

Effect of catalysts properties on selectivity in CO₂ methanation with coupling pathway of RWGS and CO methanation

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5.1. Characterization Methods

Nitrogen adsorption-desorption isotherms were conducted on a Trwastar3000 micromeritics instrument at -196 °C. Before testing, the samples were outgassed at 300 °C for 4 h. The specific surface areas were calculated according to the BET method. The average pore size distributions and the total pore volumes were obtained according to the BJH method from the desorption isotherms.

Powder X-ray diffraction (XRD) patterns were collected using a D8 Advance X-ray diffractometer citrate complexation combined with impregnation method (Bruker) with Cu K α radiation of wavelength $\lambda=0.15406$ nm at 40 kV and 100 mA. The crystallite sizes were estimated with the Scherrer equation.

The morphology of the samples was visualized using an emission scanning electron microscope (SEM) (Gemini 300, ZEISS, Germany).

The surface chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS) (ESCLAB-250Xi, Thermo-Fisher Scientific, USA), which was performed in an ultra-high vacuum chamber with a base pressure of 2×10^{-7} Pa. Samples were prepared for XPS analysis by adhering powers to carbon substrates, and all peaks were energy-calibrated relative to the C 1s peak of adventitious carbon at 284.6 eV.

Hydrogen temperature programmed reduction (H₂-TPR) was carried out by PX200 (Tianjin Peng Xiang Technology Co., Ltd) catalyst characterization system. 100 mg of fresh sample was pre-treated in high purity nitrogen at 200 °C for 2h to remove the adsorbed moisture and impurities. The sample was exposed to 5% H₂/N₂ (50 ml min⁻¹) and the samples were heated to 900 °C with a heating rate of 10 °C min⁻¹.

The H₂ temperature-programmed desorption (H₂-TPD) was conducted on an Autosorb IQ quanta chrome instrument (ASIQAC160000- 6) with a thermal conductivity detector. As for H₂-TPD, 50 mg of fresh sample was reduced in situ with H₂ at 600 °C for 2 h before the TPD tests, then cooled down to room temperature after H₂ reduction, and then flushing argon (Ar, 30 ml min⁻¹) for 30 min to detach the physically adsorbed H₂. Then the sample was heated to 500 °C with a heating rate of 10 °C min⁻¹ under a flow of 5 vol.% H₂ and 95 vol.% Ar mixture, the H₂ desorption signal was recorded by the TCD detector. The Ni dispersion (D) and the Ni metallic surface area (S_{Ni}) of N/AZ-x catalysts were determined by H₂-TPD and calculated with the following equations (1) and (2) [8, 31]:

$$D_{Ni}(\%) = \frac{2V_H \times N_A / V_m}{m \times \omega \times N_A / M} \times 100\% \quad (1)$$

$$S_{Ni} = \frac{2V_H \times N_A \times \delta_{Ni}}{m \times V_m} \quad (2)$$

where the V_H, m, and ω are the monolayer adsorption capacity of hydrogen on the catalyst surface (L), the mass of sample (g), and the Ni mass fraction, respectively. The corresponding values of the Avogadro's number (N_A), the H₂ molar volume (V_m), Ni molecular weight (M), the Ni cross-sectional area (δ_{Ni}) are 6.02×10^{23} mol⁻¹, 22.4 L mol⁻¹, 58.69 g mol⁻¹, and 0.0649 nm². The moles of desorbed H₂ were calculated by

integrating the area of the H₂-TPD profiles and using calibration pulses of pure H₂ of known quantities. The turnover frequency (TOF) was calculated as moles of CH₄ produced per mole of surface metal atoms per second using the inlet flow of CO₂, the molar gas volume, and the catalyst mass (surface metal atoms were estimated using the dispersion from H₂-TPD).

Similarly, for the CO₂/CO/NH₃-TPD, the samples were reduced in H₂ at 600 °C and cooled down under inert atmospheres. Afterwards, the samples were subjected to CO₂/Ar, CO/Ar or NH₃-TPD stream for 30 min and the physisorbed CO₂/CO species were flushed out for 30 min using an Ar stream. Then the sample was heated to 500 °C with a heating rate of 10 °C min⁻¹ under a flow of 5 vol.% CO₂/CO and 95 vol.% Ar mixture, and the CO₂/CO desorption signal was recorded by the TCD detector.

In situ DRIFTS of CO₂ methanation were measured on a Frontier FT-IR Spectrometer (PerkinElmer). The sample (reduced at 700 °C for 2h before the test) was pretreated at 200 °C for 30 min with an Ar flow of 20 ml min⁻¹, and then the background spectra of the sample were collected from 400 to 4000 cm⁻¹. Finally, a mixed gas of 3%H₂ / 12%CO₂ / 85%Ar with 10 mL min⁻¹ was injected into the chamber, and then the system was heated to the desired temperature from 150-500 °C (interval of 50 °C) while recording the spectra.

S 2. SEM images

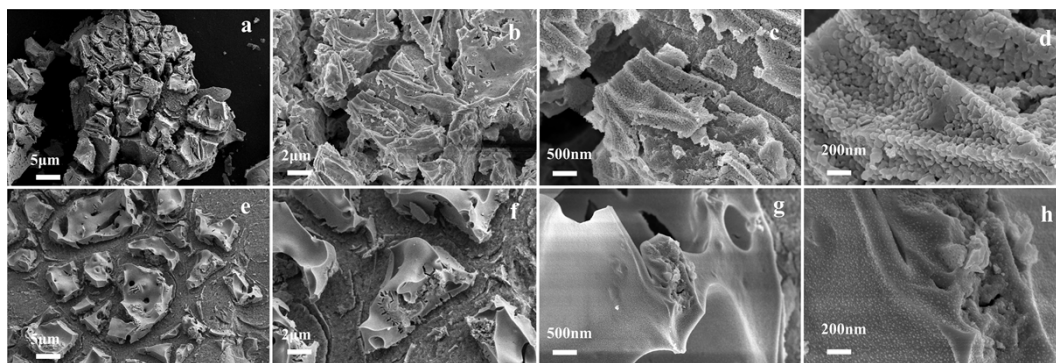


Fig. S1. SEM images: LN/AZ (a-d) and LN/AZ (e-f).