NO\textsubscript{x} Removal by Selective Catalytic Reduction with Ammonia over a Hydrotalcite-Derived NiFe Mixed Oxide

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Abstract: A series of NiFe mixed oxide catalysts were prepared via calcining hydrotalcite-like precursors for the selective catalytic reduction of nitrogen oxides (NO\textsubscript{x}) with NH\textsubscript{3} (NH\textsubscript{3}-SCR). Multiple characterizations revealed that catalytic performance was highly dependent on the phase composition, which was vulnerable to the calcination temperature. The MO\textsubscript{x} phase (M = Ni or Fe) formed at a lower calcination temperature would induce more favorable contents of Fe\textsuperscript{2+} and Ni\textsuperscript{3+} and as a result contribute to the better redox capacity and low-temperature activity. In comparison, NiFe\textsubscript{2}O\textsubscript{4} phase emerged at a higher calcination temperature, which was expected to generate more Fe species on the surface and lead to a stable structure, better high-temperature activity, preferable SO\textsubscript{2} resistance, and catalytic stability. The optimum NiFe-500 catalyst incorporated the above virtues and afforded excellent denitrification (DeNO\textsubscript{x}) activity (over 85% NO\textsubscript{x} conversion with nearly 98% N\textsubscript{2} selectivity in the region of 210–360 °C), superior SO\textsubscript{2} resistance, and catalytic stability.

Keywords: NiFe-LDH; mixed oxide; NiFe\textsubscript{2}O\textsubscript{4} spinel; NO\textsubscript{x}; NH\textsubscript{3}-SCR

1. Introduction

Emission of nitrogen oxides (NO\textsubscript{x}) is a main contributing factor to the induction of regional air pollution and ecosystem acidification [1]. During the past few decades, stringent regulations on NO\textsubscript{x} emissions have been issued worldwide and various measures have been devoted to diminish NO\textsubscript{x}, among which the removal of NO\textsubscript{x} from stationary sources by selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) has been attracting significant attention due to the low cost and high efficiency [2–4]. The most adopted SCR catalysts in practical applications are V-based catalysts, while the toxicity of active vanadium species, together with high N\textsubscript{2}O formation at high temperatures, restricts their further application [5]. Therefore, for the current situation, developing environmentally friendly substitutive catalysts with excellent efficiency, strong stability, and high SO\textsubscript{2} resistance in NH\textsubscript{3}-SCR is imperative.

Recently, great efforts have been made to exploit novel NH\textsubscript{3}-SCR catalysts, and some transition metal oxide catalysts have received wide attention [6–8]. Notably, iron-based catalysts have been considered as a potential candidate for the NH\textsubscript{3}-SCR application due to their high reactivity, cost-effectiveness, superior SO\textsubscript{2} durability, and non-toxicity. However, pure iron catalysts are subject to the limitations of a low acid amount [9] and inferior N\textsubscript{2} selectivity beyond 330 °C [10,11].

Up to now, a lot of reports have found that introducing other active ingredients (e.g., titanium oxides [12], manganese oxides [13], or tungsten oxides [2]) is an effective way to promote the denitrification (DeNO\textsubscript{x}) performance of iron-based catalysts. Especially, nickel species possess abundant surface
acidity sites [14] and a favorable ability to increase the N₂ selectivity of NH₃-SCR reactions [15,16], which was expected to be introduced into the iron-based catalytic system [17]. Furthermore, nickel oxides are considered as valuable materials to induce a synergistic effect with other active species, such as NiMnOₓ [18,19] and NiTiOₓ [20], which are very sensitive to the synthesis process.

It was reported that layered double hydroxide (LDHs) materials are excellent precursors for the preparation of metal oxide catalysts with the desired chemical and phase composition [21]. Thermal decomposition of hydrotalcite-like materials could produce layered double oxides (LDOs) possessing a relatively high surface area, which could promote the catalytic performance.

Herein, a series of economical and eco-friendly NiFe mixed oxides catalysts were prepared via calcining a hydrotalcite-like compound at various temperatures. The NH₃-SCR activity, SO₂ resistance, and stability were evaluated for the different NiFe mixed oxides catalysts. The correlations among phase composition, structure, and catalytic performance were systematically explored by XRD (X-ray diffraction), FT-IR (Fourier Transform Infrared), TG (thermogravimetric analysis), N₂ physisorption, NH₃-TPD (NH₃-Temperature Programmed Desorption), H₂-TPR (H₂-Temperature Programmed Reduction), and XPS (X-ray Photoelectron Spectroscopy). It was proved that the DeNOₓ performance was highly dependent on the phase composition of NiFe mixed oxides catalysts, which was available via adjusting the calcination temperature of NiFe-LDH. This work may serve as an important reference for LDH precursors to be tailored for potential applications in adjusting the phase component and catalytic performance.

2. Results and Discussion

NH₃-SCR reactions over NiFe mixed oxides catalysts at various calcination temperatures (400 °C, 500 °C, and 600 °C) were performed during 150–450 °C and the results are given in Figure 1A. It is clear that the NiFe-400 sample showed rather low NH₃-SCR efficiency with an obviously narrow operation temperature window. The DeNOₓ activity and temperature window for the NiFe-500 and NiFe-600 samples were promoted dramatically in comparison to that of the NiFe-400 catalyst. The NiFe-600 catalyst exhibited lower NOₓ conversion than the NiFe-500 catalyst at temperatures below 330 °C, while it behaved better in the higher temperature region, which implied that the higher calcination temperature was conducive to high-temperature SCR activity. As demonstrated in Figure 1B, all NiFe mixed oxides catalysts afforded superior N₂ selectivity: nearly 98% below 360 °C. When temperatures exceeded 360 °C, the N₂ selectivity of the NiFe-500 and NiFe-600 samples showed a slight decline compared with the NiFe-400 catalyst. Obviously, the NiFe-500 catalyst was the most promising candidate for NH₃-SCR, affording above 85% DeNOₓ activity within the widest temperature region of 210–360 °C and superior N₂ selectivity over the whole tested temperature range.

![Figure 1. Cont.](image-url)
was observed at 1601 cm$^{-1}$ while around a 5% decrease was displayed for NiFe-400. After purging off SO$_2$ tolerance under the reaction conditions of 600 ppm NO, 600 ppm NH$_3$, 5% O$_2$, 100 ppm SO$_2$ (when used), 10% H$_2$O (when used), balance N$_2$, gas hourly space velocity (GHSV) = 45,000 h$^{-1}$.

The stability is an important indicator to estimate the properties of catalysts. The stability tests were performed at 300 °C for 50 h over each catalyst under the reaction conditions of 600 ppm NO, 600 ppm NH$_3$, 5.0% O$_2$, and balanced with N$_2$. As presented in Figure 1C, the DeNO$_x$ activity of the NiFe-500 and NiFe-600 catalysts slightly fluctuated with only ±1% variance, indicating fine stability. Comparatively, the NiFe-400 sample displayed the relatively worst stability. Such different stabilities can be ascribed to the different stabilities of the mixed oxides’ structures. Thus, the NiFe-500 and NiFe-600 catalysts possessed a more stable structure in comparison with the NiFe-400 catalyst.

The presence of H$_2$O and SO$_2$ in the actual exhaust usually inhibits the NH$_3$-SCR of NO$_x$ [22]. Therefore, it is of great importance to evaluate the H$_2$O and/or SO$_2$ tolerance under the reaction conditions. The H$_2$O and/or SO$_2$ tolerance of the serial NiFe mixed oxides catalysts was investigated at 300 °C under the reaction conditions of 600 ppm NO, 600 ppm NH$_3$, 5% O$_2$, 0 or 100 ppm SO$_2$, 0 or 10.0% H$_2$O, and balanced with N$_2$. As depicted in Figure 1D, at the first stage, the NO$_x$ conversion for the NiFe-400, NiFe-500, and NiFe-600 catalysts was maintained at around 85%, 99%, and 96%, respectively. After adding 100 ppm SO$_2$ into the reaction gas, the NO$_x$ conversion decreased slightly. However, the co-existence of 100 ppm SO$_2$ and 10% H$_2$O led to a gradual decrease to some extent in NO$_x$ conversion, where the decrease was only about 2% for the NiFe-500 and NiFe-600 samples while around a 5% decrease was displayed for NiFe-400. After purging off SO$_2$ and H$_2$O, the NO$_x$ conversion gradually recovered to the original values. Thus, the NiFe-500 and NiFe-600 catalysts possessed an excellent SO$_2$ and H$_2$O resistance ability in comparison to the NiFe-400 catalyst.

XRD is an essential technology to evaluate the structure of catalysts. The XRD pattern of the NiFe-LDH precursor is presented in Figure 2A. The characteristic reflections at 20 values of 11.7°, 23.2°, 34.5°, 39.1°, 45.6°, and 59.8° can be observed, which were correspondingly indexed to the (003), (006), (012), (015), (018), and (110) planes according to the standard card (JCPDS no.15-0087). The absence of other crystalline phases hinted at the successful fabrication of NiFe-LDHs with high purity.

The FT-IR spectrum of NiFe-LDH is illustrated in Figure 2B. An intense and board peak at 3429 cm$^{-1}$ corresponded to the stretching vibration of the -OH group in the NiFe brucite-like layers, the interlayer water molecules, and the lattice water [23]. The peak that occurred at 2987 cm$^{-1}$ can be assigned to a CO$_2$–H$_2$O bridging bond [24]. The vibration of the angular deformation of H$_2$O molecules was observed at 1601 cm$^{-1}$ [23]. The peaks at 1385 cm$^{-1}$ belonged to the stretching vibrations of carbonate ions [25]. Additionally, the peak located at 676 cm$^{-1}$ might be correlated to the vibration of M-O (Fe-O, Fe-O-Ni or Ni-O) on the layer of the NiFe-LDH samples [26]. Both XRD and FT-IR data confirmed that NiFe-LDH was prepared successfully with CO$_3^{2-}$ as an interlayer anion.
The process of thermal decomposition of the NiFe-LDH precursor into mixed oxides was studied by TG coupled with MS (mass spectrometer) analysis (TG-MS). From the TG and DTG (derivative thermogravimetry) curves in Figure 3A, three major weight-loss stages were observed visually. The initial reduction in mass occurred between 80 °C and 180 °C (approximately 9 wt.%) and arose from the desorption of the surface adsorbed and interlayer water and CO₂ molecules. The second mass loss stage occurred at the temperature range of 190–350 °C (about 13 wt.%) and mainly released H₂O, CO₂, and NO₂, which were detected by online MS analysis (Figure 3B). This rapid and major mass loss can be assigned to the dehydroxylation of the inorganic layers and decomposition of interlayer anions (NO₃⁻ and CO₃²⁻) [27] accompanied by the collapse of the hydrotalcite structure. A small DTG exothermic peak at about 395 °C observed in the Figure 3A corresponds to the release of CO₂ and NO₂ in the MS curves, which was attributed to the degradation of nitrates and carbonates with high thermal stability. Based on the above, stable NiFe mixed oxides catalysts can be obtained when hydrotalcite-like precursors are calcined at over 400 °C.

An XRD analysis was performed for the serial NiFe mixed oxides catalysts, which were produced by calcining NiFe-LDH at different temperatures (400–600 °C). As exhibited in Figure 2C, the calcination temperature was an important factor affecting the formation of crystalline phase. As the calcination temperature increases from 400 °C to 600 °C, the diffraction peaks were found to significantly sharpen, representing the mushrooming of crystallinity and particle size. Meanwhile, new crystal phases progressively appeared. For the NiFe-400 sample, all diffraction peaks at 37.0°, 43.3°, 63.2°, 75.7°,
and 78.8° could be assigned to NiO phase (PDF # 44-1159). The absence of diffraction peaks of Fe species, existing in the form of oxides (e.g., FeO, Fe₂O₃, and Fe₃O₄), manifested their high dispersion or presence in the crystal lattice of NiO. The indicative diffraction peaks of NiFe₂O₄ spinel were emergent in NiFe-500 and markedly enhanced for the NiFe-600 sample, which were located at 2θ values of 30.4°, 35.6°, 53.8°, and 57.5° (PDF # 10-0325). Notably, according to the literature [28], a NiFe₂O₄ spinel possesses an inverse structure and can be written as Fe₃[FeNi]O₄, in which half of the Fe³⁺ occupies the tetrahedral sites with the octahedral sites comprised of a 1:1 ratio of Ni²⁺ and Fe²⁺ cations. It was reported that such an inverse NiFe₂O₄ spinel is a valuable material with structural stability and the possibility for bifunctional redox properties [28,29]. Combining the results in the catalytic performance tests, the NiFe₂O₄ spinel could be confirmed to be the expected phase in this system.

The nitrogen adsorption and desorption isotherms of NiFe mixed oxides catalysts are displayed in Figure 4A, in which can clearly be observed the typical shape of type IV isotherms curves (IUPAC classification), indicating the presence of 2–50 nm mesopores [30,31]. The NiFe-400 and NiFe-500 samples displayed a typical type H2 hysteresis loop that verified the existence of an “ink bottle” state structure, whereas the NiFe-600 catalyst presented the narrow type H3 hysteresis loop, demonstrating the existence of a “slit”-shaped mesopore [9,32]. Meanwhile, the pore diameter distribution of the serial catalysts can be visually observed from Figure 4B, where NiFe-500 exhibited the more intensive distribution in the region of 1–6 nm. The Brunauer–Emmett–Teller (BET) surface area and the average pore diameter of the as-prepared catalysts are listed in Table 1. The BET specific surface areas calculated by N₂ desorption isotherms were clearly seen to drop sharply with the increase of the calcination temperature in Table 1. However, the order of the catalysts by average pore diameter was NiFe-600 (15.5 nm) > NiFe-400 (5.1 nm) > NiFe-500 (4.0 nm). As discussed in the XRD analysis, with the increasing of calcination temperature, the crystallinity and particle size were both increased. Thus, the BET surface areas were decreased, which is in agreement with the literature [33]. In addition, in comparison to NiFe-400, NiFe-500 showed a smaller pore diameter, which may be due to the shrinkage of pores accompanied by the increase in crystallinity. However, for NiFe-600, a high crystallinity NiFe₂O₄ spinel was formed, which may result in the formation of a “stacked hole” with a larger pore diameter. The relatively larger specific surface area and even porous structures can provide more catalytic centers, which might account for the better DeNOₓ performance.

![Figure 4. N₂ adsorption and desorption isotherms (A) and pore diameter distribution (B) of the serial NiFe-LDO catalysts.](image-url)

The surface acidity and acid strength distribution of the NiFe mixed oxides catalysts were investigated by NH₃-TPD experiments. As illustrated in Figure 5A, the NH₃-TPD curves showed two ammonia desorption peaks for each sample in the 70–700 °C range. The first desorption peak
centered at around 120 °C corresponds to the physisorbed NH\textsubscript{3} or weakly acidic sites [34]. The other peak located at around 480 °C can be assigned to the chemical adsorbed ammonia on strong Lewis and Brønsted acidity sites [35]. The amount of total NH\textsubscript{3} adsorption and the proportion for every type of acid site were calculated from the integrated areas of the corresponding peaks. The calculation results were normalized and are listed in Table 2. It is clear that the increase of calcination temperature resulted in a dramatic reduction of ammonia adsorption and surface acidity. The desorption amount of NiFe-500 and NiFe-600 decreased by 35% and 73%, respectively. In addition, with the calcination temperature increasing from 400 °C to 600 °C, the proportion of weakly acidic sites shows an obvious rise from 34.5% to 52.4%, while the proportion of the strongly acidic sites decreased from 65.5% to 47.6%. Combined with the results of XRD and BET, we speculated that the increase of calcination temperature resulted in severe agglomeration of iron species and the acid center was covered in this process. More acid sites should be conductive to promote DeNO\textsubscript{x} activity. However, the NiFe-400 catalyst afforded the worst NH\textsubscript{3}-SCR performance though it owned the maximum acid quantity, suggesting that the number of acid sites was not the only factor to affect catalytic performance. Moreover, to our great interest, the NiFe-600 catalyst possessed the lowest number acid sites, but its high-temperature DeNO\textsubscript{x} activity was satisfactory. The DeNO\textsubscript{x} mechanism was further analyzed as below. It was confirmed that an iron-based mixed oxide catalyst would follow the Langmuir–Hinshelwood mechanism under 250 °C, where both NH\textsubscript{3} and NO would be adsorbed to all of the acid sites and then transformed to the corresponding intermediate [36]. The dramatic decrease of acid quantity for NiFe-600 resulted in the absence of adsorption of the reactant; accordingly, the low-temperature activity decreased. At medium and higher temperatures, the catalyst would fit the Eley–Rideal mechanism [31,37], where only the adsorption and activation process of NH\textsubscript{3} was conducted, generating the reaction between the adsorbed intermediate and gaseous-state NO. Therefore, the residual acid sites were still enough to absorb the majority of the NH\textsubscript{3} despite the evident decrease.

**Table 1.** Brunauer–Emmett–Teller (BET) surface areas and average pore diameter of the samples.

| Catalysts | BET Surfaces Areas (m\textsuperscript{2}/g) | Average Pore Diameter (nm) |
|-----------|--------------------------------------------|----------------------------|
| NiFe-400  | 169.3                                      | 5.1                        |
| NiFe-500  | 89.6                                       | 4.0                        |
| NiFe-600  | 20.9                                       | 15.5                       |

Figure 5. NH\textsubscript{3}-TPD profiles (A) and H\textsubscript{2}-TPR patterns (B) of the serial NiFe catalysts.

The H\textsubscript{2}-TPR technique was employed to determine the reducibility of the as-prepared NiFe mixed oxides catalysts. Over all samples, two noticeable reduction peaks are exhibited in Figure 5B. According to the literature [38,39], the reduction peak located at the lower temperature region (200–400 °C) may be assigned to the reduction of Ni\textsuperscript{2+} (Ni\textsuperscript{3+}) to Ni\textsuperscript{0} (Peak 1), and the reduction peak at the higher
temperature region (400–450 °C) could represent the reduction of Fe species (Peak 2). However, it was reported that the reduction peaks of mixed oxides usually do not correspond to only one kind of metal oxide [40]. Hence, the theoretical (denoted as E) and actual (denoted as A) H₂ consumption of each catalyst were calculated and are shown in Table 3. For all samples, the amount of total theoretical H₂ consumption was higher than that of the total actual H₂ consumption, implying the existence of an incomplete reduction of active species. Therein, the actual H₂ consumption amount of Ni species (peak 1) was higher than the theoretical values for each catalyst (A₁ > E₁), while Fe species (peak 2) were the opposite (A₂ < E₂). Therefore, the first reduction peak may be ascribed to the co-reduction of Ni as well as partial Fe species and the second peak may be only attributed to the Fe species. From Table 3, it was also clear that the NiFe-400 and NiFe-500 catalysts exhibited a similar position of reduction peaks and the NiFe-600 catalyst significantly shifted to high-temperature zones, presenting the worst reducibility for NiFe-600, which can well-explain its degraded DeNOₓ activity at a low temperature compared with the NiFe-400 and NiFe-500 catalysts.

### Table 2. Amount and proportion of NH₃ desorption of the serial catalysts.

| Catalysts | Total Amount of NH₃ Desorption a | Proportion of NH₃ Desorption (%) |  |  |
|-----------|---------------------------------|---------------------------------|  |  |
|            |                                 |                                 | Weak Acid Sites (55–300 °C) | Strong Acid Sites (300–700 °C) |
| NiFe-400   | 1                               | 34.5                            | 65.5                        |
| NiFe-500   | 0.65                            | 42.5                            | 57.5                        |
| NiFe-600   | 0.27                            | 52.4                            | 47.6                        |

a Normalized by the NH₃ desorption peaks area of the NiFe-400 sample (28,487.8 a.u.).

### Table 3. The reduction peaks temperature (°C) and H₂ consumption (mmol g⁻¹) of each catalyst.

| Catalysts | Peak 1 | Peak 2 | Total Actual H₂ Consumption | Total Theoretical H₂ Consumption |
|-----------|--------|--------|-----------------------------|----------------------------------|
|           | T₁     | A₁     | E₁             | T₂     | A₂     | E₂     |                           |                         |
| NiFe-400  | 333    | 13.99  | 13.86          | 427    | 0.59   | 0.77   | 14.58                      | 14.63                   |
| NiFe-500  | 333    | 14.21  | 14.05          | 428    | 0.41   | 0.88   | 14.62                      | 14.93                   |
| NiFe-600  | 357    | 13.68  | 12.10          | 444    | 0.95   | 2.62   | 14.63                      | 14.72                   |

where T₁ and T₂ refer to the reduction peak temperature; A₁ and A₂ refer to the actual H₂ consumption of peak 1 and peak 2, respectively; and E₁ and E₂ refer to the theoretical H₂ consumption of peak 1 and peak 2, respectively.

XPS analysis was performed to determine the surface components and valence states of elements presented on the catalyst surfaces. The XPS spectra of Fe 2p and Ni 2p₃/₂ are shown in Figure 6 and the corresponding surface atomic concentrations as well as the proportion of different valence states are listed in Table 4.

![Figure 6](image_url)  
**Figure 6.** The ideal model of catalysts with MOₓ (M = Ni or Fe) or multiple phases (MOₓ and a NiFe₂O₄ spinel).

According to Table 4, the amounts of surface Fe species showed a monotonic increase for the NiFe-400, NiFe-500, and NiFe-600 catalysts. As discussed in the XRD analysis section, when NiFe-LDH was calcined at 400 °C, iron species existed in the form of FeOₓ, which should be mostly covered by Ni...
species. With the increment of calcination temperature, NiFe$_2$O$_4$ spinels were generated. Fe species were gradually exposed or transferred to the surface of the catalysts, and the ideal model is displayed in Figure 6. It is well-known that more Fe species could result in better high-temperature activity; thus, DeNO$_x$ activity at high temperatures (>330 °C) displaying the order of NiFe-600 > NiFe-500 > NiFe-400 can be reasonable.

**Table 4.** Surface atomic concentration and oxidation states.

| Catalysts     | Fe 2p (%) | Fe$^{2+}$/Fe$^{3+}$ (%) | Ni 2p (%) | Ni$^{2+}$/Ni$^{3+}$ (%) |
|---------------|-----------|-------------------------|-----------|-------------------------|
| NiFe-400      | 1.7       | 51.4                    | 28.3      | 72.5                    |
| NiFe-500      | 2.2       | 43.8                    | 30.9      | 75.5                    |
| NiFe-600      | 5.4       | 66.5                    | 25.6      | 60.1                    |

For the XPS spectra of Fe 2p in Figure 7A, two main peaks assigned to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ can be observed centered at a binding energy of approximately 711 eV and 724 eV, respectively. By performing peak-fitting deconvolution, the Fe 2p$_{3/2}$ spectra were fitted into sub-bands located at approximately 710.9 eV and 712.7 eV, which corresponded to Fe$^{2+}$ and Fe$^{3+}$, respectively [41]. As shown in Figure 7B, the Ni 2p$_{3/2}$ spectra can be separated into three characteristic peaks at 854.1, 855.9, and 861.4 eV, which can be ascribed to the Ni$^{2+}$, Ni$^{3+}$, and satellite peaks, respectively [42]. Combined with the data in Table 2, it was clear that the Ni$^{3+}$ content on the surface of the NiFe-500 sample (75.5%) was higher than that of the NiFe-400 sample (72.5%), but the content of the surface Fe$^{3+}$ species was opposite for the two catalysts, which indicated that increasing the calcination temperature could result in a redox reaction between Ni$^{2+}$ and Fe$^{3+}$ to form Ni$^{3+}$ and Fe$^{2+}$ (Ni$^{2+}$ + Fe$^{3+}$ ↔ Ni$^{3+}$ + Fe$^{2+}$). However, the amount of surface Ni$^{3+}$ decreased to 60.1% with the increase in calcination temperature from 500 °C to 600 °C for the NiFe catalyst, which can be attributed to the formation of more high-crystallinity NiFe$_2$O$_4$ spinels, so it was difficult for the reaction (Ni$^{2+}$ + Fe$^{3+}$ ↔ Ni$^{3+}$ + Fe$^{2+}$) to occur on the surface of the catalyst. Thus, comparatively, the redox reaction (Ni$^{2+}$ + Fe$^{3+}$ ↔ Ni$^{3+}$ + Fe$^{2+}$) may more easily occur for the NiFe-500 sample. Such interaction in the bimetallic oxide was similar to that previously reported [30,43] and it was considered to be favorable for the creation of a redox cycle and further promoted the catalytic activity, especially at low temperatures.

![Figure 7. XPS spectra of the serial catalysts: (A) Fe 2p and (B) Ni 2p.](image-url)
3. Materials and Methods

3.1. Catalyst Preparation

The NiFe hydrotalcite-like precursor with the molar ratio of Ni to Fe being 4 was prepared by the urea hydrolysis method [44]. First, a urea solution and a mixed solution with Ni(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and sodium citrate in the corresponding ratio were dissolved fully with deionized water. Afterwards, the solution was transferred to a beaker and hydrothermally treated at 120 °C for 24 h. The NiFe-LDH precursors were obtained after extraction, filtration, washing, and drying at 60 °C for 12 h. Subsequently, the precursors were calcined at the required temperature (400–600 °C) for 5 h to obtain the NiFe mixed oxides. Finally, the NiFe catalysts were crushed and sieved through 40–60 mesh for catalytic evaluation.

3.2. Catalyst Characterization

XRD patterns of the samples were characterized using a DX-2700 instrument (Dandong Aolong Radiative Instrument Group Co. Ltd, Liaoning, China) with a Cu Kα radiation source (λ = 1.54184 Å, 40 KV, and 30 mA) in the 2θ range of 5–85° at a step of 8° min$^{-1}$. The FTIR spectrum was recorded on a TENSOR II FTIR spectrophotometer (Bruker, Billerica, MA, USA). The hydrotalcite-like samples were pressed into KBr pellets. TG coupled with MS analysis was employed to analyze the thermal decomposition of the NiFe-LDH precursor. A Mettler Toledo 851® thermobalance system (Balzers Ltd., Milton Keynes, UK) was used for TG measurements, which were carried out in a flow of Ar (80 mL min$^{-1}$) for a temperature range of 25–800 °C with a heating rate of 10 K min$^{-1}$. A ThermoStar Balzers MS (Balzers Ltd., Milton Keynes, UK) was used to monitor the evolved gases during the thermal decomposition process. The textural structures of the NiFe-LDO catalysts were determined using an ASAP 2460 automated gas sorption (Micromeritics, Norcross, GA, USA) analyzer through the N$_2$ adsorption-desorption equilibrium at −196 °C. The specific surface area and pore diameter were determined and calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. H$_2$-TPR and NH$_3$-TPD were performed on a TP-5080 instrument (Xianquan Industry and Trade Development Co. Ltd, Tianjin, China) coupled with MS using 0.08 g catalysts. Prior to the H$_2$-TPR test, the sample was pre-treated at 300 °C for 1 h in an Ar flow and then cooled to room temperature. Subsequently, the feeding gas was switched from Ar to 10% H$_2$/Ar (20 mL min$^{-1}$) and the temperature was increased from 30 °C to 900 °C with a heating rate of 10 K min$^{-1}$. In the case of NH$_3$-TPD, the samples were also pre-treated at 300 °C for 1 h, cooled to room temperature in a flow of He, and then saturated with 3% NH$_3$/He (25 mL min$^{-1}$) for 1 h at 50 °C. After NH$_3$ exposure, the sample was purged with He until excessive NH$_3$ was removed. Then, the TPD data were collected from 30 °C to 900 °C at a rate of 10 K min$^{-1}$ in He flow. XPS were recorded on a Thermo ESCALAB 250XI electron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with Al Kα as a radiation source (1486.6 eV). Binding energies of Ni 2p and Fe 2p were calibrated based on the graphite C 1s core level at 284.8 eV.

3.3. Catalytic Performance Tests

The NH$_3$-SCR activities over the catalysts were evaluated in a fixed-bed reactor with 0.38 g catalysts (40–60 mesh). The feed gas consisted of 600 ppm NO, 600 ppm NH$_3$, 5.0% O$_2$, 0 or 10.0% H$_2$O, 0 or 100 ppm SO$_2$, and balanced with N$_2$ at a flow rate of 350 cm$^3$ min$^{-1}$, and the gas hourly space velocity (GHSV) was 45,000 h$^{-1}$. The inlet and outlet gas concentrations of NO, N$_2$O, NO$_2$, and NH$_3$ were detected by an online Fourier-transform-IR spectrometer (MultiGas™ 6030) (MKS, Andover, MA, USA). The SCR reaction was carried out in the temperature range of 150–450 °C and the
data were recorded when the steady-state reaction was maintained after 30 min at each temperature. The NO\textsubscript{x} conversion and N\textsubscript{2} selectivity were calculated according to the following expression:

\[
\text{NO}\textsubscript{x} \text{ conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%
\]

\[
\text{N}_2 \text{ selectivity (\%)} = \frac{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}} \times 100\%
\]

where [NO]_{\text{in}} and [NH}_3]_{\text{in}} refer to the inlet concentrations of NO and NH\textsubscript{3}, respectively, and [NO]_{\text{out}}, [NO}_2]_{\text{out}}, and [N}_2\text{O}]_{\text{out}} refer to the reactor outlet concentrations of NO, NO\textsubscript{2}, and N\textsubscript{2}O, respectively.

4. Conclusions

A series of NiFe mixed oxides catalysts derived from hydrotalcite-like precursors were prepared and novelly employed as NH\textsubscript{3}-SCR catalysts. The result proposed that the ideal phase composition of NiFe mixed oxides catalysts was available via adjusting the calcination temperature of NiFe-LDH, which had a significant effect on DeNO\textsubscript{x} activity. The oxide phase formed at a lower calcination temperature is propitious for a better redox property and low-temperature activity, while the presence of NiFe\textsubscript{2}O\textsubscript{4} spinels could contribute to high-temperature activity as well as SO\textsubscript{2} resistance and stability. We testify to NiFe-500 being the optimal catalyst incorporating NiO and NiFe\textsubscript{2}O\textsubscript{4} spinels, where the virtues of the two phases were synergistically exerted and the best NH\textsubscript{3}-SCR performance was achieved.

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