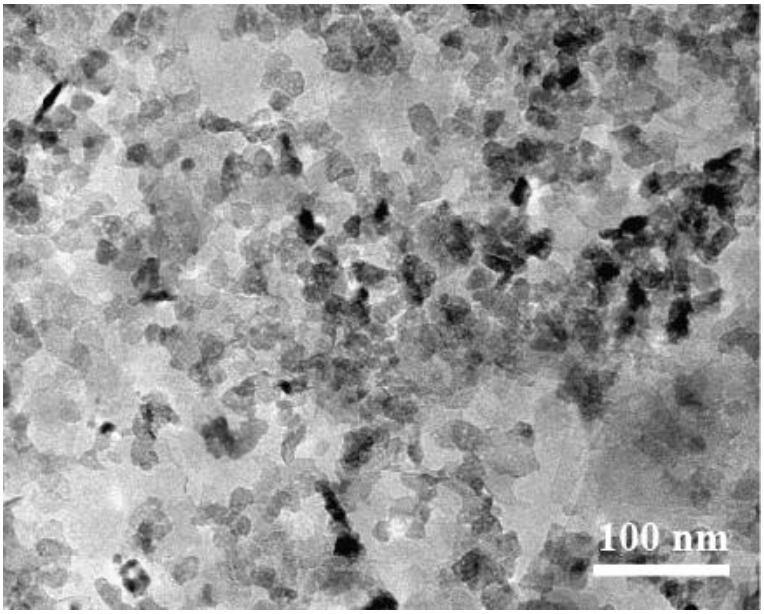

Figure S4. TEM image of the flower-like MgO collected after one run for the reaction of methanol and EC, the flower-like MgO were broken into pieces after one run reaction.

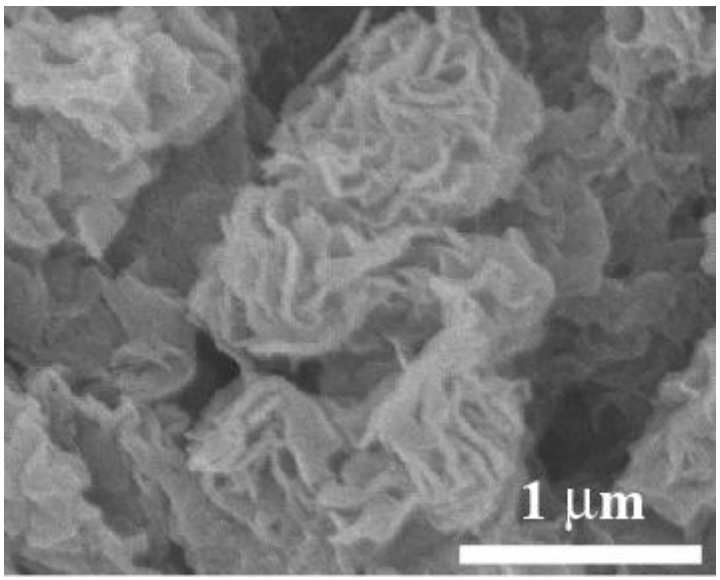

Figure S5 SEM image of the meso-SiO_2 layer after MgO being removed, the remaining SiO_2 still keeps the shape of flower.

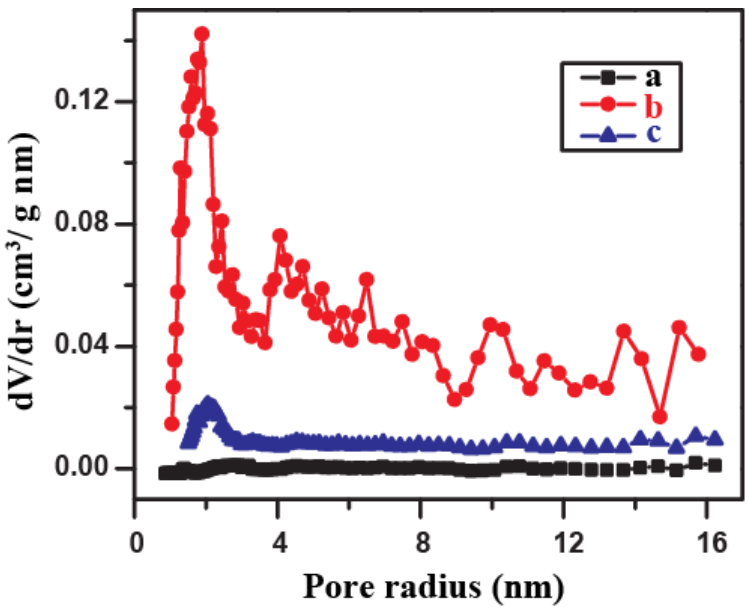

Figure S6. Non-Local Density Functional Theory (NLDFT) analysis of pore size distribution of a) MgO, b) MgO@ meso-SiO_2 composite and c) the outer SiO_2 coating of the MgO@meso-SiO_2 composite obtained after MgO being removed. The sharp raise at 1.6 nm of the SiO_2 indicates that the outer SiO_2 coating has relatively uniform mesoporous pore.