Supplementary Information

Structural effect of Ni/TiO$_2$ on CO methanation: improved activity and enhanced stability

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Table S1 Textural properties of the TiO$_2$ support and the Ni/TiO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{pore}}$ (cm$^3$/g)</th>
<th>$D_{\text{pore}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>13.2</td>
<td>0.03</td>
<td>9.1</td>
</tr>
<tr>
<td>Ni/TiO$_2$-C</td>
<td>14.1</td>
<td>0.04</td>
<td>10.2</td>
</tr>
<tr>
<td>Ni/TiO$_2$-P</td>
<td>15.1</td>
<td>0.03</td>
<td>8.5</td>
</tr>
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</table>
The Ni 2p<sub>3/2</sub> spectra of the Ni/TiO<sub>2</sub> catalysts are shown in Fig. S1. The Ni species exists in both elemental state (Ni<sup>0</sup>) centered at 851.8 eV and oxidized state (Ni<sup>2+</sup>) centered at 855.0 eV, along with a satellite located at 860.4 eV.<sup>S1, S2</sup> The oxidic Ni<sup>2+</sup> can be assigned to NiO from the air exposure. Compared to the standard binding energy (BE) of Ni<sup>0</sup> (852.9 eV), the BE of Ni<sup>0</sup> shifted negatively in catalysts, suggesting an electron transfer from TiO<sub>2</sub> to Ni.<sup>S1</sup> The Ni 2p<sub>3/2</sub> spectra of Ni/TiO<sub>2</sub>-P catalyst shows more intensive peaks, indicating a better dispersion on the surface.<sup>S3</sup> This is consistent with our conclusion that Ni/TiO<sub>2</sub>-P catalyst possesses smaller Ni particle size and higher Ni dispersion.

![Ni 2p<sub>3/2</sub> XPS spectra of Ni/TiO<sub>2</sub>-P and Ni/TiO<sub>2</sub>-C.](image_url)

**Fig. S1** Ni 2p<sub>3/2</sub> XPS spectra of Ni/TiO<sub>2</sub>-P and Ni/TiO<sub>2</sub>-C.
The dispersion of Ni nanoparticles ($D_{Ni}$) was estimated by assuming Ni nanoparticle as a sphere, following the equations: \(^{54}\)

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

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 m\(^2\), which is $1.54 \times 10^{19}$ m\(^2\) calculated for fcc Ni using the proportions of low index planes fcc (111): (100): (110) = 1: 1: 1; \(^{54}\) $\rho_0$ is the density of Ni, $8.902 \times 10^6$ g·m\(^{-3}\); $N_A$ is $6.02 \times 10^{23}$ mol\(^{-1}\); $M$ is the atomic weight of Ni, 58.69 g·mol\(^{-1}\).
**Fig. S2** TG curve of TiO$_2$.

**References**


