## Ultrasmall Ni Nanoparticles Embedded in Zr-based MOFs Give High Selectivity for CO<sub>2</sub> Hydrogenation to Methane at Low Temperature

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## **EXPERIMENTAL SECTION**

**Preparation of UiO-66 MOFs:** In a typical synthesis, 5 mL DMF solution containing 33.4 mg of ZrCl<sub>4</sub>, and 5 mL DMF solution with 25 mg of benzene-1, 4-dicarboxylic acid were mixed in the glass vial and stirred for 1 h. Then, 0.7 ml acetic acid was added, the mixture solution was sealed and placed in an oven at 120 °C for one day. After natural cooling, the resulting product was collected by centrifugation and washed for three times with DMF and then immersed in methanol for 24 h. Finally, as-synthesized UiO-66 was activated by removing the solvent under vacuum for 12 h at 50 °C.

**Preparation of Ni@UiO-66:** Ni@UiO-66 catalysts with varied Ni contents were synthesized by impregnation and reduction methods (see Scheme 1). Typically, 250 mg of Ni(NO<sub>3</sub>)<sub>2</sub>.  $6H_2O$  was dissolved in 50 mL distilled water. Then, 200 mg of UiO-66 was dispersed into the solution under continuous agitation. The mixture was stirred for 12 h at room temperature. Subsequently, the suspension was dried by rotary evaporator. Finally, the resulting solids were put in a tube furnace and heated to 250 °C for 5 h with a ramp of 5 °C min<sup>-1</sup> under nitrogen gas flow. After that, the gas was changed to 5% H<sub>2</sub>/Ar, and the furnace was still kept at this temperature for another 5 h. This nominal weight content of Ni loading was 20 wt% and the catalyst was denoted as 20Ni@UiO-66. For comparison, a series of Ni@UiO-66 samples with different amount loading of Ni were prepared under the same conditions.

**Preparation of Ni/SiO<sub>2</sub> and Ni/ZrO<sub>2</sub>:** In a brief, in one baker, 250 mg of Ni(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O was dissolved in 50 mL distilled water to form a solution. 200 mg of SiO<sub>2</sub> (of SiO<sub>2</sub>) was added into the solution and stirred for 1 h. Then, the mixture was dried by rotary evaporator. Finally, the resulting solids were calcined at 450 °C for 5 h under nitrogen gas flow and subsequently reduced in 5% H<sub>2</sub>/Ar gas flow at 450 °C for 5 h.

## Characterization

Powder X-ray diffraction (XRD) was carried out on Rigaku/Max-3A X-ray diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). The high-resolution transmission electron microscopic (HRTEM) images and EDX elemental mapping

were performed on a JEOL JEMARF200F atomic resolution analytical microscope with a spherical aberration corrector. The sample morphologies were measured on scanning electron microscopy (SEM, JEOL JSM-6330F, 15.0 kV). X-ray photoelectron spectroscopy (XPS) was measured on a Perkin–Elmer RBD upgraded PHI-5000C ESCA system. The thermo gravimetric analysis (TGA) was performed on a Shimadzu DTG-60H thermal analyzer under air gas flow at 10 °C min<sup>-1</sup> in the temperature range of 30–800 °C. Temperature-programmed reduction analysis (H<sub>2</sub>-TPR) wascarried out by heating a sample (50 mg) from 25 to 700 °C at 10 °C min<sup>-1</sup> in a gas flow of 5 vol.% H<sub>2</sub>/Ar mixture (40 mL min<sup>-1</sup>). Fourier transformed infrared (FT-IR) spectra were recorded on a Nicolet Magana-IR 750 spectrometer in a range from 400 to 4000 cm<sup>-1</sup>.

## **Catalyst evaluation**

The activity tests of the obtained catalysts for CO<sub>2</sub> hydrogenation to methane were carried out in a fixed-bed continuous-flow reactor–gas chromatography (GC) combination system. In each experiment, 100 mg of catalyst was loaded into the flow reactor. Prior to reaction, the catalysts were reduced in a mixture gas of  $H_2/CO_2 = 3/1$  at a flow rate of 20 mL min<sup>-1</sup> and 573 K for 6 h, and then cooled to 150 °C in argon. The reaction was conducted at a stationary state under reaction conditions of 1.0 MPa, 200 °C to 340 °C. A mixture of  $H_2$ , CO<sub>2</sub> and Ar (as internal standard) with a molar ratio of  $H_2$ :CO<sub>2</sub>:Ar = 72:24:4 was introduced into the reactor and the gas hourly space velocity (GHSV) was 9000 mL h<sup>-1</sup> g<sup>-1</sup>. The outlet gases were transported to the sampling valve of the GC (Agilent GC-7820), which was equipped with dual thermal conductivity and flame ionization detectors and dual columns filled with carbon molecular sieve (TDX-01) and capillary column (Porapak-Q). CO<sub>2</sub> conversion (denoted as X(CO<sub>2</sub>)), CH<sub>4</sub> and CO selectivity (denoted as S(CH<sub>4</sub>) and S(CO)) were calculated by an internal normalization method as follows:

 $X(CO_2) = \frac{C_{in(CO2)} - C_{out(CO2)}}{C_{in(CO2)}}$ 

$$S(CH_4) = \frac{C_{(CH4)}}{C_{in(CO2)} - C_{out(CO2)}}$$
$$\frac{C_{(CO)}}{S(CO)} = \frac{C_{in(CO2)} - C_{out(CO2)}}{C_{in(CO2)} - C_{out(CO2)}}$$

where  $C_{in(CO2)}$  and  $C_{out(CO2)}$  are the inlet and outlet concentrations of the corresponding gases, respectively;  $C_{(CH4)}$  and  $C_{(CO)}$  are the CH<sub>4</sub> and CO concentration of the exit gas composition during catalytic reactions.

The dispersion of Ni ( $D_{Ni}$ ) was determined by  $H_2$  pulse chemisorption and carried out on a Micromeritics AutoChem 2920 instrument. In a typical measurement, 0.1 g catalyst was packed into a reactor with a quartz tube, and treated at 300 °C for 1 hour at a heating rate of 10 °C min<sup>-1</sup> under a flow of pure  $H_2$  atmosphere. After cooling down to room temperature, the sample was purged under Ar flow at 50 sccm for 30 min. Then, 5 vol. %  $H_2$ /Ar pulses were injected until the adsorption reached saturation. Turnover frequency (TOF) of product formation was calculated according to the equation:

 $Turnover frequency (TOF) (s^{-1}) = \frac{The \ rate \ of \ product \ formation}{The \ number \ of \ Ni \ surface \ atoms}$ 



Fig. S1. SEM images of Ni/SiO $_2$  (a) and Ni/ZrO $_2$  (b).



Fig. S2. XRD patterns of Ni/ZrO<sub>2</sub> and Ni/SiO<sub>2</sub>.



Fig. S3. FT-IR spectrum of UiO-66.



Fig. S4. Thermal gravity analysis curve of UiO-66 in the range of 30-800 °C



Fig. S5. Effect of temperature on  $CO_2$  conversion for  $CO_2$  methanation over the Ni/ZrO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts



Fig. S6. Effects of Ni loading on  $CO_2$  conversion for  $CO_2$  methanation over xNi@UiO-66 catalysts at 300 °C.



Fig. S7.  $H_2$  pluse chemisorptions profiles of UiO-66 (a) and 20Ni@ UiO-66 (b).



Fig. S8. Illustration of Ni@UiO-66 catalyst.