TiO$_2$–x–Modified Ni Nanocatalyst with Tunable Metal–Support Interaction for Water–Gas Shift Reaction

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Supporting Information

ABSTRACT: The modulation of strong metal–support interaction (SMSI) plays a key role and remains a challenge in achieving the desired catalytic performance in many important chemical reactions. Herein, we report a TiO$_2$–x–modified Ni nanocatalyst with tunable Ni–TiO$_2$–x interaction via a two-step procedure: preparation of Ni/Ti mixed metal oxide (NiTi–MMO) from NiTi-layered double hydroxide (NiTi–LDH) precursor, followed by a further reduction treatment at different temperatures. A combination study (XRD, TEM, H$_2$–TPR, XPS, and in situ EXAFS) verifies that a high reduction temperature enhances the Ni–TiO$_2$–x interaction, which results in an increased coverage degree of Ni nanoparticles by TiO$_2$–x as well as electron density of interfacial Ni (Ni$^{3+}$). Moreover, the creation of a Ni$^{2+}$–O–Ti$^{3+}$ interface site (O$_x$ denotes oxygen vacancy) induced by strong Ni–TiO$_2$–x interaction serves as dual-active site to efficiently catalyze the water–gas shift reaction (WGSR). The optimized catalyst (Ni@TiO$_2$–x(450)) via tuning Ni–TiO$_2$–x interaction gives a TOF value of 3.8 s$^{-1}$, which is ~7 times larger than the conventional 15%Ni/TiO$_2$(450) catalyst. Such a high catalytic efficiency is attributed to the interface site (Ni$^{2+}$–O$_x$–Ti$^{3+}$) with medium strength of metal–support interaction, as revealed by in situ diffuse reflectance Fourier transform infrared spectroscopy (in situ DRIFTS), which promotes the synergetic catalysis between Ni$^{2+}$ and oxygen vacancy toward WGSR.

KEYWORDS: layered double hydroxide, strong metal–support interaction, water–gas shift reaction, interface structure, structure–activity correlation

1. INTRODUCTION

The water–gas shift reaction (WGSR) is widely used to produce hydrogen for many important industrial chemical processes and plays an important role in removing the presence of CO in feed streams for fuel cells.¹

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.2 \text{ kJ mol}^{-1} \]

WGSR can be practically operated at high temperature (350–450 °C) or low temperature (190–250 °C); the former process promoted by Fe–Cr catalysts gives satisfactory activity but suffers from the toxicity of Cr component.² Recently, extensive studies have been focused on the exploration of oxide supported Ni-based catalysts as a candidate for high-temperature WGSR.³–⁵ Despite their high catalytic activity, the supported Ni-based catalysts accelerate the undesired side reaction (methanation), which significantly deteriorates the H$_2$ selectivity and yield.²,⁵,⁶ Thus, a great of efforts have been devoted to developing more efficient Ni-based catalysts via tuning geometric and electronic structure to suppress methanation reaction, e.g., the formation of Ni-based alloy phase,²,⁴ the addition of alkali,⁵,⁶ or the creation of unique core–shell configuration.² Although much progress has been made, how to obtain highly efficient Ni-based catalysts via material design and synthesis exploration so as to inhibit methanation and enhance WGSR simultaneously still remains a challenging goal.

The interactions between metals and supports, especially the strong metal–support interaction (SMSI), are widely proposed as a key factor in determining catalytic performances toward important chemical reactions (including CO and hydrocarbon oxidation, the water–gas shift reaction and hydrogenation reactions).⁸–¹⁰ With respect to WGSR, both experimental and computational studies revealed that a cooperative interaction between metals and oxygen vacancies of reducible oxides supports would dominate the reactivity of catalysts.¹¹,¹² Typical phenomena induced by classical SMSI include an encapsulation...
of metal by support, or electron transfer from support to metal after high-temperature reduction of TiO2-supported VIII group metals, which significantly alter two key properties of catalysts, i.e., the geometric and electronic effect.11 The encapsulation of metal by reducible oxides support could preferentially block low-coordinated metal sites (e.g., defects) which activate methanation but enlarge the highly active interface sites for WGSR.14 However, it is rather difficult to control a suitable encapsulation of metal with an unique interfacial electronic structure by conventional preparation methods, since a modulation deflection would induce overencapsulation of active sites. Therefore, a detailed, systematic research for the modulation of metal–support interactions would be valuable to achieve an optimal trade-off of geometric/electronic effect and resulting largely improved catalytic performance.

In the present work, a NiTi-layered double hydroxide precursor (NiTi−LDH) was synthesized by a facile urea decomposition method developed by our group15 with the advantage of highly distributed Ni2+ and Ti4+ at an atomic-ordered level in the hydroxide layers. By means of annealing and subsequently reducing at different temperatures, the TiO2−x phase modified Ni nanoparticles (denoted as Ni@TiO2−x) were obtained, which showed finely tunable Ni−TiO2−x interaction. A combination study including XRD, HRTEM, H2-TPR, in situ EXAFS, and XPS confirms that Ni−TiO2−x interaction strengthens gradually as the reduction temperature rises from 400 to 600 °C, accompanied by the increased coverage of Ni nanoparticle by TiO2−x and enhanced electron density of interfacial Ni (NiOx). Notably, the strong electronic metal–support interactions (EMSI) between TiO2−x and Ni results in the formation of surface site O−−Ti3+ (O2− denotes oxygen vacancy) and concomitant interface site Ni−O−−Ti3+, which act as dual active sites as required for WGSR. Moreover, in situ DRIFTS results demonstrate that the interface site (NiOx−O2−−Ti3+) with medium strength of metal–support interaction promotes a desirable modulation of coverage degree and electron density of Ni, accounting for the optimal catalytic performance toward WGSR. By virtue of a tunable Ni−TiO2−x interaction based on an LDH precursor approach, a new strategy in tailoring active sites of supported metal catalysts with desired selectivity has been developed.

2. RESULTS AND DISCUSSION

2.1. Structural and Morphological Characterizations.

The NiTi−LDH precursor with Ni/Ti ratio of ~3 was prepared by a urea decomposition method reported by our group.15 The XRD pattern of NiTi−LDH precursor (Figure 1a) shows a series of diffraction peaks at 12.0°, 24.5°, 33.3°, 37.8°, and 59.7°, which belong to a characteristic feature of NiTi−LDH phase.15 SEM and TEM images (Figure S1) give a mean lateral size of 180 ± 30 nm and a thickness of 4−10 nm for the NiTi−LDH nanoplatelets. After calcination at 500 °C, the NiTi−LDH precursor transforms to a mixed metal oxide phase (NiTi−MMO), as shown in Figure 1b. The diffraction peaks at 37.2°, 43.5°, 63.0°, and 75.5° are indexed to a cubic NiO phase (JCPDS 47-1049); while the weak broad reflection at 25.3° corresponds to anatase TiO2 phase (JCPDS 21-1272). Finally, the NiTi−MMO was reduced in a H2 atmosphere at 400, 450, 500, and 600 °C, respectively, so as to obtain the TiO2−x phase modified Ni nanoparticles (denoted as Ni@TiO2−x). For the four reduction samples, XRD shows the disappearance of cubic NiO phase, accompanied by the observation of three reflections at 44.5°, 51.8°, and 76.4° attributed to a fcc Ni phase (Figure 1c−f).16 In addition to the metallic Ni, diffraction peaks of anatase are also observed (Figure 1c−f). Notably, as the reduction temperature rises from 400 to 600 °C, Ni@TiO2−x(400), Ni@TiO2−x(450) and Ni@TiO2−x(500) give a very close particle size of Ni (~13.0 nm) calculated by the Scherrer equation (Table 1); only a small growth of Ni particle (~14.5 nm) is observed for Ni@TiO2−x(600). This suggests a resistance of Ni against sintering at high temperature, possibly due to the strong interaction between Ni and TiO2−x. For comparison, a reference sample, 15%Ni/TiO2(450) (16.9% of Ni loading) was prepared by the conventional impregnation method (Figure S2A), whose XRD pattern shows both fcc Ni and anatase phase.

TEM measurements were performed to further investigate the morphology and structural features of these four Ni@TiO2−x samples (Figure 2). It is observed that Ni nanoparticles (~55% of Ni loading) are well-dispersed within the TiO2−x matrix with a high density (Figure 2A1−D1). HRTEM images (Figure 2A2−D2) show the TiO2−x phase (particle size: 5−7 nm) anchoring on the surface of single Ni nanoparticle: the lattice fringe of 0.203 nm corresponds to the {111} plane of cubic Ni phase; while that of 0.350 nm is indexed to the {101} plane of rhomboic TiO2 phase. The selected electron diffraction and TEM images of various Ni@TiO2−x catalysts are shown in Figure S3, which further reveals that TiO2−x, coating partially overlayers on the surface of Ni nanoparticles. HAADF−STEM and STEM−EDS measurements were carried out for the Ni@TiO2−x(450) sample to further explore the surface encapsulation structure (Figures S4 and S5). The STEM−EDS line scan spectrum of one individual Ni nanoparticle shows a dosed distribution of Ti and O on the surface of Ni with a molar ratio of ~1:2. Elemental mapping analysis based on HAADF−STEM−EDS displays a similar Gaussian distribution, indicating a modification of TiO2 overlayer on the surface of Ni nanoparticle. Moreover, it is found that the Ni dispersion calculated from CO chemiadsorption is remarkably lower than that estimated from the Ni particle size (Table 1), further demonstrating the decoration of TiO2−x on the Ni surface. The coverage degree of Ni nanoparticle is determined by CO chemiadsorption over these four Ni@TiO2−x samples (Table 1), which shows an increase from 66% to 92% with the enhancement of reduction temperature from 400 to 600 °C. According to previous reports, the encapsulation of metal by support oxide layer is a typical characteristic of SMSI results.
phenomenon. Thus, the partial coverage of Ni nano-particles by TiO$_2$ suggests the formation of SMSI in these four Ni@TiO$_2$ samples. In addition, the particle size of Ni (Figure 2A1−D1) increases slightly from $\sim$11.7 to $\sim$13.8 nm as the reduction temperature rises from 400 to 600 °C, indicating this SMSI between Ni and TiO$_2$ effectively suppresses the growth of Ni nanoparticles. This is in agreement with the XRD results. In the case of conventional 15%Ni/TiO$_2$(450) sample, the encapsulation of Ni (particle size: $\sim$8.2 nm) by TiO$_2$ is also observed with a 87% of coverage degree (Figure S2B,C and Table 1).

To further investigate the sample reducibility and the interaction between Ni species and TiO$_2$ phase, H$_2$-TPR experiments were performed (Figure 3). The TPR profile of NiO/TiO$_2$ (the precursor of conventional Ni/TiO$_2$ sample) (Figure 3a) shows two hydrogen consumption peaks: the one

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$g$^{-1}$)</th>
<th>Ni species content (wt %)</th>
<th>Ni crystallite size (nm)</th>
<th>mean Ni particle size (nm)</th>
<th>metal Ni dispersion (%)</th>
<th>surface metallic Ni conc (mmol g$^{-1}$)</th>
<th>metal Ni dispersion (%)</th>
<th>coverage degree of Ni (%)</th>
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<tr>
<td>Ni@TiO$_2$−x (400)</td>
<td>133.6</td>
<td>49.7</td>
<td>12.6</td>
<td>11.8</td>
<td>1.48</td>
<td>0.125</td>
<td>4.3</td>
<td>66</td>
</tr>
<tr>
<td>Ni@TiO$_2$−x (450)</td>
<td>115.9</td>
<td>54.2</td>
<td>13.0</td>
<td>12.5</td>
<td>1.02</td>
<td>0.094</td>
<td>4.0</td>
<td>75</td>
</tr>
<tr>
<td>Ni@TiO$_2$−x (500)</td>
<td>110.1</td>
<td>56.4</td>
<td>13.3</td>
<td>11.7</td>
<td>0.77</td>
<td>0.074</td>
<td>4.3</td>
<td>82</td>
</tr>
<tr>
<td>Ni@TiO$_2$−x (600)</td>
<td>111.7</td>
<td>55.6</td>
<td>14.5</td>
<td>13.8</td>
<td>0.29</td>
<td>0.027</td>
<td>3.5</td>
<td>92</td>
</tr>
<tr>
<td>15%Ni/TiO$_2$ (450)</td>
<td>53.1</td>
<td>16.9</td>
<td>8.8</td>
<td>8.2</td>
<td>0.83</td>
<td>0.024</td>
<td>6.2</td>
<td>87</td>
</tr>
</tbody>
</table>

$^{a}$Ni species content was determined by inductively coupled plasma−atomic emission spectroscopy (ICP−AES). $^{b}$Crystallite size was determined by XRD with the Scherrer equation. $^{c}$Mean Ni particle size was determined by TEM images. $^{d}$Metal Ni dispersion and surface metallic Ni concentration were calculated based on the results of CO pulse chemiadsorption at 200 K (described in the Experimental Section). $^{e}$Ni dispersion was estimated on the basis of Ni particle size measured by TEM. $^{f}$Coverage degree of Ni nanoparticle was calculated based on the results of CO pulse chemiadsorption and Ni particle size measured by TEM (described in the Experimental Section).

Figure 2. (A$_1$−D$_1$) TEM images of the four Ni@TiO$_2$−x samples (inset: the histogram of size distribution of Ni nanoparticles). (A$_2$−D$_2$) HRTEM images of a single Ni nanoparticle selected from A$_1$−D$_1$, respectively.

Figure 3. H$_2$-TPR profiles of (a) NiO/TiO$_2$ (b) NiTi−MMO.
at ~290 °C is assigned to the reduction of bulk NiO which interacts weakly with TiO₂, and the main peak centered at 375 °C is attributed to the reduction of highly dispersed NiO phase in strong interaction with TiO₂. In the case of NiTi–MMO sample obtained from calcination of NiTi–LDH, the reduction peak of bulk NiO (~290 °C) weakens extremely; while the peak of well-dispersed NiO species (~405 °C) becomes dominant and shifts toward higher temperature (Figure 3b). This indicates a significantly enhanced interaction between NiO and TiO₂ species in the NiTi–MMO sample. In the NiTi–LDH precursor, both Ni and Ti are dispersed at an atomic level, which induces the decoration of NiO phase by TiO₂ phase during the calcination process. Moreover, the amount of H₂ consumption for TiO₂ species (~2.18 Å). This could lead to a strong interaction between NiO and TiO₂ and thus increased reduction temperature of NiTi–MMO. Notably, in the high temperature range, an additional shoulder peak in 500–630 °C is observed in Figure 3b, which is assigned to the reduction of TiO₂ species. Moreover, the amount of H₂ consumption for NiTi–MMO and NiO–TiO₂ is calculated to be 11.2 mmol g⁻¹ and 3.15 mmol g⁻¹, respectively. This indicates that the NiO phase was reduced to metal Ni accompanied by a partial reduction of Ti⁴⁺ to Ti³⁺ for NiTi–MMO, resulting in the formation of O−–Ti³⁺ site (O− denotes oxygen vacancy). A similar phenomenon was also reported in the TiO₂-modified group VIII metal catalysts with SMSI.

In situ EXAFS spectroscopy was performed to investigate the detailed structure (Figure 4), and the normalized Ni K-edge XANES spectra for these four Ni@TiO₂−x samples are shown in Figure 4A. The Ni@TiO₂−x(400) displays a slightly stronger white line (at ~8352 eV) relative to Ni foil, while the XANES spectra of the other three Ni@TiO₂−x samples are rather close to the Ni foil. This indicates the coexistence of metallic Ni and NiO phase in Ni@TiO₂−x(400) but the predominant metallic state of Ni in other three Ni@TiO₂−x samples. Notably, the absorption edge displays a slight shift toward low photon energy relative to the Ni foil, which indicates the enrichment of electron on the Ni atom (denoted as Ni°) in these four Ni@TiO₂−x samples (Figure 4A and inset). This can be attributed to the electron excursion from TiO₂−x to the interfacial Ni atom, caused by strong Ni–TiO₂−x interaction, which is in agreement with previous reports about SMSI effect on TiO₂-supported group VIII metals. Moreover, from Ni@TiO₂−x(400) to Ni@TiO₂−x(600), the absorption edge shifts to low photon energy gradually, suggesting an enhanced electronic metal–support interaction (EMSI) and concomitantly increased electron density of interfacial Ni atom (Ni°).

In addition, as shown in the Fourier-transform EXAFS spectra at Ni K-edge (Figure 4B), the metallic Ni–Ni distance for Ni@TiO₂−x samples decreases gradually with the increment of reduction temperature, indicating an enhancement of bonding interaction between metal Ni and TiO₂−x support. Ni@TiO₂−x(600) show a smallest metallic Ni–Ni distance (~2.12 Å) compared with Ni foil (~2.18 Å).

The normalized Ti K-edge XANES spectra of Ni@TiO₂−x and anatase reference (Figure 4C) can be divided to two regions: pre-edge feature (photon energy< 4984 eV) and post-edge feature (photon energy> 4984 eV), respectively. The post-edge region of anatase reference shows a white line peak at ~4987 eV (labeled as C) and three resolveable peaks (denoted as B₁, B₂, and B₃) in the range from 4993 to 5006 eV. In comparison with anatase reference, the white line peak of four Ni@TiO₂−x samples decreases gradually with the increment of reduction temperature, indicating an enhancement of bonding interaction between metal Ni and TiO₂−x support. Ni@TiO₂−x(600) show a smallest metallic Ni–Ni distance (~2.12 Å) compared with Ni foil (~2.18 Å).

The normalized Ti K-edge XANES spectra of Ni@TiO₂−x and anatase reference (Figure 4C) give information about the local Ti–O coordination environment. For symmetric octahedral anatase reference (six-coordinated Ti–O structure), three prepeaks in the range from 4967 to 4976 eV are observed, labeled as A₁, A₂, and A₃ corresponding to transitions of the core electron to Ti 3d⁴p⁴s-hybridized states. Furthermore, the pre-edge features of Ti XANES spectra (Figure 4CD) give information about the local Ti–O coordination environment. According to both the pre-edge A₁ energy (~4970.5 eV) and its predominant feature, it is concluded that these Ni@TiO₂−x samples have a large fraction of five-coordinated Ti atoms, which is associated with the presence of oxygen vacancies (i.e., O−–Ti²⁺ site). The formation of electron-enriched Ni site (Ni°) in this work strongly suggested the presence of strong electronic interaction between Ni atoms and O−–Ti²⁺ sites at Ni–TiO₂ interface, which leads to the electron transfer from Ti³⁺ to Ni atom and the resulting Ni°–O−–Ti³⁺ interface site. A similar interface structure was also reported in TiO₂-supported noble metal catalysts with SMSI. For the sample of 15%Ni/TiO₂(450), the normalized Ni K-edge show the similar electron transfer from TiO₂−x to interfacial Ni atom (Figure S6A and inset), indicating that there are also significantly electron transfer in the conventional Ni/TiO₂.
catalyst. But Ti K-edge XANES spectra are very similar to that of anatase reference (Figure S6B), which indicates the presence of six-coordinated Ti$^{4+}$−O structure.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the influence of Ni−TiO$_2$$_{−x}$ interaction on the surface electronic structure (Figure 5). Figure 5A shows the Ni 2p spectra with a deconvolution by Gaussian peak fitting method for these four Ni@TiO$_2$$_{−x}$ samples. The deconvoluted peaks at ~852.4, ~853.9, ~855.2, and ~860.5 eV are assigned to the Ni$^{0}$ state, Ni$^{2+}$ state, and their two satellite peaks, respectively. Notably, in lower binding energy region relative to Ni$^{0}$ state, one additional peak at ~851.0 eV is observed, which is assigned to the electron-enriched Ni atom (Ni$^{2+}$). This indicates the electron transfer from TiO$_2$$_{−x}$ to metallic Ni, in accordance with the results of Ni K-edge XANES spectra. Furthermore, from Ni@TiO$_2$$_{−x}$(400) to Ni@TiO$_2$$_{−x}$(600), the ratio of Ni$^{2+}$ peak (Table S1) increases gradually along with a shift to low binding energy. This confirms that a higher reduction temperature leads to a stronger electronic interaction between metal Ni and TiO$_2$$_{−x}$ and accordingly a larger electron density of interfacial Ni atom (Ni$^{2+}$). Figure 5B shows Ti 2p spectra of these Ni@TiO$_2$$_{−x}$ samples. A broad Ti 2p$_{3/2}$ peak is observed between 455 and 460 eV, which can be deconvoluted to two peaks at ~458.5 and ~457.5 eV, respectively, corresponding to Ti$^{4+}$ and Ti$^{3+}$ state. It should be noted that ratio of Ti$^{3+}$ peak (Table S1) increases gradually from Ni@TiO$_2$$_{−x}$(400) to Ni@TiO$_2$$_{−x}$(600), suggesting the enhancement of oxygen vacancies (i.e., O$^−$−Ti$^{3+}$ sites). Moreover, O 1s spectra can be deconvoluted to four peaks at ~529, ~530.2, ~531.3, and ~532.3 eV (Figure S7), which are assigned to surface adsorption oxygen species at the oxygen vacancy, lattice oxygen, surface hydroxyl group, and the adsorption of H$_2$O molecule, respectively. The dependence of oxygen vacancy concentration on temperature shows a similar tendency observed in the Ti 2p$_{3/2}$ spectra. As mentioned above, there is a positive relationship between the amount of Ni$^{2+}$ and Ti$^{3+}$ from Ni@TiO$_2$$_{−x}$(400) to Ni@TiO$_2$$_{−x}$(600), which originates from enhanced interaction between Ni atom and O$^−$−Ti$^{3+}$ site with increased Ni$^{2+}$−O$^−$−Ti$^{3+}$ interface site. This is in accordance with the results of in situ EXAFS spectroscopy. In contrast, as shown in Figure S8 and Table S1, the sample of Ni/TiO$_2$ shows a relatively low ratio of Ni$^{2+}$ and Ti$^{3+}$.

2.2. Catalytic Performances and Active-Site Determination toward WGSR. The catalytic performances of these four Ni@TiO$_2$$_{−x}$ samples toward the water–gas shift reaction (WGSR) were studied. Figure 6A shows CO conversion as a function of reaction temperature at a weight hourly space velocity (WHSV) of 66000 mL g$_{cat}^{-1}$ h$^{-1}$. The 15%Ni/TiO$_2$(450) sample shows a poor activity, whose maximal level of CO conversion is only 36.9% at 450 °C. Moreover, the TiO$_2$−Ni catalyst prepared by the traditional sol-gel hydrolysis method shows a poor activity with the maximal CO conversion of 23.2% at 450 °C and a reaction rate of 7.07 μmol CO g$_{cat}^{-1}$ s$^{-1}$ at 350 °C (Figure S9). In contrast, the four Ni@TiO$_2$$_{−x}$ samples give CO conversions of up to 97% at 350 °C, indicating a rather high catalytic activity at a lower temperature. It is well-known that for nickel-based catalysts, methanation as the side reaction occurs easily, leading to the consumption of hydrogen and the formation of byproduct CH$_4$. Moreover, the modulation of metal–support interactions can also significantly influence the selectivity of catalytic reaction. Senanayake et al. reported a new type of metal–support interaction between small Ni particles and ceria, in which CO methanation can be inhibited due to electronic perturbations induced by ceria on the surface of Ni. In situ and theoretical studies showed that the support effect...
substantially enhanced the O–H bond cleavage owing to the electronic metal–support interactions (EMSI). Furthermore, Matsubu et al. reported a facile method to control the strong metal–support interactions over Rh/TiO₂ catalysts through modulating the pretreatment atmosphere, which significantly enhanced the selectivity of CO₂ hydrogenation to CO. Figure 6B shows the selectivity toward CO₂ at the maximum CO conversion over the four Ni@TiO₂−ₓ samples at 350 °C and 15%Ni/TiO₂ at 450 °C, respectively. The 15%Ni/TiO₂(450) sample displays a CO₂ selectivity of 98% but a poor activity (CO conversion of 36.9%). However, Ni@TiO₂−ₓ samples exhibit a comparable CO₂ selectivity but still maintain a very high activity. As discussed above, the results of XANES spectra (Ni–K edge and Ti–K edge) and XPS spectra show a moderate strength of electronic metal–support interactions (EMSI) for the sample of Ni@TiO₂−ₓ(450); simultaneously, it exhibits the optimal activity (CO conversion: 99.3%) and CO₂ selectivity (95%). This indicates that EMSI significantly influences the catalytic performance of Ni@TiO₂−ₓ catalysts. In addition, the long-term catalytic stability of Ni@TiO₂−ₓ(450) is further investigated (Figure 6C), which gives a catalytically stable performance with a constant percentages of CO conversion to CO₂ (95%) throughout 100 h. TG-MS measurements over the fresh and used Ni@TiO₂−ₓ(450) catalyst were performed (Figure S10A), and the results showed some coking on the surface of used catalyst. No obvious change in its morphology or structure was observed after 100 h on stream (Figure S10B–D). Furthermore, the used catalyst can be regenerated to its original activity via a reduction treatment in a H₂/N₂ (2:3, v/v) at 450 °C for 4 h.

To establish a structure–activity correlation for these Ni@TiO₂−ₓ catalysts, the reaction rate and turnover frequency (TOF) values were calculated at a low level of CO conversion (<10%). From Ni@TiO₂−ₓ(400) to Ni@TiO₂−ₓ(600) with

Table 2. Catalytic Performances of Various Samples for WGSR

<table>
<thead>
<tr>
<th>catalyst</th>
<th>surface Ni concentration (mmol g⁻¹)</th>
<th>Ti³⁺/(Ti³⁺ + Ti⁴⁺) ratio</th>
<th>coverage ratio of Ni (%)</th>
<th>CO conversion (X_CO) (%)</th>
<th>CO₂ selectivity (S_CO₂) (%)</th>
<th>TOF (s⁻¹)</th>
<th>reaction rate (μmol CO g⁻¹cat s⁻¹)</th>
<th>Activation Energy (E_a) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni@TiO₂−ₓ(400)</td>
<td>0.125</td>
<td>54.4</td>
<td>66</td>
<td>99.6</td>
<td>90.5</td>
<td>2.3</td>
<td>291.1</td>
<td>62 ± 2</td>
</tr>
<tr>
<td>Ni@TiO₂−ₓ(450)</td>
<td>0.094</td>
<td>65.7</td>
<td>75</td>
<td>99.3</td>
<td>95.1</td>
<td>3.8</td>
<td>356.8</td>
<td>59 ± 1</td>
</tr>
<tr>
<td>Ni@TiO₂−ₓ(500)</td>
<td>0.074</td>
<td>70.5</td>
<td>82</td>
<td>98.8</td>
<td>93.6</td>
<td>1.8</td>
<td>133.2</td>
<td>63 ± 3</td>
</tr>
<tr>
<td>Ni@TiO₂−ₓ(600)</td>
<td>0.027</td>
<td>84.2</td>
<td>92</td>
<td>97.3</td>
<td>92.6</td>
<td>1.9</td>
<td>50.8</td>
<td>62 ± 2</td>
</tr>
<tr>
<td>15%Ni/TiO₂(450)</td>
<td>0.024</td>
<td>15.7</td>
<td>87</td>
<td>36.9</td>
<td>98.0</td>
<td>0.5</td>
<td>12.8</td>
<td>73 ± 4</td>
</tr>
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</table>

aTi³⁺/(Ti³⁺ + Ti⁴⁺) ratio was calculated from Ti 2p XPS spectra. bX_CO represents the CO conversion of the four Ni@TiO₂−ₓ samples at 350 °C and Ni/TiO₂ at 450 °C, respectively. cS_CO₂ is the CO₂ selectivity of the four Ni@TiO₂−ₓ samples at 350 °C and Ni/TiO₂ at 450 °C, respectively.
enhanced coverage degree of Ni nanoparticle (Table 2), the TOF value increases first and then decreases, and the maximum TOF (3.8 s⁻¹) presents in the sample of Ni@TiO₂₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋xFigure 8. (A) In situ DRIFTS spectra of (a) Ni@TiO₂₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋xFigure 8 and Figures S12 and S13). It has been reported that at a relatively low temperature (100°−170 K) the CO molecule can adsorb on the surface of TiO₂ support with a stretching frequency above 2100 cm⁻¹.13 In this work, however, the whole IR band is below 2100 cm⁻¹, and the dominant band (1800−2000 cm⁻¹) is due to bridge CO adsorption on the surface of metallic Ni at 25 °C. For the 15% Ni/TiO₂(450) sample, one single IR band centered at ~2055 cm⁻¹ is observed, corresponding to the linearly adsorbed CO on the surface of metallic Ni (Figure S12). It should be noted that this band disappears after flushing with He for 5 min, indicating a weak adsorption of CO on the Ni surface (Figure S12) associated with its poor catalytic activity. In the case of Ni@TiO₂₋ₓ₋ₓ₋xFigure 21 of medium chemiadsorption strength site (E_a) are calculated from the Arrhenius plots (Figure 7B and Table 2). The Ni@TiO₂₋ₓ₋ₓ₋ₓ₋ₓ₋xFigure 21 catalyst shows the lowest E_a (59 kJ mol⁻¹), in accordance with its optimal activity. The reference sample 15%Ni/TiO₂(450), with the lowest reaction rate and TOF value, gives the largest E_a (73 kJ mol⁻¹). This indicates that the active site of Ni@TiO₂₋ₓ₋ₓ₋ₓ₋xFigure 21 catalysts may be different from the conventional Ni/TiO₂ one. Correspondingly, it is observed that the reaction rate as a function of Ni concentration (Figure 7C) or Ti³⁺/(Ti³⁺ + Ti⁴⁺) ratio (Figure 7D) exhibits a volcano shape, with the maximum reaction rate (356.8 µmol CO g⁻¹ s⁻¹) obtained for Ni@TiO₂₋ₓ₋ₓ₋ₓ₋xFigure 21 in Ni/TiO₂ catalyst. In addition, for the conventional Ni/TiO₂ catalyst, the reaction rate shows a nonlinear relationship with the surface metallic Ni concentration (Figure S11A) or Ti³⁺/(Ti³⁺ + Ti⁴⁺) ratio (Figure S11B). As the surface Ni concentration increases, the reaction rate over Ni/TiO₂ catalyst enhances gradually. In contrast, the reaction rate declines progressively along with the increase of Ti³⁺/(Ti³⁺ + Ti⁴⁺) ratio. This indicates that only Ni or oxygen defect cannot serve as the exclusive active site. It has been reported that in catalytic system of WGS, the metal site activates CO whereas oxygen vacancy adsors and activates H₂O.11,12 This dual-active-site catalysis is necessary for WGSR. In this work, Ni−TiO₂ interface structure (Ni²⁺−O−Ti³⁺ site) may dominate the reactivity: Ni²⁺ serves as active site for CO while O facilitates the activation of H₂O. In addition, Ni@TiO₂₋ₓ₋ₓ₋ₓ₋xFigure 21 in this work exhibits the highest the reaction rate (356.8 µmol CO g⁻¹ s⁻¹) and TOF value (3.8 s⁻¹), which is superior to supported Ni-based catalysts and even some noble-metal catalysts reported previously (Table S2).

To identify the intrinsic active site, in situ DRIFTS spectra were performed over these Ni@TiO₂₋ₓ₋ₓ₋ₓ₋xFigure 21 samples and 15% Ni/TiO₂(450) after CO chemiadsorption at 25 °C (Figure 8 and Figures S12 and S13). It has been reported that at a relatively low temperature (100°−170 K) the CO molecule can adsorb on the surface of TiO₂ support with a stretching frequency above 2100 cm⁻¹.13 In this work, however, the whole IR band is below 2100 cm⁻¹, and the dominant band (1800−2000 cm⁻¹) is due to bridge CO adsorption on the surface of metallic Ni at 25 °C. For the 15% Ni/TiO₂(450) sample, one single IR band centered at ~2055 cm⁻¹ is observed, corresponding to the linearly adsorbed CO on the surface of metallic Ni (Figure S12). It should be noted that this band disappears after flushing with He for 3 min, indicating a weak adsorption of CO on the Ni surface (Figure S12) associated with its poor catalytic activity. In the case of Ni@TiO₂₋ₓ₋ₓ₋xFigure 21 catalysts, the DRIFTS spectra of stable CO adsorption state are obtained after flushing with He for 30 min (Figure 8A and Figure S13A−D). The IR band above 2000 cm⁻¹ can deconvoluted to two peaks at ~2065 and ~2035 cm⁻¹, respectively, which are assigned to linearly adsorbed CO on low-coordinated Ni atom and on Ni atom with increased electron density (Ni²⁺). In general, the adsorption of CO on Ni prefers a linear state on top sites at room temperature, giving IR bands above 2000 cm⁻¹. Meanwhile, the encapsulation of Ni by metal oxide favors CO linear adsorption but restrains bridge adsorption, as shown in Ni/TiO₂ in this work.

Previous studies have shown that the strength of CO adsorption (CO stretching frequency) is closely associated with the electronic density of interfacial metal, especially due to electronic effect of reducible support.40,41 In this work, the electron-enriched Ni²⁺ increases the back-donation of Ni d-electrons into the 2π* antibonding orbital of CO, which enhances the strength of CO chemiadsorption on Ni²⁺−O−Ti³⁺ interface site. For instance, for these four Ni@TiO₂₋ₓ₋xFigure 21 samples, in addition to linear CO adsorption, a dominant broad IR band located in the range 1800−2000 cm⁻¹ is observed, which is attributed to bridge CO adsorption (i.e., 2-fold CO species bound to Ni) with a weaker C=O bond but a stronger C–O bond than that of the linearly adsorbed CO (Figure S12). This is related to the existence of unique Ni²⁺−O−Ti³⁺ interface structure: the Ni²⁺ site significantly increases the back-donation of Ni d-electrons into the 2π* antibonding orbital of CO, accounting for the bridge
adsorption and the correspondingly high ratio of bridge adsorption to linear adsorption (denoted as $X_{B−L}$, Table S3) for these four Ni@TiO$_2$−x samples. Moreover, the shortened Ni−Ni bond distance caused by SMSI (as confirmed by EXAFS) promotes a change in CO adsorption from linear to bridge state. Since the presence of a large proportion of bridge sites promotes the activation of CO but inhibits the C−O bond rupture (the rate-determining step for methanation),$^{[56]}$ a high catalytic activity but a low CH$_4$ selectivity in this work is observed for Ni@TiO$_2$−x samples. In contrast, for Ni/TiO$_2$, the relatively high coverage degree of Ni is likely to block low-coordinated Ni sites (associated with the methanation); however, the absence of Ni$^{2+}$−O−Ti$^{3+}$ interface site results in a rather low catalytic activity.

In situ DRIFTS spectra were further performed to identify the interfacial structure (Ni$^{2+}$−O−Ti$^{3+}$ interface site) with different strength of metal−support interaction, in which CO was used as a probe molecule. According to the lower frequency of bridge modes representing a stronger chemiadsorption of CO on Ni sites,$^{[6]}$ IR spectrum below 2000 cm$^{-1}$ can be further deconvoluted to three peaks at $\sim$1945, $\sim$1890, and $\sim$1835 cm$^{-1}$ (Figure 8A), which are attributed to the weak ($B_w$), medium ($B_m$), and strong ($B_s$) bridge CO chemiadsorption, respectively. Based on the deconvolution results, the ratios of each bridge site to total bridge sites (denoted $X_{B_w}$, $X_{B_m}$, and $X_{B_s}$ respectively) were calculated. Subsequently, the surface concentration of each bridge site can be estimated according to the surface concentration of metallic Ni, the bridge-to-linear adsorption ratio ($X_{B−L}$) and $X_{B_w}$ (listed in Table S3). A linear correlation between WGS reaction rate and concentration of the $B_w$ site is obtained (Figure 8B), indicating that the interfacial site (Ni$^{2+}$−O−Ti$^{3+}$) with medium strength of metal−support interaction serves as the optimal active site. In comparison, there is no positive correlation between the reaction rate and the concentration of the $B_m$ site or $B_s$ site. The results show that interface sites with too weak or too strong metal−support interaction impose a significant influence on the CO chemiadsorption on the surface of metal Ni, which results in a low efficiency of WGSR. Operando DRIFTS measurements under WGSR conditions were performed over Ni@TiO$_2$−x catalysts from 423 to 673 K (Figure S14). The CO adsorption species is not observed at relatively low temperatures (Figure S14A−C) but can be detected at 573, 623, and 673 K (Figure S14D−F) with a variable adsorption mode. According to the results, CO chemiadsorption species can serve as active intermediate species at 573, 623, and 673 K, respectively, as shown in Figure S14. The adsorption type of CO changes from linear to bridge chemiadsorption at elevated temperature. The active intermediate species and the mechanism of WGS reaction under operando conditions can be revealed by SSITKA-MASS combined with operando DRIFTS, which deserves a deep investigation in our future study. As shown in HRTEM, in situ EXAFS and XPS, the sample of Ni@TiO$_2$−x(450) shows a relatively moderate electron density of interfacial Ni (Ni$^{2+}$), promoting the medium chemiadsorption of CO, while a relatively moderate coverage degree of Ni nanoparticle facilitates the exposure of these sites. Therefore, an optimal trade-off between the number of active sites and geometric/electronic structure is obtained via tuning SMSI at the metal−support interface, resulting in the largely enhanced catalytic performance of Ni@TiO$_2$−x(450) toward WGSR.

3. CONCLUSION

In summary, a TiO$_2$−x-modified Ni nanocatalyst with tunable Ni−TiO$_2$−x interaction was prepared based on the calcination of the NiTi−LDH precursor followed by reduction at different temperatures ranging from 400 to 600 °C. The as-obtained Ni@TiO$_2$−x(450) catalyst shows largely enhanced catalytic performance (a reaction rate of 356.8 pmol CO s$^{-1}$ min$^{-1}$ and a TOF of 3.8 s$^{-1}$) for WGSR. A combination study including XRD, HRTEM, H$_2$-TPR, in situ EXAFS and XPS verifies that with the increase of reduction temperature, the Ni−TiO$_2$−x interaction is strengthened gradually accompanied by increased coverage degree of Ni nanoparticles and electron density of interfacial Ni (Ni$^{2+}$). This strong Ni−TiO$_2$−x interaction results in O$_2$−Ti$^{3+}$ site and concomitantly Ni$^{2+}$−O−Ti$^{3+}$ interface site, which provide the necessary dual-active-site required for WGSR. Moreover, in situ DRIFTS spectra further demonstrate that the interfacial site (Ni$^{2+}$−O−Ti$^{3+}$) with medium strength of metal−support interaction promotes a desirable modulation of coverage degree and electron density of Ni, accounting for the excellent catalytic performance toward WGSR.

4. EXPERIMENTAL SECTION

4.1. Materials. Analytical grade chemicals including TiCl$_4$, Ni(NO$_3$)$_2$·6H$_2$O, and urea were purchased from Sigma-Aldrich and used without further purification. The commercial TiO$_2$ (anatase) was purchased from Aladdin Co. Deionized water was used in the entire experimental process.

4.2. Synthesis of Ni@TiO$_2$−x and Ni/TiO$_2$ Catalyst. Synthesis of Ni@TiO$_2$−x. The NiTi−LDHs precursors with a molar ratio of [Ni$^{2+}$]/[Ti$^{4+}$] = 3/1 was synthesized by a urea decomposition method reported by our group.$^{[15]}$ In a typical procedure, 2.00 g of NiTi−LDH was calcinated in air at 500 °C for 4 h with a heating rate of 2 °C min$^{-1}$, followed by cooling to room temperature to obtain the mixed metal oxide (NiTi−MMO). Subsequently, the resulting NiTi−MMO was reduced in a H$_2$/N$_2$ (2:3, v/v) stream for 4 h at 400, 450, 500, and 600 °C, respectively, with a heating rate of 5 °C min$^{-1}$. The resulting products were slowly cooled to room temperature in a N$_2$ stream for subsequent catalytic evaluation, which were denoted as Ni@TiO$_2$−x(400), Ni@TiO$_2$−x(450), Ni@TiO$_2$−x(500), and Ni@TiO$_2$−x(600), respectively.

Synthesis of Ni/TiO$_2$. Ni/TiO$_2$ as a reference sample was prepared by a conventional impregnation method. TiO$_2$ (anatase, 3.00 g) was dispersed in a Ni(NO$_3$)$_2$·6H$_2$O solution (2.22 g, 5.0 mL). The slurry was stirred at room temperature for 3 h, aged for 24 h, and then dried at 60 °C for 12 h. The obtained solid sample was calcinated in air at 500 °C for 4 h with a heating rate of 5 °C min$^{-1}$, followed by cooling to room temperature, to obtain a mixture of NiO/TiO$_2$. The resulting NiO/TiO$_2$ sample was reduced in a H$_2$/N$_2$ (2:3, v/v) at 400, 450, 500, 600 °C for 4 h with a heating rate of 5 °C min$^{-1}$, to obtain the final 15%Ni/TiO$_2$(400), 15%Ni/TiO$_2$(450), 15%Ni/TiO$_2$ (500), and 15%Ni/TiO$_2$(600), respectively.

Synthesis of TiO$_2$−Ni. TiO$_2$−NiO (15%) precursor was prepared by the traditional sol−gel hydrolysis method reported previously.$^{[12]}$ A similar calcination and reduction process as described above were performed to obtain the TiO$_2$−Ni sample as a reference catalyst.

4.3. Characterizations. Powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer using Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 30 mA with a scanning rate of 5° min$^{-1}$ and a 2θ angle ranging from 3° to
90°. Scanning electron microscope (SEM) of the sample was performed on a Zeiss Supra 55 with an accelerating voltage of 20 kV. High-resolution transmission electron microscopy (HRTEM) was carried out on a JEM-3010 at an accelerating voltage of 200 kV. High-angle annular dark-field scanning TEM-energy-dispersive X-ray spectroscopy (HAADF-STEM) images were obtained on a JEOL2101F instrument using an electron probe (diameter 0.5 nm) with a diffraction camera length of 10 nm. CO chemiadsorption was performed in a quartz tube reactor on an automated catalyst characterization system (AutoChem 2920) from Micromeritics equipped with an online mass spectrometry (MS). In a typical process, 100 mg of sample was first prereducted at 400, 450, 500, and 600 °C for 1 h, respectively, followed by flushing with high purity He for 1.0 h and then the temperature was decreased to 200 K. Subsequently, successive pulses of CO were introduced, using He as the carrier gas (50 mL min⁻¹), until a stable mass signal of CO was obtained. The dispersion of metal Ni (D (%), eq 1) was calculated on the basis of CO chemiadsorption value:

\[ D(\%) = \frac{5SV_{CMNi}}{m_{WNi}} \times 100 \]  

(1)

The theoretical dispersion of metal Ni (Dt (%), eq 2) estimated based on Ni particle size measured by TEM and spherical model:

\[ D_t(\%) = \frac{3M_{Ni}F}{2N_A R_{Ni} \rho_{Ni} \sigma} \times 100 \]  

(2)

The coverage degree of Ni nanoparticle (θ) was calculated according to the CO chemiadsorption value and Ni particle size measured by TEM, based on the following equation:

\[ \theta = \left( 1 - \frac{\sigma N_m m_{Ni}}{W_m R_{Ni}^2} \right) \times 100 \]  

(3)

\[ m_{Ni} = \frac{4\pi R_{Ni}^3}{3} \]  

(4)

where \( M_{Ni} \), \( m_{Ni} \), \( V_{ab} \), \( W_{ab} \), and \( \rho_{Ni} \) are the molecular weight of Ni, the weight of sample (g), the volume of chemiadsorbed CO, the weight fraction of Ni, and the metal density of Ni, respectively. \( V_{ab} \) is the molar volume of CO at the standard temperature and pressure (STP); \( d \) is the reduction degree of Ni; SF is the stoichiometric factor, which is assumed as 1:1 for CO: Ni; \( N_A \) is the Avogadro’s number; \( \rho_{Ni} \) is the density of metal Ni; \( \sigma \) is the atomic cross-sectional area (0.0649 nm²); \( n \) is CO chemiadsorption value per gram catalyst (mmol g⁻¹); \( m_{Ni} \) is the quality of single Ni nanoparticle (g); \( R_{Ni} \) is the average semidiameter of the Ni nanoparticle measured by TEM.

Hydrogen temperature-programmed reduction (H₂-PR) was measured on a Micromeritics ChemiSorb 2070 with a thermal conductivity detector (TCD). In a typical process, 100 mg of the sample was sealed in a quartz tube reactor and pretreated in a Ar atmosphere at 200 °C for 2 h, followed by reduction in a stream of H₂/Ar (1:9, v/v; a total gas flow of 40 mL min⁻¹) with a heating rate of 10 °C min⁻¹ up to 900 °C. The specific surface area measurements were performed on the basis of the Brunauer–Emmett–Teller (BET) method using a Quantachrome Autosorb-1C-VP analyzer. The chemical compositions of prepared samples were determined using a Shimadzu ICPS-7500 inductively coupled plasma–atomic emission spectrometer (ICP–AES). In situ extend X-ray absorption fine structure spectroscopy (EXAFS) at the Ni and Ti K-edge was performed at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). The typical energy of the storage ring was 2.5 GeV with a maximum current of 250 mA. The Si (111) double crystal monochromator was used. The powdered sample was first pressed into sheet and loaded into a reactor cell equipped with polyimide windows. The sample sheet was reduced in a H₂/He stream at different temperatures ranging from 400 to 600 °C in the reactor cell, followed by flushing (50 mL min⁻¹) with high purity He for 1.0 h. The reduced sample was slowly cooled to 350 °C (in accordance with reaction temperature) in a He stream, and then the EXAFS spectra at the Ni or Ti K-edge were collected. X-ray photoelectron spectra (XPS) were recorded on a Thermo VG Escalab 250 X-ray photoelectron spectrometer equipped with Al Kα radiation (1486.6 eV) and a beam diameter of 100 μm. The Ni@TiO₂ samples were reduced in a microquartz tube reactor and were stored in the same tube until the XPS measurements were performed. In situ diffuse reflectance Fourier transform infrared spectroscopy (in situ DRIFTS) was performed in an in situ reaction cell on a VERTEX 70 spectrometer equipped with a MCT narrow-band detector.

### 4.4. Catalytic Evaluation for the Water Gas Shift Reaction

The catalytic evaluation of Ni-based catalysts was carried out using a microquartz tube reactor with an interior diameter of 8 mm at atmospheric pressure, equipped with an online GC-2014C Shimadzu gas chromatograph. Prior to the catalytic reaction, 0.2 g of catalyst was pretreated in a gaseous mixture of H₂ and N₂ (2:3, v/v; a total gas flow of 100 mL min⁻¹) at different temperatures ranging from 400 to 600 °C for 1 h, and then cooled to 200 °C in Ar. Water was fed into a vaporizer (150 °C) by using a HPLC pump, and the resulting steam was mixed with reactant gases before entering the reactor. Subsequently, a mixture of CO, H₂O and Ar (an internal standard) with a molar composition of 6% CO, 24% H₂O, and 70% Ar was introduced into the reactor with a total flux of 220 mL min⁻¹, and a weight hourly space velocity (WHSV) was maintained at 66000 mL gcat⁻¹ h⁻¹. The CO conversion was measured in the temperature range 200–500 °C, with a 3 h of balance time at each temperature. The composition of outlet gases was analyzed online using a GC-2014C gas chromatograph with a TDX-01 column and TCD detector. The total conversion of CO was calculated according to the following equation:

\[ X_{CO, total} = \frac{[CO_{out}] + [CH₄_{out}]}{[CO_{in}] + [CO_{out} + [CH₄_{out}]} \]  

(5)

For the calculation of turnover frequency (TOF) and reaction rate, a total gas flow rate of 220 mL min⁻¹ over catalyst (diluted with powder quartz sand) was employed in order to keep the total CO conversion below 10%. The TOF value and reaction rate were calculated according to the following equations:

\[ \text{TOF} = \frac{\text{Mol of CO converted}}{\text{mol of metallic Ni surface atom} \times \text{time (s)}} \]  

(6)

\[ \text{reaction rate} = \frac{\text{Mol of CO converted}}{\text{mass of catalyst (g) \times \text{time (s)}}} \]  

(7)
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REFERENCES


