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


# Supporting information

# Modulating the methanation activity of Ni by the crystal phase of $TiO_2$

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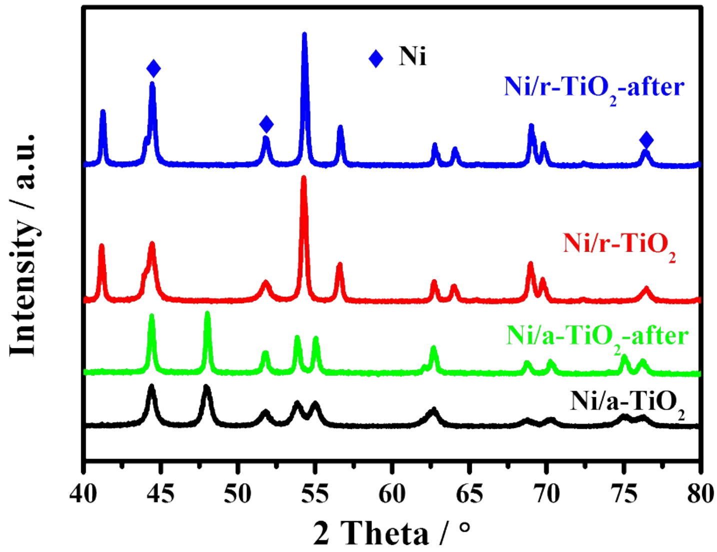



**Figure S1.** XRD patterns of Ni/a-$TiO_2$ and Ni/r-$TiO_2$ catalysts before and after reaction test in Figure 1c.

**Table S1.** Surface areas of $TiO_2$ and the corresponding Ni/$TiO_2$ catalysts.

| Sample | $S_{BET}$ ($m^2 \cdot g^{-1}$) |
|---|---|
| a-$TiO_2$ | 96.3 |
| r-$TiO_2$ | 51.7 |
| Ni/a-$TiO_2$ | 61.7 |
| Ni/r-$TiO_2$ | 28.4 |

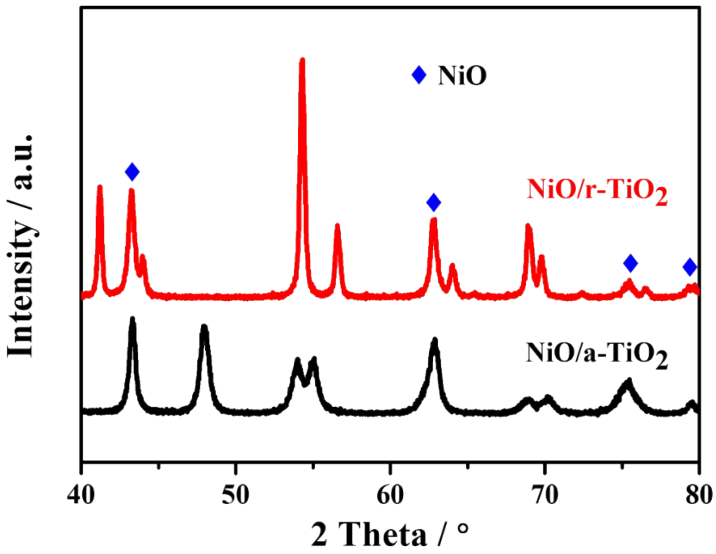



**Figure S2.** XRD patterns of the freshly prepared NiO/a-$TiO_2$ and NiO/r-$TiO_2$.

**Table S2.** The particle size of NiO in the fresh catalysts.

| Sample | [a]NiO (nm) |
|---|---|
| NiO/a-$TiO_2$ | 18.6 |
| NiO/r-$TiO_2$ | 18.1 |

[a] The NiO particle size in the fresh catalysts, estimated from XRD.

**Table S3.** The amount of $H_2$ adsorbed over Ni/a-$TiO_2$ and Ni/r-$TiO_2$ catalysts.

| Sample | [a]$H_2$ adsorption amount (mmol) |
|---|---|
| Ni/a-$TiO_2$ | 0.0089 |
| Ni/r-$TiO_2$ | 0.0161 |
| [a]: The catalyst mass is 401.0 mg. | |

The dispersity of Ni nanoparticles is estimated according to $H_2$-TPD ($D_{H_2-TPD}$) by the following equations[1]:

$$D_{H_2-TPD} = \frac{N_H}{N_{Ni}}$$

$$N_{Ni} = \frac{m \cdot c}{M}$$

Where $N_H$ is the mole number of H atoms measured from $H_2$-TPD; $N_{Ni}$ is the total mole number of Ni; $m$ is the mass of fresh catalysts, 401.0 mg and c is the Ni loading in the fresh catalysts; $M$ is the atomic weight of Ni, $58.69\ g{\cdot}mol^{-1}$.

The dispersity of Ni nanoparticles ($D_{XRD}$) was estimated by assuming Ni nanoparticle as a sphere, following the equations: [1]

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

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

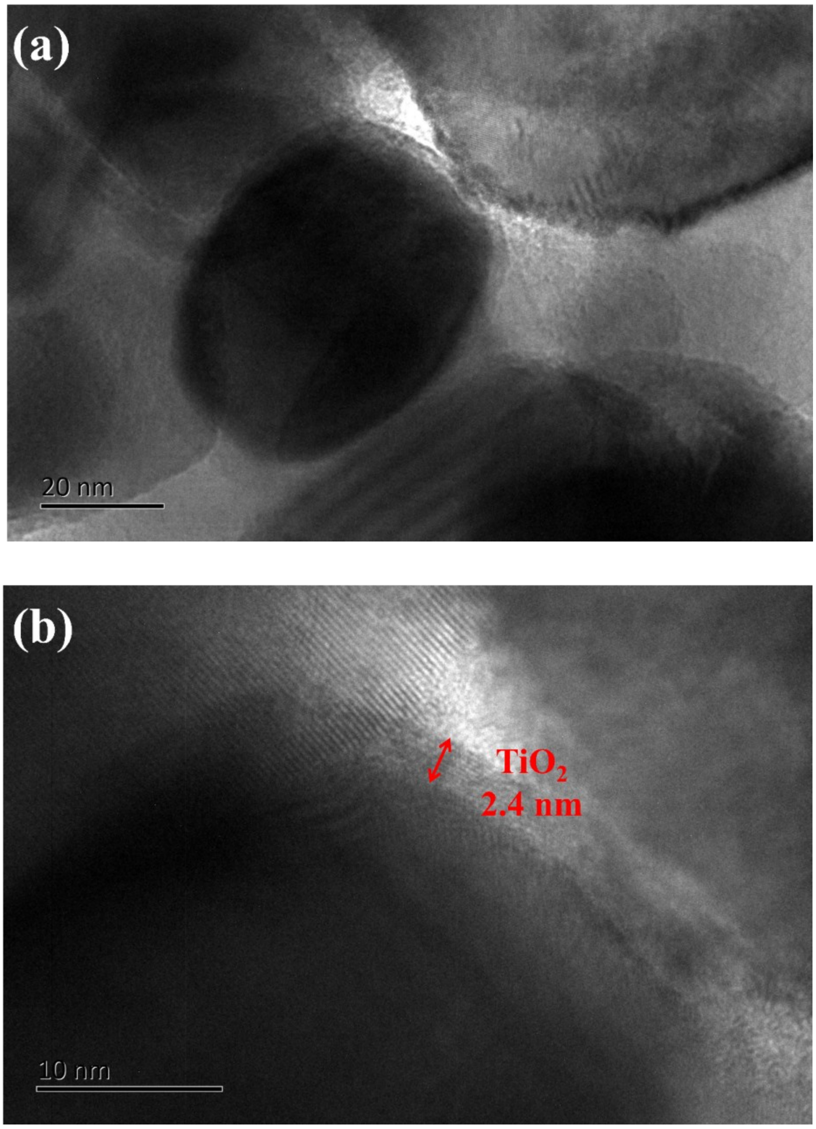
Where $n_s$ is the number of Ni atoms on the surface of the sphere; $n$ is the total number of Ni atoms in the sphere; $d$ is the mean diameter of Ni nanoparticles obtained from XRD; $a_m$ is the number of surface Ni atoms per unit $m^2$, which is $1.54 \times 10^{19}\ m^{-2}$ calculated for fcc Ni using the proportions of low index planes fcc(111):(100):(110)=1:1:1;[1] $\rho_0$ is the density of Ni, $8.902 \times 10^6\ g{\cdot}m^{-3}$; $N_A$ is Avogadro's constant, $6.02 \times 10^{23}\ mol^{-1}$; $M$ is the atomic weight of Ni, $58.69\ g{\cdot}mol^{-1}$.

TOF as defined as the CO converting per Ni site per time, is calculated by the following equations:

$$TOF = \frac{CO\ conversion\ rate\ (mol \cdot g_{cat}^{-1} \cdot h^{-1})}{Numbers\ of\ surface\ Ni\ atoms\ (mol \cdot g_{cat}^{-1})}$$

$$= \frac{\frac{WHSV \times S_{CO} \times CO\ conversion}{V_m}}{Numbers\ of\ surface\ Ni\ atoms\ (mol \cdot g_{cat}^{-1})}$$

The numbers of surface Ni atoms were determined by $H_2$-TPD. $S_{CO}$ is the volume fraction of CO in the feed gas, 23.75%; CO conversion is 20.0% for Ni/a-$TiO_2$ and 16.8% for Ni/r-$TiO_2$; $V_m$ is the standard gas volume, 22400 ml/mol; WHSV is the total space velocity, which is $6 \times 10^4\ \mathrm{ml \cdot g_{cat}^{-1} \cdot h^{-1}}$ for Ni/a-$TiO_2$ and $6 \times 10^6\ \mathrm{ml \cdot g_{cat}^{-1} \cdot h^{-1}}$ for Ni/r-$TiO_2$.


(a)
20 nm
(b)
TiO2
2.4 nm
10 nm

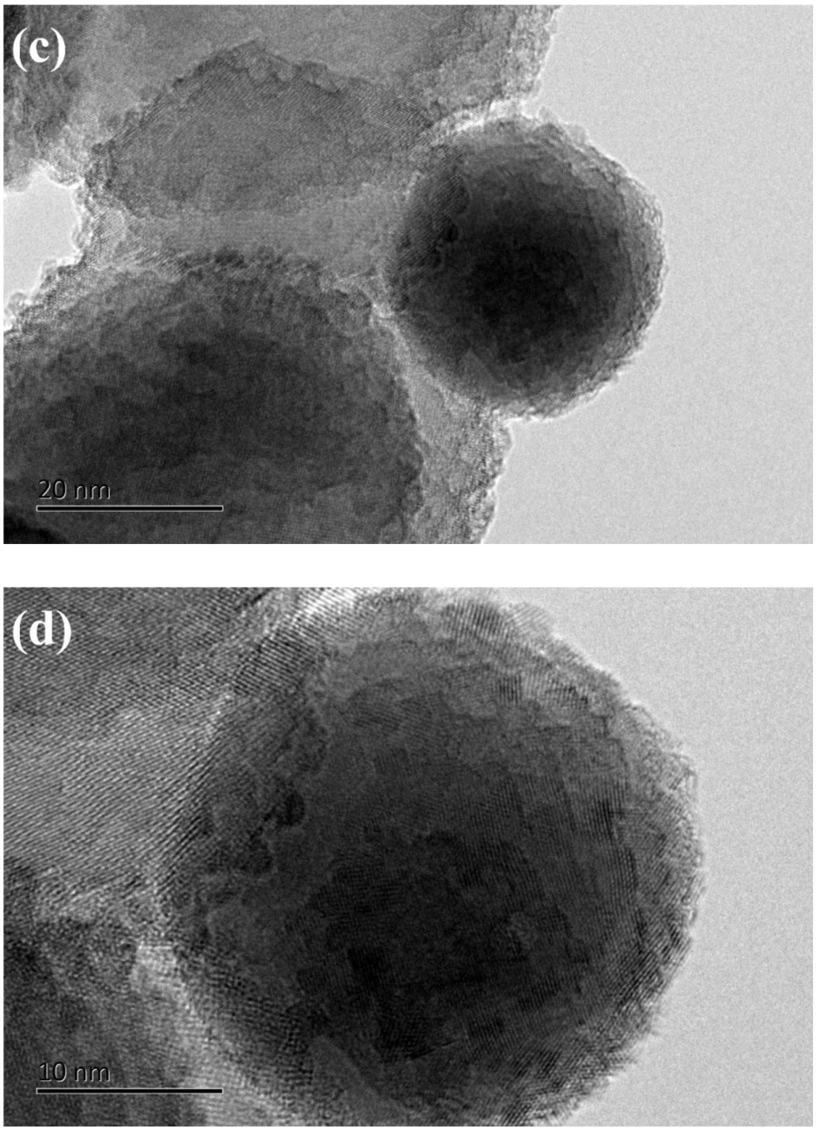



**Figure S3.** TEM images. (a) and (b) Ni/a-$TiO_2$; (c) and (d) Ni/r-$TiO_2$ after reaction at 500 °C.

## Reference

1. G. Bergeret and P. Gallezot, in *Handbook of Heterogeneous Catalysis*, eds. G. Ertl, H. Knözinger, F. Schüth and J. Weitkamp, Wiley-VCH, 2008, pp. 738-765.