Addition of Sodium Additives for Improved Performance of Water-Gas Shift Reaction over Ni-Based Catalysts

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ABSTRACT: The effect of Na loading on water-gas shift reaction (WGSR) activity of Ni@TiO₂−xNa (x = 0, 0.5, 1, 2, and 5 wt %) catalysts has been investigated. Herein, we report sodium-modified Ni@TiO₂ catalysts (denoted as Ni@TiO₂−xNa) derived from Ni₃Ti₁-layered double hydroxide (Ni₃Ti₁-LDH) precursor. The optimized Ni@TiO₂−1Na catalyst exhibits enhanced catalytic performance toward WGSR at relatively low temperature and reaches an equilibrium CO conversion at 300 °C, which is much superior to those for most of the reported Ni-based catalysts. The H₂-temperature-programmed reduction (H₂-TPR) result demonstrates that the Ni@TiO₂−1Na catalyst has a stronger metal–support interaction (MSI) than the sodium-free Ni@TiO₂ catalyst. The presence of stronger MSI significantly facilitates the electron transfer from TiO₂ support to the interfacial Ni atoms to modulate the electronic structure of Ni atoms (a sharp increase in Ni° species), inducing the generation of more surface sites (Ov−Ti³⁺) accompanied by more interfacial sites (Ni°−O−Ti³⁺), revealed by X-ray photoelectron spectroscopy (XPS). The Ni°−O−Ti³⁺ interfacial sites serve as dual-active sites for WGSR. The increase in the dual-active sites accounts for improvement in the catalytic performance of WGSR. With the tunable Ni−TiO₂ interaction, a feasible strategy in creating active sites by adding low-cost sodium additive has been developed.

1. INTRODUCTION

Water-gas shift reaction (WGSR) is an important industrial reaction to produce hydrogen and displays a vital role in the removal of CO in the feed gas for fuel cells.¹⁻⁷ From the thermodynamic reaction equation (CO + H₂O ↔ CO₂ + H₂, ΔH = −41.2 kJ mol⁻¹), WGSR is an exothermic and reversible reaction, which is thermodynamically favored at low temperature and kinetically favored at high temperature. Despite the temperature effect in thermodynamics and dynamics is contradictory, the balance can be achieved by a two-stage WGSR system to realize the high content of CO conversion in the industry. In such a WGSR system, the high-temperature stage (350-450 °C) uses Fe₂O₃−Cr₂O₃ catalysts and the low-temperature stage (190-250 °C) employs Cu−ZnO catalysts. However, the Fe₂O₃−Cr₂O₃ catalysts suffer from sintering and toxicity from the Cr element. Recently, Ni-based catalysts have been extensively employed in the high-temperature WGSR, selective hydrogenation, ethanol steam reforming, and dry reforming of methane by virtue of their advantages such as low cost, abundant resources, and excellent catalytic performance.⁸⁻¹² Although Ni-based catalysts show some advantages in high-temperature WGSR, they give unsatisfactory activity and expedite the undesired methanation side reaction, which consumes hydrogen and therefore lower the selectivity.¹³,¹⁴ Previous research studies have shown that the addition of alkali metal can improve the catalytic performance toward WGSR and suppress methanation by modifying the active sites and preventing the formation of surface carbonyl species, which serve as the intermediate of methanation reaction.²,¹³⁻¹⁶ Flytzani-Stephanopoulos et al. reported that silica- or alumina-supported Pt-based catalysts with small amounts of alkali addition could significantly enhance the catalytic activity toward low-temperature WGSR.¹⁷,¹⁸ Both experimental data and density functional theory (DFT) calculations suggested that Pt-alkali-Ox(OH) species was the active site, giving the Pt-based catalyst superior efficiency in low-temperature WGSR. Furthermore, they studied mononuclear gold steadily dispersed on an inert support with alkali additives for low-temperature WGS reaction.¹⁹ A suppression of methanation phenomenon was reported by Park et al., who revealed that potassium-modified Ni-based catalysts showed higher H₂ production and CO conversion than potassium-free Ni-based catalysts. This was further substantiated by Kwai et al., who uncovered that the addition of a certain amount of alkali could enhance the catalytic activity and selectivity of WGSR by promoting H₂O dissociation on O₂-absent ceria and inhibiting the formation of the subcarbonyl species.¹³,¹⁴ Additionally, alkali promotion in TiO₂-supported Pt-based
catalysts was also investigated. It was discovered that Pt nanoparticles were partially covered by 2–4 NaO2 layers with 2–4 wt % sodium addition. The strong interaction between Pt metal and promoter through Pt–O–Na promoted the formation of highly active sites for WGSR and hindered the sintering of Pt nanoparticles as well. From all the above research studies, we can find that the addition of alkali not only plays a crucial role in optimizing the activity and selectivity of the catalytic reaction but also inhibits metal nanoparticles sintering from each other.

Since the different loadings of alkali have varied effects on catalysts, it is of great interest to investigate the effect of alkali loading on the catalytic activity toward WGS reaction. To the best of our knowledge, there are few research studies devoted to investigating the Na promotion on TiO2-supported Ni nanocatalysts for WGSR. The previous research demonstrated that the strong interaction between Ni nanoparticles and TiO2 overlayer induced the formation of O2–−Ti5+ surface sites accompanied by the generation of Ni6+–O2–−Ti5+ interfacial sites, which performed as dual-active sites for WGSR. Moreover, by the aid of in situ and operando characterization methods, a fundamental understanding of the catalysis mechanism was proposed: the H2O molecule dissociates on the Ni6+–O2–−Ti5+ interfacial sites (Niδ+ participates in the dissociation of H2O) to produce hydrogen and active oxygen species and then active oxygen species react with CO molecule adsorbed on the surface of Ni nanoparticles to generate CO2. TiO2 is a commonly used support in WGSR, and Ti element can be introduced to the host layers of the layered double hydroxides (LDHs). The LDHs are a type of two-dimensional functional materials that have shown potential applications in heterogeneous catalysis as precursors and metal cations and are highly dispersed in the host layers at the atomic level. We use NiTi1-LDHs as a precursor, followed by calcination and reduction processes to acquire TiO2-based catalysts, which is stable at the reaction temperature. On the basis of these previous conclusions, we continue to investigate the effect of varied Na loading on the catalytic performance toward WGSR.

A low-loading sodium promotion effect on the Ni@TiO2 catalyst for the high-temperature WGSR has been proved. Herein, the sodium-modified Ni@TiO2 catalysts (denoted as Ni@TiO2-SNa) are synthesized by a topotactic transformation method from the NiTi1-LDH precursor, followed by impregnation, calcination, and reduction processes. The optimal Ni@TiO2-SNa catalyst exhibits excellent catalytic performance toward WGSR. Compared with the sodium-free Ni@TiO2 catalyst, Ni@TiO2-SNa catalyst has a stronger metal–support interaction (MSI) evidenced by H2-temperature-programmed reduction (H2-TPR) experiments. X-ray photoelectron spectroscopy (XPS) reveals that the stronger MSI greatly promotes the electron transfer from TiO2 support to the interfacial Ni atoms to modify the electronic structure of Ni atoms (a sharp increase in the Niδ+ species), resulting in the generation of more interfacial sites (Niδ+–O2–−Ti5+), which performed as dual-active sites for WGSR. The increase in the dual-active sites for WGSR accounts for an enhancement in catalytic performance.

2. RESULTS AND DISCUSSION

2.1. Morphological Characterization. The NiTi-LDH precursor (Ni/Ti molar ratio: 3:1) was prepared via a urea decomposition method developed by our group, whose X-ray diffraction (XRD) pattern (Figure 1, curve a) displayed a series of characteristic reflections at 2θ 12.1, 24.5, 33.3, 38.0, and 59.6°, which were assigned to the NiTi=−CO2-LDH phase. As shown in scanning electron microscopy (SEM) images (Figure S1), NiTi-LDHs display a favose-like morphology consisting of numerous interlaced nanosheets. Calcination at 500 °C in air results in NiTi-LDH precursor transforming to the corresponding mixed-metal oxide (NiTi-MMO), as shown in Figure 1 (curve b). Transmission electron microscopy (TEM) images show a uniform distribution of NiTi-MMO in Figure S2. A series of diffraction peaks at 37.2, 43.3, 63.0, and 75.4° are ascribed to the NiO phase (PDF #47-1049), while one weak diffraction peak at 25.3° belongs to anatase TiO2 (PDF #21-1272). With the introduction of sodium by impregnation, followed by calcination treatment, the original diffraction peaks of NiTi-MMO show no obvious change observed by XRD in Figure S3. Finally, a subsequent reduction in a H2 atmosphere at 450 °C gave sodium-modified Ni@TiO2 catalysts. Figure 1 (curve c–f) displays the disappearance of the NiO phase, accompanied by the appearance of three diffraction peaks at 44.5, 51.9, and 76.4°, which are indexed to the metallic Ni phase (PDF #04-0850). The reflections of anatase TiO2 are observed as well. Besides, a broad diffraction peak at approximately 12° can be obviously observed in Figure 1 (curve c–f), which can be attributed to the background peak based on Figure S4a. Additionally, the diffraction peaks between 30 and 40° are related to the Na2O species, which might be assigned to Na2O (PDF #03-065-2978) or NaO2 (PDF #01-077-0207) at a high Na loading, as shown in Figure 1g. With the aid of the Scherrer equation, four Ni@TiO2-SNa samples show a similar particle size of Ni (Table S1), indicating that the addition of Na displays a negligible effect on the particle size of Ni.

TEM measurements were carried out to further study the size distribution of Ni and the structural features of five Ni@TiO2-SNa samples (Figure 2). The TEM images of five samples show that Ni nanoparticles are highly dispersed on the TiO2 support with nearly the same particle size. High-resolution TEM (HRTEM) images display explicit lattice fringe of 0.350 and 0.203 nm, which are assigned to the {101} plane of anatase TiO2 phase and the {111} plane of the Ni phase, respectively. Furthermore, it is observed that the periphery of Ni nanoparticles is partially covered by TiO2 overlayers in five Ni@TiO2-SNa samples, as shown in the HRTEM images. According to the previous works, encapsulating metal nanoparticles with oxide overlayers is regarded as a typical characteristic of a strong MSI. Therefore, the phenomenon with Ni nanoparticles covered by TiO2 over-
layers reveals the formation of strong MSI in five Ni@TiO\textsubscript{x}-X\textsubscript{Na} samples. Moreover, with the addition of Na, no obvious change in the particle size of Ni is observed, which is consistent with the XRD results (Table S1).

### 2.2. Structural Investigation.
H\textsubscript{2}-TPR experiments were carried out to study the interaction between the Ni species and support and the reducibility of sodium-modified NiTi-MMO (denoted as NiTi-MMO-\textsubscript{X}Na). As for sodium-free NiTi-MMO (Figure 3, curve a), the H\textsubscript{2}-TPR profile shows two reduction peaks. The first reduction peak at \(\sim 284^\circ\text{C}\) is attributed to the reduction of bulk NiO in weak interaction with TiO\textsubscript{2} support, while the main reduction peak centered at 400 °C can be assigned to the reduction of the well-dispersed NiO phase, which interacts strongly with TiO\textsubscript{2} \textsuperscript{8,28} in accordance with TEM results. An interesting phenomenon was observed when Na adds to NiTi-MMO. Compared with the sodium-free NiTi-MMO sample, the two corresponding reduction peaks of NiTi-MMO-\textsubscript{X}Na become more notable and shift to a higher temperature (Figure 3, curve b), indicating a stronger interaction between the NiO species and TiO\textsubscript{2} \textsuperscript{8,14}. However, with the inclusion of more Na, the excess sodium is most probably deposited on the surface of catalysts based on the Na 1s spectra of Ni@TiO\textsubscript{x}-2Na and Ni@TiO\textsubscript{x}-5Na, as shown in Figure S5, which results in a decrease in the reducibility of the catalysts at higher Na loading of 2 and 5% \textsuperscript{13,14,20}. Also, the decrease in the reducibility of the samples causes a shift to higher reduction temperature (Figure 3, curves c and d). A similar phenomenon is observed in the case of alkali-doped Pd/Fe\textsubscript{2}O\textsubscript{3} \textsuperscript{29} and alkali-doped Pt/CeO\textsubscript{2} catalysts. \textsuperscript{30} Moreover, the decrease in the reducibility of the catalysts at higher Na loading of 2 and 5% can also be proved by the results of XPS analysis (Table 1). Noteworthily, an additional shoulder peak of sodium-free NiTi-MMO in 500–630 °C high-temperature region is ascribed to the reduction of the TiO\textsubscript{2} species. \textsuperscript{8,31} Moreover, with the addition of 1% sodium, the shoulder peak becomes more remarkable due to further reduction of the TiO\textsubscript{2} species (from Ti\textsuperscript{4+} to Ti\textsuperscript{3+}) to generate more O\textsubscript{v} and Ti\textsuperscript{3+}, resulting in the formation of more O\textsubscript{v}−Ti\textsuperscript{3+} sites. Therefore, the stronger interaction between NiO species and TiO\textsubscript{2} in the NiTi-MMO-1Na sample results in an increase in the reduction temperature of NiO species and the reducibility of TiO\textsubscript{2}. In addition, another weak reduction peak of sodium-modified NiTi-MMO in 220–240 °C is assigned to the reduction of gathered NiO nanoparticles. \textsuperscript{8} A similar phenomenon of a shift in the reduction peak toward higher temperature was observed.

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the effect of sodium on the surface electronic structure of Ni@TiO\textsubscript{x}-X\textsubscript{Na} catalysts and the electronic interaction between the TiO\textsubscript{2} support and metallic Ni. Figure 4A displays the Ni 2p spectra of these Ni@TiO\textsubscript{x}-X\textsubscript{Na} samples. The binding energies of Ni\textsuperscript{2+}, Ni\textsuperscript{3+}, and their two satellite peaks are \(\sim 852.6, \sim 854.4, \sim 855.6\), and \(\sim 860.1\) eV, respectively. \textsuperscript{13,14} Noteworthily, one additional and prominent peak at \(\sim 851.0\)

| catalysts | Ni\textsuperscript{2+}/(Ni\textsuperscript{2+} + Ni\textsuperscript{3+}) (%) | O\textsubscript{v} (%) | Ti\textsuperscript{3+}/(Ti\textsuperscript{3+} + Ti\textsuperscript{4+}) (%) |
|-----------|---------------------------------|-----------------|---------------------------------|
| Ni@TiO\textsubscript{x}-0Na | 27.2 | 31.8 | 47.3 |
| Ni@TiO\textsubscript{x}-0.5Na | 43.3 | 32.9 | 52.5 |
| Ni@TiO\textsubscript{x}-1Na | 50.6 | 46.9 | 83.6 |
| Ni@TiO\textsubscript{x}-2Na | 48.3 | 39.6 | 77.9 |
| Ni@TiO\textsubscript{x}-5Na | 44.1 | 36.4 | 40.4 |

Figure 2. (A1–E1) TEM images of the five Ni@TiO\textsubscript{x}-X\textsubscript{Na} samples: (A1) Ni@TiO\textsubscript{x}-0Na, (B1) Ni@TiO\textsubscript{x}-0.5Na, (C1) Ni@TiO\textsubscript{x}-1Na, (D1) Ni@TiO\textsubscript{x}-2Na, and (E1) Ni@TiO\textsubscript{x}-5Na. The inset shows the size distribution histograms of Ni nanoparticles. (A2–E2) The corresponding HRTEM lattice fringe images.

Figure 3. H\textsubscript{2}-TPR profiles of NiTi-MMO-\textsubscript{X}Na: (a) NiTi-MMO-0Na, (b) NiTi-MMO-1Na, (c) NiTi-MMO-2Na, and (d) NiTi-MMO-5Na.

Table 1. Surface Composition Calculated from XPS

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eV in the lower binding energy region is observed, which is attributed to the electron-enriched Ni species (Ni$^{\delta-}$).\textsuperscript{8} The appearance of Ni$^{\delta-}$ suggests that electron transfer from TiO$_x$ to metallic Ni is induced by strong MSI, implying a strong electronic interaction between metal Ni and TiO$_x$. Interestingly, the Ni$^{\delta-}$ peak (Figure 4A, curve c) remarkably strengthens as Na loading is increased from 0 to 1 wt %, indicating a stronger MSI with the presence of sodium, which is consistent with the H$_2$-TPR result. Further increasing the Na addition causes the decay of the Ni$^{\delta-}$ peak. Figure 4C displays the Ti 2p spectra of these Ni@TiO$_x$-XNa catalysts. By employing the Gaussian peak fitting method, the broad peak between 454 and 460 eV can be deconvoluted to two peaks at \(\sim 458.2\) and \(\sim 457.5\) eV, which are assigned to the Ti$^{4+}$ and Ti$^{3+}$ states, respectively.\textsuperscript{32,33} The formation of Ti$^{3+}$ indicates the generation of O$_{\varepsilon}$ according to the stoichiometric ratio (two Ti$^{3+}$ accompanied by one O$_{\varepsilon}$), which is also proved by the O 1s XPS spectra (Figure 4B), thereby leading to the formation of O$_{\varepsilon}$. 

Figure 4. XPS spectra of the Ni@TiO$_x$-XNa catalysts for (A) Ni 2p, (B) O 1s, and (C) Ti 2p: (a) Ni@TiO$_x$-0Na, (b) Ni@TiO$_x$-0.5Na, (c) Ni@TiO$_x$-1Na, (d) Ni@TiO$_x$-2Na, and (e) Ni@TiO$_x$-5Na.

Figure 5. (A) Ni$^{\delta-}$/(Ni$^{\delta-}$ + Ni$^0$) ratio, (B) O$_{\varepsilon}$, (C) Ti$^{3+}$/(Ti$^{3+}$ + Ti$^{4+}$) ratio, and (D) turnover frequency (TOF) value as a function of the loading of Na.
and then declines, and the optimal Na loading is 1 wt %, which increases, the catalytic activity toward WGSR enhances as a function of reaction temperature. As the addition of Na to the WGS reaction conditions. Figure 6A shows CO conversion as a function of reaction temperature over the five Ni@TiO$_2$-XNa samples (WGS reaction conditions: 5.2% CO, 61.5% Ar, 33.3% H$_2$O; weight hourly space velocity (WHSV) of 14850 mL g$^{-1}$ h$^{-1}$). (B) CO$_2$ selectivity over five Ni@TiO$_2$-XNa samples at 300 °C. (C) Plots of CO conversion vs reaction time at 300 °C over the Ni@TiO$_2$-1Na sample.

of the O$_{\delta^-}$-Ti$^{3+}$ sites. Additionally, the XPS spectra of O 1s for these Ni@TiO$_2$-XNa catalysts are deconvoluted to four peaks at ~529.0, ~530.0, ~531.0, and ~532.0 eV, which are assigned to the oxygen vacancy (O$_v$), lattice oxygen, the surface hydroxyl group, and adsorbed H$_2$O molecules, respectively, as shown in Figure 4B. A similar tendency is obtained for Ti$^{3+}$ and O$_v$ dependent on the loading of sodium as the Ni $2p_1/2$ (Ni$^{2+}$) spectra mentioned above.

The surface elemental relative concentration of various catalysts was calculated from the area of deconvoluted peaks of XPS spectra, as shown in Tables 1 and S2. Based on the results of Table 1, the surface Ni$^{2+}$/(Ni$^{2+}$ + Ni$^0$) ratio, O$_v$ and Ti$^{3+}$/(Ti$^{3+}$ + Ti$^{4+}$) ratio as a function of the loading of Na were studied, illustrated in Figure 5A-C, respectively. The ratio of Ti$^{3+}$ and O$_v$, in other words, O$_v$-Ti$^{3+}$ sites, increases first and then decreases, which shows a similar tendency with Ni$^{2+}$ as Na loading is increased from 0 to 5 wt %, and the maximum is also acquired with 1 wt % Na loading. Moreover, the interaction between Ni and O$_v$-Ti$^{3+}$ sites at the Ni-TiO$_2$ interface results in the formation of the Ni$^{2+}$-O$_v$-Ti$^{3+}$ interfacial site. On the basis of these results, the ratio of Ni$^{2+}$, O$_v$, and Ti$^{3+}$ (i.e., Ni$^{2+}$-O$_v$-Ti$^{3+}$ sites) shows a trend in volcanic shape with an increase in Na loading and Ni@TiO$_2$-1Na exhibits the highest ratio of these, as shown in Figure 5.

With the evidence from H$_2$-TPR, the Ni@TiO$_2$-1Na catalyst has a stronger MSI than sodium-free Ni@TiO$_2$ catalyst and the presence of a stronger MSI significantly enhances the electron transfer from the TiO$_2$ support to the interfacial Ni atoms to modify the electronic structure of Ni atoms (a sharp increase in the Ni$^{2+}$ species), leading to the generation of more surface sites (O$_v$-Ti$^{3+}$) accompanied by more interfacial sites (Ni$^{2+}$-O$_v$-Ti$^{3+}$). In addition, when the sodium content exceeds 1 wt %, the excess sodium deposited on the surface of catalysts inhibits the reduction of support and hinders the electron transfer from the support to the interfacial Ni, which will cause the decrease of Ni$^{2+}$, O$_v$ and Ti$^{3+}$ (i.e., Ni$^{2+}$-O$_v$-Ti$^{3+}$ sites), as displayed in Table 1 and Figure 5.

2.3. Catalytic Evaluation. The catalytic performance of these five Ni@TiO$_2$-XNa catalysts toward water-gas shift reaction was evaluated from 200 to 450 °C under the same WGS reaction conditions. Figure 6A shows CO conversion as a function of reaction temperature. As the addition of Na increases, the catalytic activity toward WGSR enhances first and then declines, and the optimal Na loading is 1 wt %, which is well in accordance with the trend of the Ni$^{2+}$-O$_v$-Ti$^{3+}$ interfacial sites certified by XPS. The effect of Na addition on the catalytic activity of the Ni@TiO$_2$-XNa catalysts is more pronounced at lower temperatures (below 250 °C), as shown in Figure S6. The CO conversion of the Ni@TiO$_2$-1Na catalyst is 30.1% at 225 °C, while that of the other four catalysts is below 15%. Initially, as Na loading increases from 0 to 1 wt %, the CO conversion increases slightly. The optimized Ni@TiO$_2$-1Na catalyst exhibits the most superior performance over the whole testing temperature range among the Ni@TiO$_2$-XNa catalysts. Concretely, the Ni@TiO$_2$-1Na catalyst exhibits excellent catalytic performance toward WGSR at a relatively low temperature (the CO conversion is 41.3% at 250 °C), the CO conversion is close to 100% at 300 °C, which is more superior to those of most of the reported Ni-based catalysts. The product consists of CO$_2$ and CH$_4$. Therefore, it is CO methanation that consumes further CO, which results in reaching the equilibrium CO conversion predicted by thermodynamics. Besides, Figure 6B displays the CO$_2$ selectivity over five Ni@TiO$_2$-XNa samples at 300 °C. The five Ni@TiO$_2$-XNa samples exhibit a similar CO$_2$ selectivity (~93%) at 300 °C, indicating that the Na addition has little impact on product distribution. Combined with the XPS results, the addition of 1 wt % Na enhances the catalytic activity due to the generation of increased O$_v$-Ti$^{3+}$ sites with more Ni$^{2+}$-O$_v$-Ti$^{3+}$ interfacial sites. Correspondingly, the TOF value as a function of the loading of Na is shown in Figure 5D. As the Na loading increases from 0 to 5 wt %, the TOF value increases first and then decreases, a similar tendency to the CO conversion, and the maximum TOF value is obtained for the Ni@TiO$_2$-1Na sample. Moreover, we tested the catalytic stability of the optimal catalyst (Ni@TiO$_2$-1Na). Figure 6C shows a slight drop in CO conversion from 97 to 92% during the 60 h thermal stability test, which was performed at 300 °C over the Ni@TiO$_2$-1Na sample. According to previous research studies, Ni catalysts suffer from deactivation probably due to some coking deposited on the surface of the spent catalysts.

It has been acknowledged that the metal site affects CO activation adsorption and oxygen vacancy adsorbs and activates H$_2$O in WGSR.$^{34-37}$ In this work, the Ni$^{2+}$-O$_v$-Ti$^{3+}$ interfacial sites are responsible for WGSR, in which Ni$^{2+}$ adsorbs CO while O$_v$ accounts for H$_2$O activation adsorption and dissociation.$^{6,21}$ Therefore, more surface and interfacial
sites will greatly facilitate $\text{H}_2\text{O}$ dissociation, the rate-determining step of WGSR.\textsuperscript{8,38} The further increment in Na loading beyond 2--5 wt %, however, causes a catalytic activity decay of the catalysts. The Ni@TiO$_2$-5Na catalyst presents the lowest activity with the equilibrium CO conversion at 350 °C, which is 50 °C higher than that in the Ni@TiO$_2$-1Na catalyst. With the inclusion of 2 and 5% Na, the excess sodium is most probably deposited on the surface of catalysts that formed the overlayers, resulting in a decrease in the reducibility of the catalysts.\textsuperscript{13,14,20} The decrease in the reducibility of the catalysts can be proved by the results of XPS analysis (Table 1). The deposition of excess Na hinders the reduction of support and restrains electron transfer from TiO$_2$ to metallic Ni, which causes the decrease in the dual-active sites (i.e., Ni$^{2+}$--O$_{\text{ad}}$--Ti$^{3+}$ sites) confirmed by XPS. Moreover, the excess sodium deposited on the surface of catalysts might form overlayers, which restricts the contact between the active sites and reactants. As a result, the performance toward the WGS reaction declines. Therefore, the low Na loading (below 2 wt %) has a stimulative effect on catalytic activity in the Ni@TiO$_2$-XNa system. With the increasing Na loading, deterioration in catalytic activity in WGSR can be ascribed to the decrease in the active sites blocked by excessive Na.

3. CONCLUSIONS

In summary, sodium-modified Ni@TiO$_2$-XNa catalysts with tunable Ni--TiO$_2$ interaction were prepared via the topotactic transformation method from the Ni$_2$Ti$_1$-LDH precursor. The effect of varying sodium loadings on these Ni@TiO$_2$-XNa catalysts has been investigated in detail to understand the role of sodium in influencing the catalytic performance in WGSR. Initially, the Ni@TiO$_2$-XNa catalysts show enhanced catalytic performance toward WGSR as Na addition increases from 0 to 1 wt %. The optimal loading is obtained with 1 wt % Na addition. The Ni@TiO$_2$-1Na catalyst displays excellent catalytic performance due to the stronger MSI, which induces more dual-active sites evidenced by H$_2$-TPR and XPS. Further increasing the Na addition causes a decline in the catalytic performance due to excessive sodium deposited on the surface of the catalysts.

4. EXPERIMENTAL SECTION

4.1. Materials. All of the analytical grade reagents including Ni(NO$_3$)$_2$·6H$_2$O, TiCl$_4$, urea (CO(NH$_2$)$_2$), and NaNO$_3$ were purchased from Sigma Aldrich and used without further purification. Deionized (DI) water was used in the whole experimental process.

4.2. Preparation of Ni@TiO$_2$-XNa Catalysts. The NiTi-LDH precursor with [Ni$^{2+}$]/[Ti$^{4+}$] = 3:1 was prepared via a urea decomposition method reported by Wei and co-workers.\textsuperscript{8} Concretely, urea (0.1 mol), Ni(NO$_3$)$_2$·6H$_2$O (0.006 mol), and deionized water (100 mL) were mixed in a round-bottomed flask to form a uniformly stable solution with continuous stirring. A 0.25 mL of TiCl$_4$/HCl solution (1:1 (v/v)) was then added into the mixture under vigorous stirring for several minutes. Finally, the resulting mixture was heated to 90 °C with stirring for 24 h, and the resulting precipitate was washed centrifugally with deionized water several times and dried in a vacuum at 60 °C overnight to obtain the NiTi-LDH precursor. Typically, 2.0 g of NiTi-LDHs was calcinated at 500 °C for 4 h with the heating rate of 2 °C min$^{-1}$, which transformed into nickel--titanium mixed-metal oxide (NiTi- MMO). The obtained NiTi-MMO was then doped with sodium by a wet-impregnation method. The loading of sodium in NiTi-MMO-XNa was varied with $X = 0, 0.5, 1, 2,$ and 5 wt %. The weight percentages of sodium refer to the final weight percentages of sodium in the Ni@TiO$_2$-XNa catalysts.

The typical process for synthesizing NiTi-MMO-XNa is as follows: a certain weight of NiTi-MMO was added to different concentrations of NaNO$_3$ aqueous solution under magnetic stirring to get a slurry. The slurry was continuously stirred at room temperature until the water had evaporated completely. Subsequently, the mixture was dried at 60 °C overnight, followed by calcination at 500 °C for 2 h in static air with the heating rate of 2 °C min$^{-1}$. Before catalytic evaluation, the resulting NiTi-MMO-X Na catalyst was reduced in a H$_2$/N$_2$ (5:6, v/v) stream at 450 °C for 2 h (heating rate: 5 °C min$^{-1}$), followed by cooling down to 25 °C in a N$_2$ stream. The obtained samples were denoted as Ni@TiO$_2$-XNa.

4.3. Characterization. The X-ray diffraction (XRD) analysis was carried out on a Rigaku XRD-6000 diffractometer by employing Cu Ka radiation ($\lambda = 0.15418$ nm) with the accelerating voltage and current of 40 kV and 30 mA, respectively. The XRD patterns were recorded over a 2θ range of 3–90° with a scanning rate of 5 °C min$^{-1}$. The morphology of the samples was explored using a Zeiss SUPRA 55 scanning electron microscope (SEM) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were conducted to study the particle size and structure of the samples on a JEOL JEM-2100 high-resolution transmission electron microscope with an accelerating voltage of 200 kV.

H$_2$-temperature-programmed reduction (H$_2$-TPR) tests were carried out on a Micromeritics ChemiSorb 2070 instrument equipped with a thermal conductivity detector (TCD). Nearly 100 mg of the sample was put in a quartz reactor and pretreated in a high-purity Ar stream at 200 °C for 2 h, followed by cooling to room temperature. Then, a total flow rate of 40 mL min$^{-1}$ of H$_2$/Ar (1:9, v/v) was introduced into the sample and the temperature was increased up to 900 °C at a heating ramp rate of 10 °C min$^{-1}$. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG Escalab 250 XPS spectrometer to analyze the electronic structure of the catalyst surface. The Ni@TiO$_2$-XNa samples were reduced in a microquartz tube reactor and kept in it until XPS measurements had been carried out.

4.4. Catalytic Evaluation. The WGSR activity of the Ni@TiO$_2$-XNa catalysts was performed in a microquartz tube reactor (interior diameter: 8 mm) at atmospheric pressure, equipped with an online gas chromatograph (GC-2014C Shimadzu). Prior to the catalytic evaluation, the catalysts were fully dispersed in quartz sand, pretreated at 450 °C for 2 h in a H$_2$/N$_2$ (5:6, v/v) stream at atmospheric pressure with a total gas flow of 110 mL min$^{-1}$, and then cooled down to 175 °C in high-purity N$_2$. The quartz sand is to cause the samples to disperse uniformly and ensure that catalysts fully touch the reactants. After the temperature dipped below 175 °C, the reactant gas (composition: 5.2%CO/33.3%H$_2$O/61.5%Ar; total gas flow: 124 mL min$^{-1}$) was introduced into the fixed-bed reactor, using Ar as the internal standard, and the total weight hourly space velocity (WHSV) was kept at 14850 mL g$_{\text{cat}}^{-1}$ h$^{-1}$. The catalytic performance toward WGSR was evaluated from 200 to 450 °C with the step of 25 °C. WGSR is an exothermic and reversible reaction, it takes some time to
approach the chemical equilibrium at each testing temperature. The CO conversion fluctuated before reaching a chemical equilibrium. Therefore, the evaluation was maintained for 2 h to acquire an accurate CO conversion at each testing temperature. The concentrations of the reactants and the products in the outlet of the reactor were analyzed by an online gas chromatograph with a TCD detector and TDX-01 column, using He as a carrier gas. The total CO conversion was calculated on the basis of the following equation

\[ X_{\text{CO-total}} = \frac{[\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}}}{[\text{CO}]_{\text{in}} + [\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}}} \]  

(1)

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05677.

SEM image of the NiTi-LDH precursor; TEM images of NiTi-MMO; CO conversion as a function of low reaction temperature (Figures S1–S6); physicochemical properties and TOF of various catalysts; and surface elemental relative concentration from XPS (Tables S1 and S2) (PDF)

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Notes
The authors declare no competing financial interest.

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