Supporting Information

Screening transition metals (Mn, Fe, Co, Cu) promoted Ni-based CO_2 methanation bimetal catalysts with advanced low-temperature activities

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Experimental

S1. The fabrication of the mesoporous Ce-Zr solid solution support

Mesoporous Ce-Zr solid solution material ($Ce_{0.8}Zr_{0.2}O_2$) was synthesized by evaporation-induced self-assembly (EISA) strategy reported elsewhere.[1, 2] In the process of synthesizing the material, 1.0 g P123 (Mav = 5800, $EO_{20}PO_{70}EO_{20}$, Aladdin) was first dissolved in 20.0 ml anhydrous ethanol (C_2H_5OH, Sinopharm Holding Chemical Reagent Co., Ltd.) with vigorous magnetic stirring. Then, 8 mmol $Ce(NO_3)_3 \cdot 6H_2O$ (Shanghai Macklin Bio-Chem Co., Ltd., China) and 2 mmol $ZrOCl_2 \cdot 8H_2O$ (Shanghai Aladdin BioChem Co., Ltd., China) were sequentially added to above P123 solution with vigorous magnetic stirring until the solution became transparent. The transparent solution was stirred into a culture dish and covered with a PE membrane with small holes. The final solution was moved to a culture dish and placed in a 60 °C convection oven with relative humidity less than 50% for solvent volatilization and template assembly. After experiencing 48 h EISA process, the golden yellow dried gel in the culture dish was transferred to the crucible and calcined at 500 °C for 5 h. The final mesoporous Ce-Zr solid solution with the 80/20 Ce/Zr molar ratio was abbreviated as M-Ce80Zr20.

S2. The preparation of the catalysts

The $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ (Shanghai Aladdin Bio-Chem Co., Ltd., China) were selected as the metal precursors and all the Ni-based bimetal catalysts were prepared by the incipient impregnation method using the M-Ce80Zr20 as the support. The weight percentages of the Ni and transition metal (T = Mn, Co, Fe, Cu) were controlled at 12.0 wt.% and 3.0 wt.%, respectively. The catalyst precursors were dried in the 60 °C convection oven for overnight and then calcined at 600 °C for 5 h. The final bimetal

catalysts with 12 wt.% Ni and 3 wt.% transition metals were denoted as 12Ni3T/M-Ce80Zr20 (T =

Mn, Co, Fe, Cu). Besides, the Ni-Co bimetal catalysts with different Ni (*x* wt.%) and Co (*y* wt.%)

loading amounts (*x* + *y* = 15) were also prepared with the same protocol and the final catalysts

were defined as *x*Ni*y*Co/M-Ce80Zr20.

S3. Catalyst characterizations

The X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a XRD-6100

diffractometer (Shimadzu, Japan) with Cu Kα radiation and scanning rate of 3°/min in the range of

20°–80°.

The N_2 physisorption analysis was carried out on an Autosorb-iQ-AG-MP instrument

(Quantachrome, US). For each test, the sample was pretreated by degassing at 300 °C for 3 h. The

Brunauer-Emmett-Teller (BET) specific surface area, Barret-Joyner-Halenda (BJH) pore volume,

and pore size distribution of the sample were calculated based on the N_2 adsorption branch of the

isotherm.

Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED),

scanning transmission electron microscopy (STEM) images, and energy-dispersed spectroscopy

(EDS) mapping were taken on a high-resolution transmission electron microscopy (FEI TECNAI G2

F20) at an accelerated voltage of 200 kV. The sample was uniformly dispersed in absolute ethanol

with the assistance of the ultrasonic and then dropped on the copper grid sample holder coated

with carbon layer.

The valence state and composition of the surface elements in the catalysts were

characterized by X-ray photoelectron spectroscopy (XPS) on the Escalab 250Xi (Thermo Fisher

Scientific, US) spectrometer with the focused monochromatic Al-K source as the incident ray. The

binding energy of the catalyst was calibrated by using C1s (284.5 eV) as the internal standard.

The H_2 temperature programmed reduction (H_2-TPR) analyses of the catalysts were carried

out on a micro fixed reactor with a LC-D200 mass spectrometer (TILON, US) as the detector. In a

specific test, 200 mg sample was loaded in a quartz tube (i.d. = 5.0 mm). The sample was firstly

purged with Ar (20.0 mL/min) at 300 °C for 30 min before the regular analysis. Then, the 5 vol.% H_2-95 vol.% Ar mixture stream (50.0 mL/min) was introduced. After the baseline of the H_2 mass signal (m/z = 2) was stable, the temperature was programmatically increased from 25 °C to 800 °C with the rate of 20 °C/min and the H_2 mass signal was recorded with the LC-D200 mass spectrometer during the whole H_2-TPR process.

The CO_2 temperature programmed desorption (CO_2-TPD) analyses of the samples were analyzed on the same apparatus of the H_2-TPR described above. Specifically, 100 mg of catalyst was loaded and absorbed CO_2 in CO_2 stream (10.0 mL/min) at 25 °C for 30 min. Then, the sample was purged by the Ar stream until the CO_2 baseline (m/z = 44) was stable. Finally, the sample was programmatically heated from 25 °C to 800 °C with a ramp of 20 °C/min under Ar stream (40.0 mL/min) and the CO_2 signal during the CO_2-TPD was recorded by the mass spectrometer.

Temperature Programmed surface reaction (TPSR) of the CO_2 methanation were performed on the same reactor as the H_2-TPR and CO_2-TPD. Specifically, the 200 mg of catalyst was loaded for each test. Before the TPSR test, the catalyst was reduced with the mixture of 50 vol.%H_2-50 vol.%N_2 mixture stream (20 mL/min) at 500 °C for 180 min. Then, the reduced catalyst was purged by the Ar stream (20.0 mL/min) until cooled down to room temperature. The feed gases consisting of 80 vol.%H_2-20 vol.%CO_2 (3.0 mL/min) and Ar (47.0 mL/min) were introduced into the catalyst bed until their baselines were stable. Finally, the TPSR of CO_2 methanation was carried out by increasing the reaction temperature from 25 °C to 500 °C with the heating rate of 10 °C/min. The trends of the reactants and products were recorded by the mass spectrometer.

The *in-situ* DRIFTS of CO_2 methanation was carried out on the Nicolet IS50 spectrometer equipped with a MCT detector. The detector was firstly cooled in liquid nitrogen and then the background and fundamental vectors were collected in vacuum condition. The $CO_2/H_2/N_2$ mixture gas was fed into the reactor cell and the temperature increased from 25 °C to 450 °C with the

heating rate of 10 °C/min. The reactor was cooled with circulating water during the test. The spectrum of sample was scanned from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 7 cm^{-1} and 32 scans at each temperature.

S4. Catalyst evaluation

Catalytic activity tests were conducted in a micro fixed bed reactor equipped with a quartz tube (i.d. = 10 mm) and the reaction quartz tube was placed vertically in a tube furnace. The temperature of the reaction was detected and controlled by the thermocouple located in the center of the catalyst bed. The gas flows of the feed gases are controlled by the mass flow controllers (MFC, Brooks Instrument) and the ratio of the reactants (H_2/CO_2) is controlled at 4/1 without any dilution. The reaction pressure are controlled at 1.0 atm and the reaction temperature is investigated in the range of 200-450 °C. For each test, 100 mg catalyst is loaded and the space velocity is set as 12000 mL/(g·h). Before catalytic reactions, the catalyst in the reactor was firstly pre-reduced with H_2/N_2 = (10.0/10.0 mL/min) at 500 °C for 2 h. The Perkin Elmer GC-680 gas chromatograph equipped with thermal conductivity detector (TCD) and the hydrogen flame detector (FID) were used for online analysis of the products.

References

(1) Xu, L.; Lian, X.; Chen, M.; Cui, Y.; Wang, F.; Li, W.; Huang, B. CO_2 methanation over Co-Ni bimetal-doped ordered mesoporous Al_2O_3 catalysts with enhanced low-temperature activities, *Int. J. Hydrogen Energy*, **2018,** 43, 17172-17184.

(2) Xu, L.; Song, H.; Chou, L. Mesoporous nanocrystalline ceria-zirconia solid solutions supported nickel based catalysts for CO_2 reforming of CH_4, *Int. J. Hydrogen Energy*, **2012**, 37, 18001-18020.