Supplementary Information

Structural effect of Ni/TiO₂ on CO methanation: improved activity and enhanced stability

Jie Zhang, Xinyu Jia and Chang-jun Liu*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072,

China

* Corresponding author. Tel.: +86 22 27406490.

E-mail addresses: cjL@tju.edu.cn (C.-J. Liu).

Table S1 Textural properties of the TiO_2 support and the Ni/TiO_2 catalysts.

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{pore} (nm)
TiO_2	13.2	0.03	9.1
Ni/TiO_2-C	14.1	0.04	10.2
Ni/TiO_2-P	15.1	0.03	8.5

The Ni $2p_{3/2}$ spectra of the Ni/TiO$_2$ catalysts are shown in Fig. S1. The Ni species exists in both elemental state (Ni^0) centered at 851.8 eV and oxidized state (Ni^{2+}) centered at 855.0 eV, along with a satellite located at 860.4 eV.[S1, S2] The oxidic Ni^{2+} can be assigned to NiO from the air exposure. Compared to the standard binding energy (BE) of Ni^0 (852.9 eV), the BE of Ni^0 shifted negatively in catalysts, suggesting an electron transfer from TiO$_2$ to Ni.[S1] The Ni $2p_{3/2}$ spectra of Ni/TiO$_2$-P catalyst shows more intensive peaks, indicating a better dispersion on the surface.[S3] This is consistent with our conclusion that Ni/TiO$_2$-P catalyst possesses smaller Ni particle size and higher Ni dispersion.
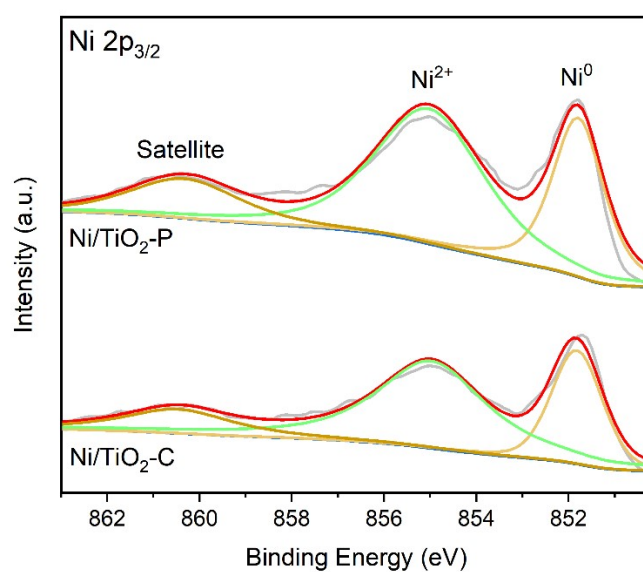

Fig. S1 Ni $2p_{3/2}$ XPS spectra of Ni/TiO$_2$-P and Ni/TiO$_2$-C.

The dispersion of Ni nanoparticles (D_{Ni}) was estimated by assuming Ni nanoparticle as a sphere, following the equations: [S4]

$$D_{Ni} = \frac{n_s}{n} = \frac{4\pi \cdot R^2 \cdot a_m}{\dfrac{\dfrac{4\pi}{3} \cdot R^3 \cdot \rho_0}{M} \cdot N_A}$$

$$R = \frac{d}{2}$$

Where n_s is the number of Ni atoms on the surface of the sphere; n is the total number of Ni atoms in the sphere; d is the mean diameter of Ni nanoparticles obtained from XRD; a_m is the number of surface Ni atoms per unit m², which is 1.54×10^{19} m⁻² calculated for fcc Ni using the proportions of low index planes fcc (111): (100): (110) = 1: 1: 1;[S4] ρ_0 is the density of Ni, 8.902×10^6 g·m⁻³; N_A is 6.02×10^{23} mol⁻¹; M is the atomic weight of Ni, 58.69 g·mol⁻¹.
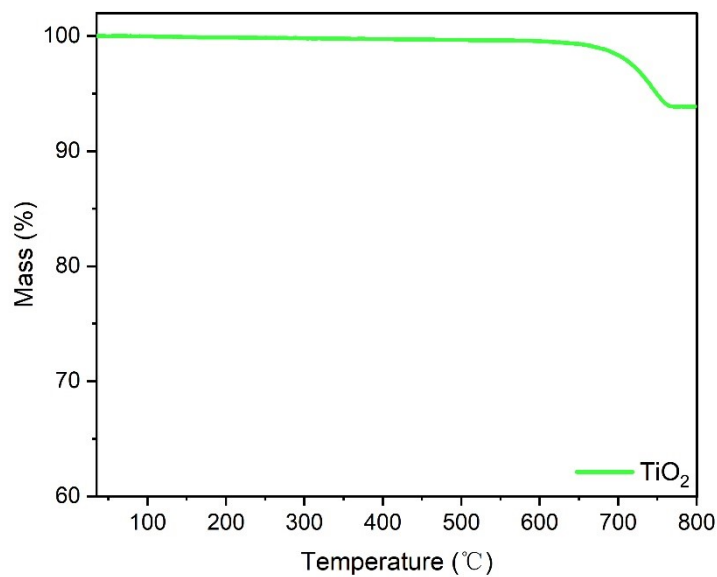
Fig. S2 TG curve of TiO$_2$.

References

[S1]   W. Lin, H. Cheng, L. He, Y. Yu and F. Zhao, *J. Catal.*, 2013, **303**, 110-116.

[S2]   J. Wang, K. Chang, Z. Sun, J. H. Lee, B. M. Tackett, C. Zhang, J. G. Chen and

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[S3]   N. Rui, X. Zhang, F. Zhang, Z. Liu, X. Cao, Z. Xie, R. Zou, S. D. Senanayake,

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[S4]   Y. Lin, Y. Zhu, X. Pan and X. Bao, *Catal. Sci. Technol.*, 2017, **7**, 2813-2818.