Synthesis of Co-Mn Oxides with Double-Shelled Nanocages for Low-temperature Toluene Combustion

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Characterizations

Powder X-ray diffraction (XRD) was performed on a PANalytical X'Pert Pro diffractometer using Cu-K$_\alpha$ radiation. N$_2$ physisorption measurement was performed on an ASAP 2020 apparatus having the sample degassed in vacuo at 180 °C for at least 6 h before measurement. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out using an Ultima 2 spectrometer. H$_2$ temperature-programmed reduction (H$_2$-TPR) was performed over an AutoChem II 2920 equipment with a thermal conductivity detector (TCD). The sample was pre-treated under Ar flow (30 mL/min) at 400 °C for 0.5 h. After cooling to room temperature, the sample was exposed to a gas flow of 10% H$_2$/Ar (30 mL/min) while its temperature was raised to 800 °C at a rate of 5 °C/min. O$_2$-TPD-MS experiment was carried out on a Micromeritics Autochem II 2920 instrument equipped with a Hiden QIC-20 mass spectrometer.

Experiments of oxygen temperature-programmed surface reaction (O$_2$-TPSR) were performed on the apparatus that was used for H$_2$-TPR. Before each run, the sample was treated in He at 300 °C for 0.5 h. With the sample cooled to 50 °C, the He flow was switched to pulse injections of 10% toluene/Ar until saturation of toluene adsorption, and the sample was then purged with He for 10 min. Finally, the TPSR run was started with the sample ramped at 5 °C/min to 500 °C under a flow of 3% O$_2$/He (40 mL/min). A mass spectrometer (Cirrus) was used for on-line monitoring of effluent gases. The signals at mass-to-charge (m/z) ratio of 18 (H$_2$O), 28 (CO), 44 (CO$_2$) and 91 (toluene) were monitored. For the CO profile, the contribution of CO as m/z = 28 fragment of CO$_2$ was deducted. X-ray photoelectron spectroscopy (XPS) analysis was performed on Physical Electronics Quantum 2000 equipped with monochromatic Al-K$_\alpha$ source (K$_\alpha$ = 1,486.6 eV) at 300 W under UHV condition. Catalyst charging was compensated by an electron flood gun during measurement. Transmission Electron Microscope (TEM) and high-resolution transmission electron microscopy (HR-TEM) measurements were carried out on a JEM-2010 microscope operating in bright field mode at 200 kV. Raman spectra of samples were collected at ambient condition on a Renishaw spectrometer, using a laser beam (λ= 532 nm) for

excitation. Scanning TEM (STEM)-EDS was carried out over a JEM-2010 microscope operating at 200 kV.

Temperature-programmed desorption (TPD) and temperature-programmed surface reactions (TPSR) of toluene were carried out on the apparatus that was employed for H_2-TPR experiments. In a typical TPD run, 0.05 g of catalyst was treated in He at 300 °C for 30 min, and subsequently cooled down to room temperature. Then the catalyst was exposed to toluene (flushed in by Ar at -10 °C) for 0.5 h followed by purging with He for 30 min (to remove physically adsorbed toluene). Temperature programming was then initiated at a heating rate of 10 °C/min to raise the catalyst temperature to 600 °C. A mass spectrometer (Cirrus) was used for on-line monitoring of effluent gases. The signals at mass-to-charge (m/z) ratios of 28 (CO), 44 (CO_2) and 91 (toluene) were monitored, and the contribution of m/z = 28 fragment of CO_2 was deducted from the CO profile. Toluene-TPSR was conducted following a procedure similar to that of toluene TPD except that there was the introduction of a flow of 3 % O_2/He (30 mL/min) during the rise of temperature.
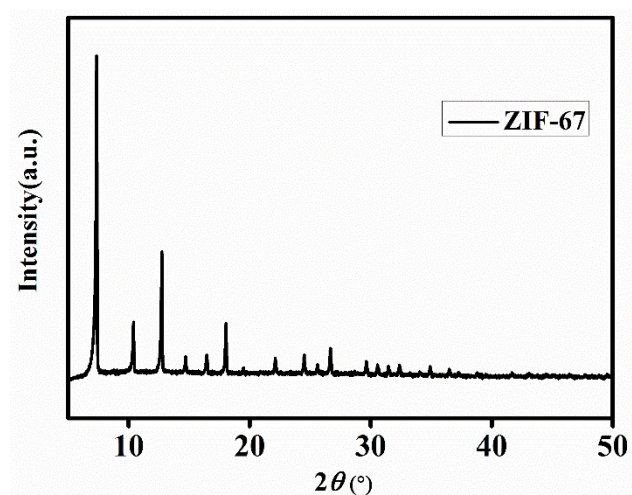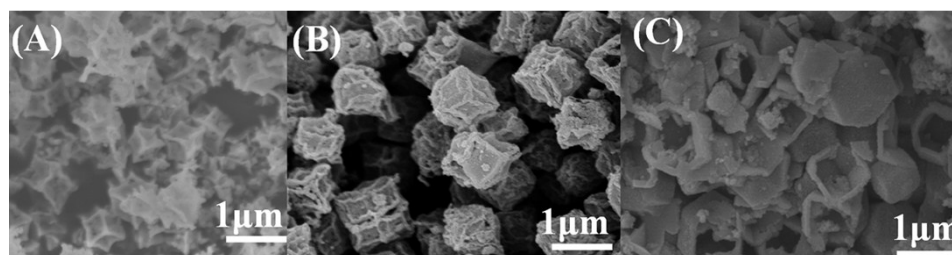
Figure S1 XRD pattern of ZIF-67.

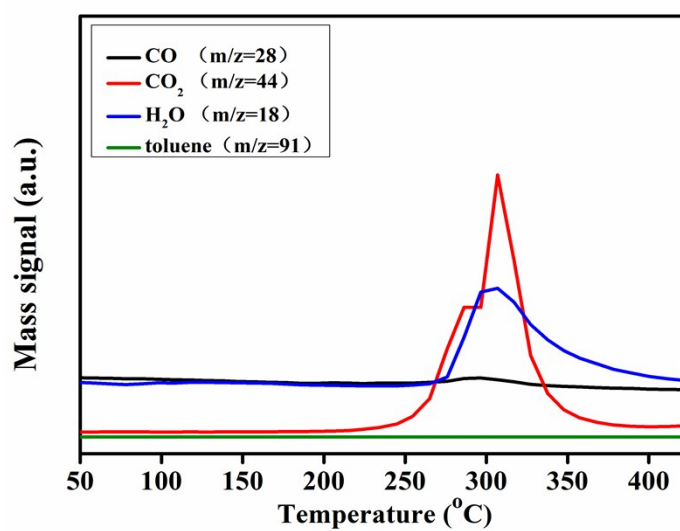**Figure S2** SEM images of (A) Co_1Ni_1 BHNCs, (B) Co_1Cu_1 BHNCs and (C) Co_1Fe_1 BHNCs.

Figure S3 O_2-TPSR profiles of Co_1Mn_1 BHNCs.