Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Methanation of CO_2 and reverse water gas shift reactions on Ni/SiO_2 catalysts: The influence of particle size on selectivity and reaction pathway

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Table S1 Characterization of the 0.5 wt% and 10 wt% Ni/SiO_2 catalysts

Catalyst	CO adsorption (μmol/g cat.)	Ni surface area[a] (m^2/g)	Ni particle size[b] (nm)
0.5 wt% Ni/SiO_2	8.5	0.33	nd[c]
10 wt% Ni/SiO_2	68.8	2.68	9

[a] Estimated from CO chemisorption.

[b] Estimated from the XRD spectra in Figure 1.

[c] The XRD pattern was too weak to be observed.

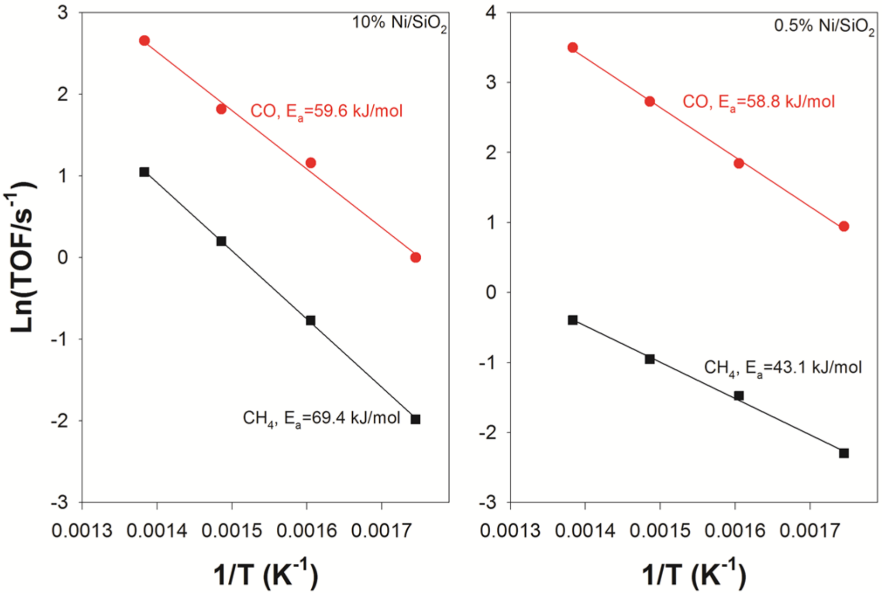

Fig. S1 Arrhenius plots for the TOF of CO CH_4 formation from CO_2 hydrogenation on Ni/SiO_2 catalysts.

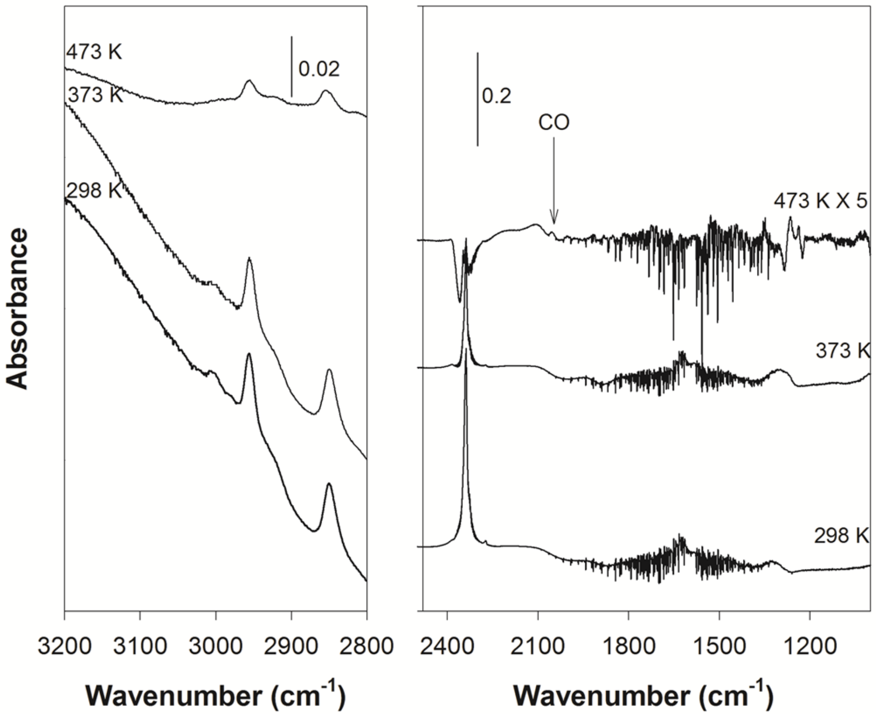

Fig. S2 IR spectra of H_2 and CO_2 co-adsorbed on the 0.5 wt% Ni/SiO_2 catalyst at various temperatures. All experiments were performed by passing a pure CO_2 stream (20 mL/min) over the catalysts for 20 min at 298 K, followed by purging the CO_2 with a He stream (20 mL/min). The IR spectra were recorded to monitor the adsorbed CO_2 on Ni/SiO_2 under a H_2 stream at elevated temperatures.

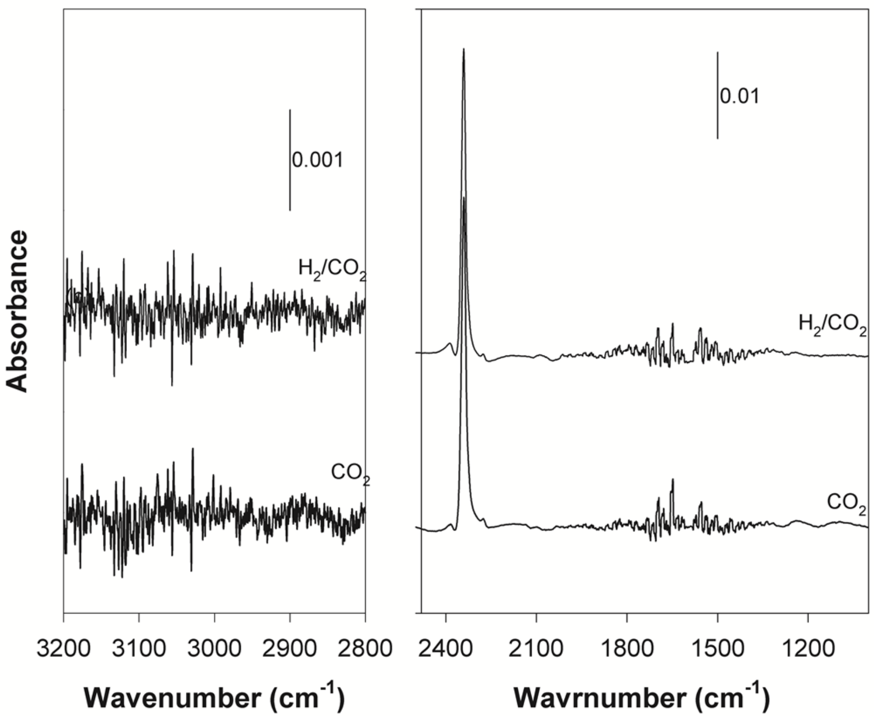

Fig. S3 IR spectra of CO_2 and H_2/CO_2 adsorbed on the SiO_2 at room temperature. All experiments were performed by passing a pure CO_2 stream (20 mL/min) over the catalysts for 20 min at 298 K, followed by purging the CO_2 with a He stream (20 mL/min). The IR spectrum of H_2 and CO_2 co-adsorption was recorded to monitor the adsorbed CO_2 on SiO_2 under a H_2 stream at room temperature.

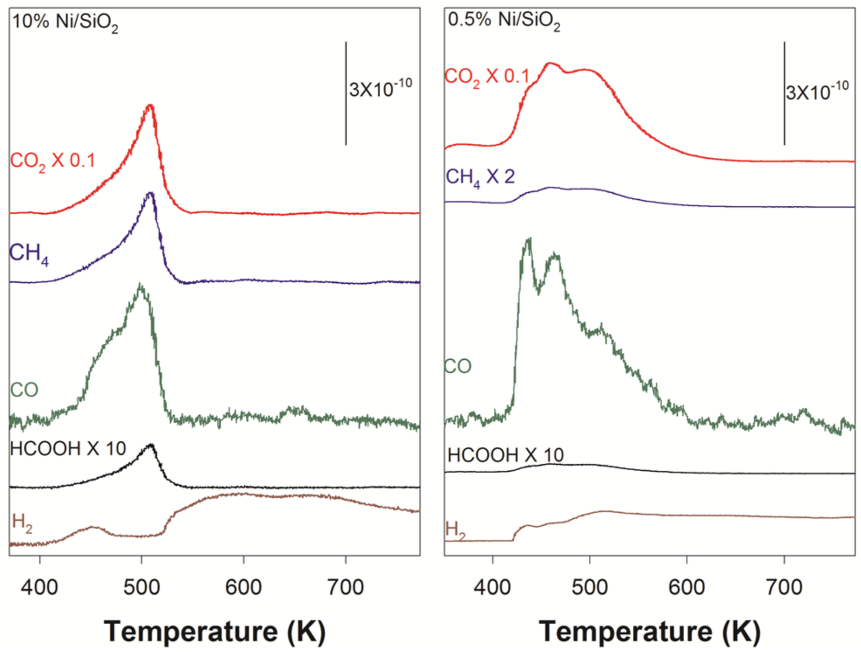

Fig.S4 TPD spectra of the 0.5 wt% and 10 wt% Ni/SiO_2 catalysts at 298 K after a 1-μL dose of formic acid.

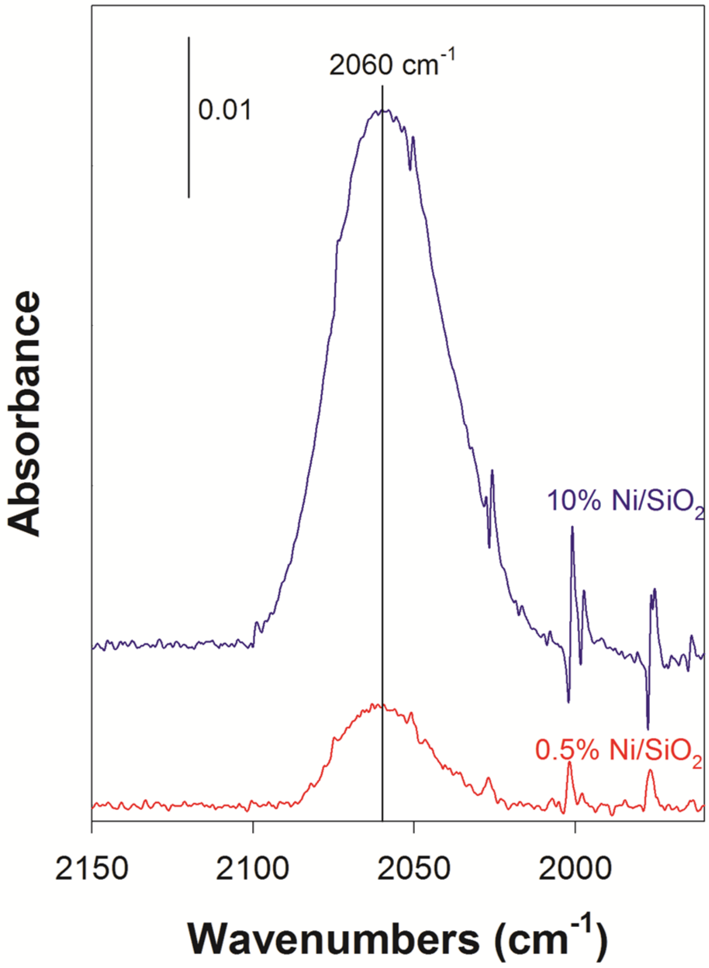

Fig. S5 IR spectra of the CO adsorbed on the reduced 0.5 wt% and 10 wt% Ni/SiO$_2$ catalysts at 298 K.

Appendix

Far away from equilibrium conditions, the steady-state rate of CO_2 hydrogenation to form CO and CH_4 *via* parallel and consecutive reaction network is described by the following equations:

The possible reaction network of CO_2 hydrogenation can be described:

(1) $H_2+CO_2 \rightarrow CO+H_2O$

(2) $3H_2+CO \rightarrow CH_4+H_2O$

(3) $4H_2+CO_2 \rightarrow CH_4+2H_2O$

(A) parallel pathway:

$$\frac{r_{CO}}{r_{CH_4}} = \frac{k_1 P_{H_2}^{1.1} P_{CO_2}^{0.06}}{k_3 P_{H_2}^{1.1} P_{CO_2}^{0.06}} = \frac{k_1}{k_3}$$

Selectivity of CH_4: $S_{CH_4} = \frac{r_{CH_4}}{r_{CO} + r_{CH_4}} = \frac{k_3}{k_1 + k_3}$

(B) consecutive pathway:

$$\frac{r_{CO}}{r_{CH_4}} = \frac{k_1 P_{H_2}^{0.3} P_{CO_2}^{0.5} - k_2 P_{H_2}^{0.3} P_{CO_2}^{0.5} X_{CO_2}}{k_2 P_{H_2}^{0.3} P_{CO_2}^{0.5} X_{CO_2}} \quad (\mathrm{X}_{\mathrm{CO}_2}: \mathrm{CO}_2 \text{ conversion})$$

Selectivity of CH_4: $S_{CH_4} = \frac{r_{CH_4}}{r_{CO} + r_{CH_4}} = \frac{k_2 P_{H_2}^{0.3} P_{CO_2}^{0.5} X_{CO_2}}{k_1 P_{H_2}^{0.3} P_{CO_2}^{0.5}} = \frac{k_2}{k_1} X_{CO_2}$