

Supporting Information

Three-dimensional flower-like nickel phyllosilicates for CO₂ methanation: Enhanced catalytic activity and high stability

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S1 Experimental Section

S1.1 Catalytic performance measurement

CO₂ methanation reaction was carried out in a fixed bed reactor equipped with a quartz tube at 0.1 MPa in the temperature range of 300–550 °C with an interval of 50 °C. The catalyst (0.1 g, 20–40 mesh) diluted with quartz sands (5.0 g) was uploaded in a quartz tube with an inner diameter of 8 mm. The addition of the quartz sand can avoid the generation of hotspot in the catalyst bed due to its high heat conductivity. The influence of heat and mass transfers was examined and eliminated before the catalytic tests. The catalyst was reduced at 600, 700 or 800 °C in pure H₂ (100 mL min⁻¹) for 1 h and then cooled to the starting reaction temperature in H₂. The reaction gas of H₂ and CO₂ as well as N₂ (as the internal standard) were introduced into the reactor at a molar ratio of H₂/CO₂/N₂=12/3/5 at a total flow rate of 100 mL min⁻¹. Inlet and outlet gases were analyzed online by a Micro GC (3000A; Agilent Technologies). The concentrations of H₂, N₂, CH₄, and CO in the gas products were detected by a TCD detector connected to a Molecular Sieve column, while the components of CO₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ were separated by a Plot Q column and analyzed by another TCD. In addition, a lifetime test of CO₂ methanation was performed at 450 °C and 0.1 MPa. Here, the CO₂ conversion, CH₄ selectivity, and CH₄ yield are defined as bellow:

$$\text{CO}_2 \text{ conversion: } X_{\text{CO}_2} (\%) = \frac{V_{\text{CO}_2,\text{in}} - V_{\text{CO}_2,\text{out}}}{V_{\text{CO}_2,\text{in}}} \times 100 \quad (1)$$

$$\text{CH}_4 \text{ selectivity: } S_{\text{CH}_4} (\%) = \frac{V_{\text{CH}_4,\text{out}}}{V_{\text{CO}_2,\text{in}} - V_{\text{CO}_2,\text{out}}} \times 100 \quad (2)$$

$$\text{CH}_4 \text{ yield: } Y_{\text{CH}_4} (\%) = \frac{V_{\text{CH}_4,\text{out}}}{V_{\text{CO}_2,\text{in}}} \times 100 \quad (3)$$

where, X is the conversion of CO₂, S is the selectivity of CH₄, Y is the CH₄ yield, $V_{\text{CO}_2,\text{in}}$ and $V_{\text{CO}_2,\text{out}}$ are the volume flow rates of CO₂ at the inlet and outlet of the reactor at standard temperature

and pressure (STP), mL s⁻¹.

The normalized rate and activation energy for CO₂ methanation over the catalysts were measured at 0.1 MPa with the catalyst loading of 1.0 g (20–40 mesh) diluted with 3.0 g quartz sands (20–40 mesh). In order to lower the CO₂ conversion in the range of 5–10%, the experiments were performed at different total gas flow rates of 50, 100 and 200 mL min⁻¹ at the temperatures of 200, 210 and 220 °C. The rate was determined using the following equation:

$$Rate(r) = \frac{F_{CO_2} \times X_{CO_2}}{W} = \frac{X_{CO_2}}{W/F_{CO_2}} \quad (4)$$

Where F_{CO_2} represents the flow of the CO₂ in mol s⁻¹, W is the weight of the catalyst in g, and X_{CO_2} the CO₂ conversion. The variations of X_{CO_2} with respect to W/F_{CO_2} were plotted, and then the rates of reaction were calculated at various temperatures from the slope of linear portion. The activation energy was calculated using the Arrhenius equation.

S1.2 Hydrothermal treatments of catalysts in the 100% steam

To evaluate the hydrothermal stability of the catalysts, 0.20 g of the calcined N/M-P-30 or N/M-Im was set in the center of a tube furnace at 600 °C; simultaneously, a 100% steam flow produced by heating a flask containing deionized water was continuously charged for 6 h. The obtained sample was denoted as “N/M-P-30-H” or “N/M-Im-H”, respectively.

S2 Results and Discussion

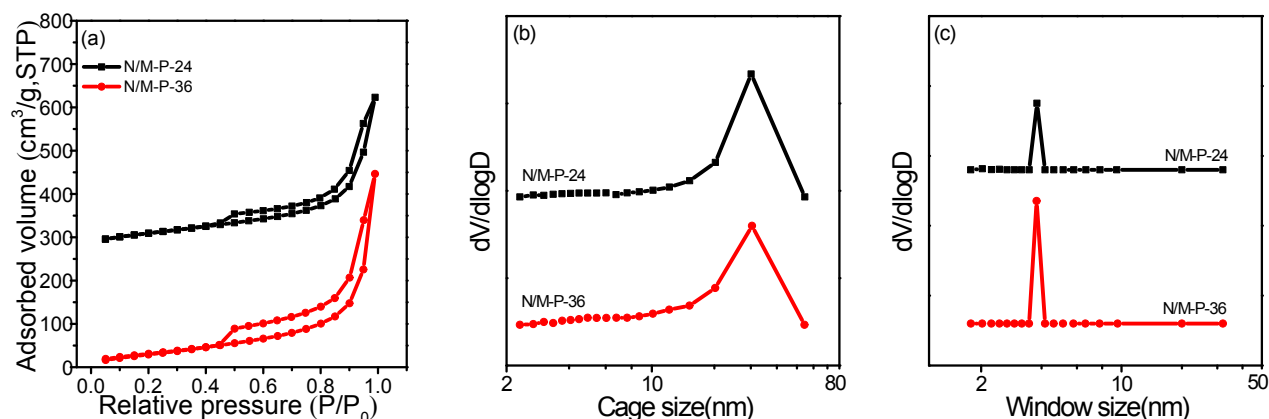


Figure S1. N₂ adsorption results of the calcined catalysts: (a) adsorption-desorption isotherms; (b) the BdB cage size distribution curve obtained from the adsorption branch; and (c) the BdB window size distribution curve obtained from desorption branch.

Table S1. Physical and chemical properties of the calcined catalysts.

Samples	Ni content ^a (wt.%)	S _{BET} ^b (m ² g ⁻¹)	V _p ^c (cm ³ g ⁻¹)	D _c ^d (nm)	D _w ^e (nm)
N/M-P-24	25.46	202.1	0.82	30.6	3.8
N/M-P-36	31.87	191.2	0.75	30.6	3.8

^aNi contents determined by ICP analysis;

^bSurface area, derived from BET equation;

^cPore volume, obtained from the volume of nitrogen adsorbed at the relative pressure of 0.99;

^dD_c, Cage size, calculated from the adsorption branches of the N₂ adsorption isotherms based on the BdB sphere model;

^eD_w, Window size, calculated from the desorption branches of the N₂ adsorption isotherms based on the BdB sphere model.

Table S2. Ni crystal size and Ni particle size of N/M-P-30-600 and N/M-P-30-800 catalysts.

Samples	Ni crystal size ^a (nm)	Ni particle size ^b (nm)
N/M-P-30-600	3.4	–
N/M-P-30-800	5.3	5.4

^aNi crystal size, calculated by the XRD diffraction peak ($2\theta = 44.6$) using the Debye-Scherrer equation;

^bAverage particle size, estimated from the TEM images.