

## Supplementary material

# A Facile Fabrication of Supported Ni/SiO<sub>2</sub> Catalysts for Dry Reforming of Methane with Remarkably Enhanced Catalytic Performance

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### *Calculation of the Equilibrium Conversion in DRM Reaction*

**Table S1.** The equilibrium conversions of CH<sub>4</sub> and CO<sub>2</sub>, H<sub>2</sub>/CO molar ratio, and selectivity to H<sub>2</sub>O calculated by HSC chemistry 6.0.

Feeding gas and product gas	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	CO	H <sub>2</sub> O
Initial molar composition (mol)	45.0	45.0	10.0	0	0	0
Equilibrium composition (mol)	4.14	2.18	10.0	79.8	83.7	1.96
Conversions of CH <sub>4</sub> and CO <sub>2</sub> (%)	91.0	95.0	---	---	---	---
Equilibrium H <sub>2</sub> /CO molar ratio	---	---	---	0.95	---	---
Selectivity to H <sub>2</sub> O (%)	---	---	---	---	---	2.3

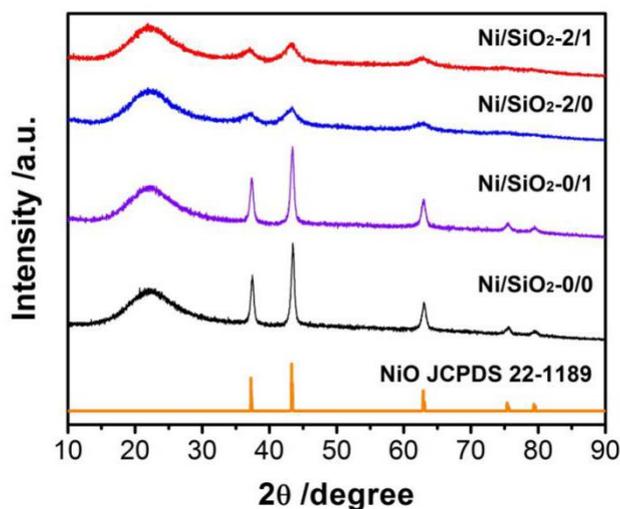
Reaction conditions: 800 °C, 1 bar.

In order to evaluate the catalytic activity in DRM reaction, equilibrium conversions of CH<sub>4</sub> and CO<sub>2</sub> were calculated by software HSC chemistry 6.0. The initial composition of feeding gas and product gas was set at CH<sub>4</sub> (45 mol), CO<sub>2</sub> (45 mol), N<sub>2</sub> (10 mol), H<sub>2</sub> (0 mol), CO (0 mol), and H<sub>2</sub>O (0 mol), while operating conditions were set at 800 °C and 1 bar. The calculated results are shown in Table S1.

**Table S2.** BET surface area, pore volume and pore size of the SiO<sub>2</sub> support and as-prepared Ni/SiO<sub>2</sub> catalysts.

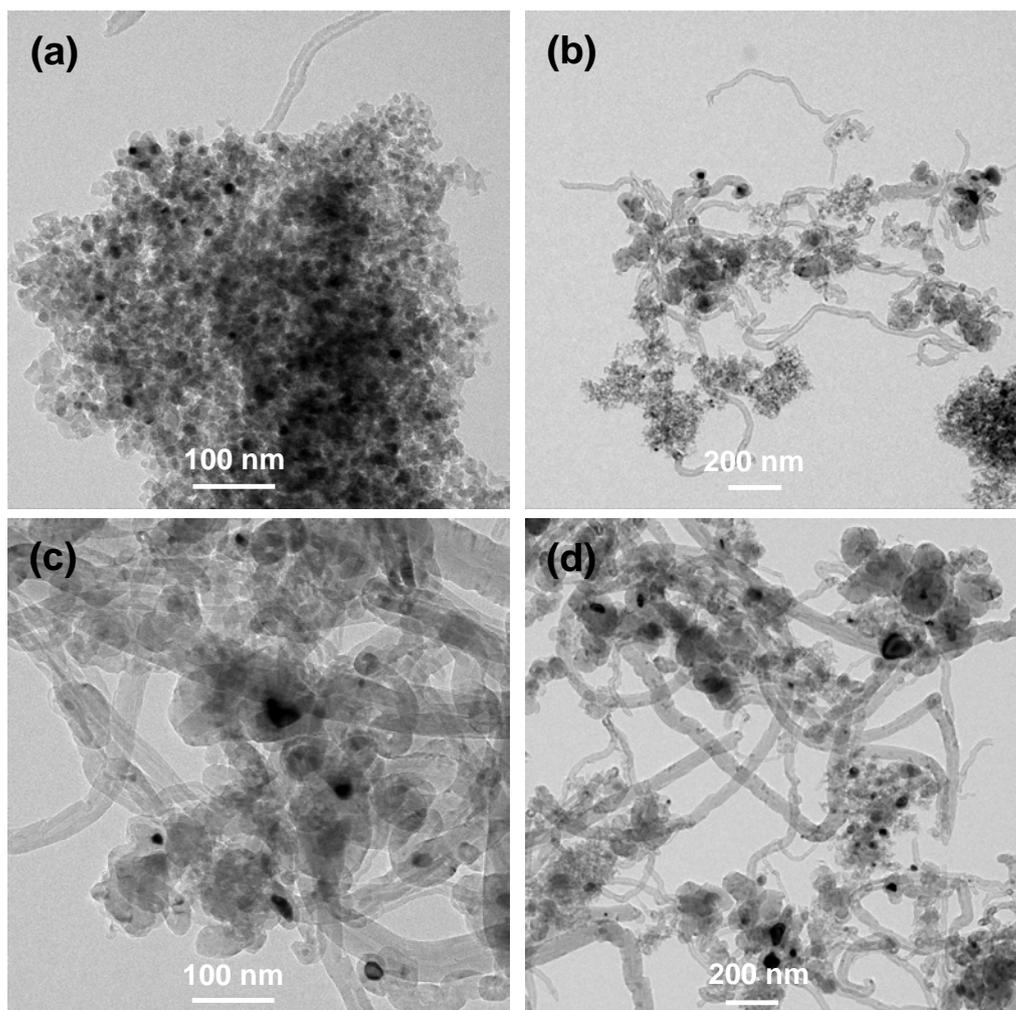
Sample		SiO <sub>2</sub> support	Ni/SiO <sub>2</sub> -0/0	Ni/SiO <sub>2</sub> -0/1	Ni/SiO <sub>2</sub> -2/0	Ni/SiO <sub>2</sub> -2/1
BET surface area (m <sup>2</sup> /g)	Fresh	188.8	161.2	159.7	172.2	175.1
	Reduced	-	162.6	167.0	169.9	165.9
	Spent	-	89.9	95.0	121.0	118.3
Pore volume (cm <sup>3</sup> /g)	Fresh	1.17	0.97	0.81	0.84	0.80
	Reduced	-	0.99	0.99	0.82	0.88
	Spent	-	0.37	0.36	0.39	0.50
Pore size (nm)	Fresh	17.6	15.6	17.5	15.5	16.2
	Reduced	-	15.5	15.5	15.5	15.5
	Spent	-	17.5	16.2	13.8	16.8

Table S2 shows the BET surface area, pore volume and pore size of the SiO<sub>2</sub> support and as-prepared Ni/SiO<sub>2</sub> catalysts. It can be seen clearly that, compared with SiO<sub>2</sub> support, the BET surface area, pore volume and pore size slightly decreased over all prepared fresh and reduced Ni/SiO<sub>2</sub> catalysts. However, they became distinctly different after 50-hours of reaction, which should be ascribed to the carbon deposits on the catalyst. The Ni/SiO<sub>2</sub>-0/0 with the largest Ni nanoparticle size led to the decrease of surface area to the largest extent from 162.6 to 89.9 m<sup>2</sup>/g. In contrast, the Ni/SiO<sub>2</sub>-2/1 prepared by the combustion method with both C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> as the fuel and NH<sub>4</sub>NO<sub>3</sub> as the combustion improver gave the lowest decrease in the BET surface area from 165.9 to 118.3 m<sup>2</sup>/g due to its smallest Ni nanoparticle size.



**Fig. S1** XRD patterns of fresh Ni/SiO<sub>2</sub> catalysts prepared with the combustion method by using different ratios of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> to NH<sub>4</sub>NO<sub>3</sub>.

Fig. S1 shows the XRD patterns of as-prepared fresh Ni/SiO<sub>2</sub> catalysts. It is clear that all fresh Ni/SiO<sub>2</sub> catalysts exhibit the apparent diffraction peaks at 2θ values of 37.3°, 43.2°, 63.0°, 75.4°, and 79.4° assigned to the NiO (JCPDS 22-1189). In the case of Ni/SiO<sub>2</sub>-0/1, the presence of only NH<sub>4</sub>NO<sub>3</sub> as the combustion improver did not obviously affect the intensity of sharp peaks compared to the Ni/SiO<sub>2</sub>-0/0 which indicates the large NiO crystallite nanoparticles. In contrast, the addition of C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> fuel brought about a remarkable decrease in the nanoparticle size of NiO as reflected by much weaker and broader diffraction peaks over Ni/SiO<sub>2</sub>-2/0 and Ni/SiO<sub>2</sub>-2/1 catalysts.



**Fig. S2** TEM images of spent Ni/SiO<sub>2</sub>-0/0 catalyst ((a) and (b)) and Ni/SiO<sub>2</sub>-2/1 catalyst ((c) and (d)) after 50-hours of reaction.