

Supporting Information

High catalytic performance of mesoporous zirconia supported nickel catalysts for selective CO methanation

Aihua Chen, Toshihiro Miyao, Kazutoshi Higashiyama, Mashiro Watanabe

Experimental Section

Mesoporous ZrO₂, denoted as m-ZrO₂, was prepared following the procedure described by Yan et al. by employing a triblock copolymer (Pluronic F127, M_{av} = 12600, EO106PO70EO106, Sigma-Aldrich) as a template [1, 2]. In detail, F127 1 g was dissolved in 10 mL of ethanol at room temperature. Then, 1.61 g (5 mmol) of ZrOC128H₂O was added to the above solution with vigorous stirring. The mixture was covered with a PE film. After being stirred for at least 2 h at room temperature, the homogenous sol was transferred to an oven and underwent solvent evaporation. After 2 days of aging under the desired temperature (40 °C) and humidity (50%), the gel product was dried at 100 °C for 24 h. The resulting sample was calcined at 400 °C with a ramp rate of 1°C/min and held for 4 h. Ni with different amount was loaded into m-ZrO₂ through conventional incipient-wetness impregnation step with an aqueous solution of Ni (ZnO)₃·2H₂O. After drying at 110 °C for 12 h, the sample was calcined at 400 °C for 5 h. The X-ray powder diffraction of the samples was carried out with a Rigaku D/MAX-2000 diffractometer using Cu K α radiation. Transmission electronic microscopy (TEM) was recorded on a JEOL-2700 under a working voltage of 200 kV. The nitrogen adsorption and desorption isotherms at 78.3 K were measured using an ASAP 2020 analyzer. The surface areas were calculated by Brunauer-Emmett-Teller (BET) equation. Before measurement, each sample was pretreated at 300 °C for 1 h. The catalytic activity tests were performed through a fixed-bed quartz tubular reactor at atmospheric pressure. The catalyst powder was shaped and sieved into pellets with diameters of 1.2-2.0 mm. Before reaction, the catalyst was pretreated at 400 °C with H₂ for 1 h. An on-line gas chromatograph with a thermal conductivity detector (TCD) and flame ionization detector (FID) was used to analyze the inlet and outlet gas composition.

The conversion of CO and CO₂, and the selective of CO methanation were calculated from the following equations.

$$\text{CO conversion } (X_{\text{CO}}, \%) = \frac{\text{Inlet CO} - \text{Outlet CO}}{\text{Inlet CO}} \times 100$$

$$\text{CO}_2 \text{ conversion } (X_{\text{CO}_2}, \%) = \frac{\text{Outlet CH}_4 - (\text{Inlet CO} - \text{Outlet CO})}{\text{Inlet CO}_2} \times 100$$

$$\text{CO-Selectivity (\%)} = \frac{\text{Inlet CO} - \text{Outlet CO}}{\text{outlet CH}_4} \times 100$$

Reference:

- 1 Q. Yuan, Q. Liu, W Song, W. Feng, W Pu, L. Sun, Y. Zhang, C Yan, *J. Am. Chem. Soc.*, 2007, **129**, 6698.
- 2 Q. Yuan, L.L. Li, S. L. Lu, H. H. Duan, Z. X. Li, Y. X. Zhu, C. H. Yan, *J. Phys. Chem. C* 2009, **113**, 4117.

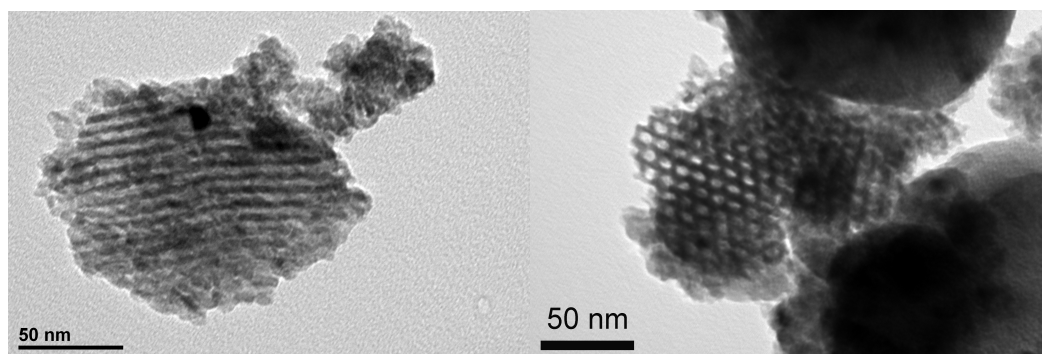


Fig. S1 TEM images of 7%Ni/m-ZrO₂.