Highly selective catalytic reduction of NO via SO₂/H₂O-tolerant spinel catalysts at low temperature

Xuanxuan Cai¹ · Wei Sun¹ · Chaochao Xu¹ · Limei Cao¹ · Ji Yang¹

Received: 12 March 2016 / Accepted: 8 June 2016 / Published online: 15 June 2016
© The Author(s) 2016. This article is published with open access at SpringerLink.com

Abstract Selective catalytic reduction of NOₓ by hydrogen (H₂-SCR) in the presence of oxygen has been investigated over the NiCo₂O₄ and Pd-doped NiCo₂O₄ catalysts under varying conditions. The catalysts were prepared by a sol-gel method in the presence of oxygen within 50–350 °C and were characterized using XRD, BET, EDS, XPS, Raman, H₂-TPR, and NH₃-TPD analysis. The results demonstrated that the doped Pd could improve the catalyst reducibility and change the surface acidity and redox properties, resulting in a higher catalytic performance. The performance of NiCo₁.₉₅Pd₀.₀₅O₄ was consistently better than that of NiCo₂O₄ within the 150–350 °C range at a gas hourly space velocity (GHSV) of 4800 mL g⁻¹ h⁻¹, with a feed stream containing 1070 ppm NO, 10,700 ppm H₂, 2 % O₂, and N₂ as balance gas. The effects of GHSV, NO/H₂ ratios, and O₂ feed concentration on the NO conversion over the NiCo₂O₄ and NiCo₁.₉₅Pd₀.₀₅O₄ catalysts were also investigated. The two samples similarly showed that an increase in GHSV from 4800 to 9600 mL h⁻¹ g⁻¹, the NO/H₂ ratio from 1:10 to 1:1, and the O₂ content from 0 to 6 % would result in a decrease in NO conversion. In addition, 2 %, 5 %, and 8 % H₂O into the feed gas had a slightly negative influence on SCR activity over the two catalysts. The effect of SO₂ on the SCR activity indicated that the NiCo₁.₉₅Pd₀.₀₅O₄ possesses better SO₂ tolerance than NiCo₂O₄ catalyst does.

Keywords SCR · NOₓ · Hydrogen · Flue gas · Gas treatment · SO₂/H₂O-tolerant

Introduction Nitrogen oxides (NOₓ), including NO, NO₂, N₂O, N₂O₃, N₂O₄, and N₂O₅, are mainly derived from fossil fuel combustion (Costa and Efstathiou 2007b). NOₓ are the major air pollutants that are greatly hazardous to human health and the environment (Xiaoling et al. 2012), causing negative effects such as photochemical smog, acid rain, ozone depletion, ground-level ozone, and greenhouse effects (Qi et al. 2006). A number of techniques have been developed to reduce the emission of NOₓ. Among them, the selective catalytic reduction of NOₓ by ammonia (NH₃-SCR) is a well-known and widely industrialized NOₓ control technology for stationary sources such as power plants and nitric acid plants (Li et al. 2010b). Generally, V₂O₅-WO₃ (MO₃)/TiO₂ is employed as NH₃-SCR catalysts (Grossale et al. 2008). However, many problems are encountered in the use of NH₃-SCR technology, namely catalyst deterioration, NH₃ slip (emissions of unreacted toxic ammonia), ash odor, air heater fouling, and a high running cost (Olympiou and Efstathiou 2011).

H₂-SCR has many advantages; for instance, hydrogen as a reductant does not induce any second pollutants and has high activity to reduce NOₓ efficiently at the lowest possible...
temperature (Kim and Hong 2010; Machida et al. 2001). Especially for industrial sites where H₂ is readily available, H₂-SCR is regarded as a possible alternative for NH₃-SCR. The catalyst is the most central technology in any H₂-SCR process, and its performance directly affects the removal of nitrogen oxides (Koebel et al. 2001; Weirong et al. 2012). Currently, the catalysts of H₂-SCR primarily contain supported noble metal oxides (Jun Yub et al. 2003; Yang and Jung 2009), among which the Pt-based and Pd-based catalysts have been revealed to possess good catalytic activity at relatively low temperatures (Chiarello et al. 2007; Costa and Efstathiou 2007a; Qing et al. 2010; Schott et al. 2009). For example, Costa and Efstathiou (2007a) had reported that the Pt/MgO-CeO₂ catalyst exhibited a maximum of 95 % NO conversion and 78–92 % N₂ selectivity within the 100–400 °C range. Higher than 90 % NO₃⁻ conversion within 170–300 °C was presented in the Pd/SiO₂ catalyst (Qing et al. 2010). Chiarello et al. (2007) investigated the catalytic reduction of NOₓ by H₂ over Pd-based catalysts with a support consisting of LaCoO₃. The 0.5 wt% Pd/LaCoO₃ catalyst exhibited a maximum of approximately 100 % NO conversion and over 78 % N₂ selectivity at 150 °C.

Nevertheless, noble metals are rare and expensive and they are sensitive to sulfur poisoning. These factors limit their large-scale applications. Therefore, new highly efficient catalysts need to be searched to replace Pt-based and Pd-based catalysts for H₂-SCR for NOₓ. Due to their low price, ready synthesis, and good redox property, transition metal oxides have been widely used as catalysts in various reactions (Auxilia et al. 2014; Chiu et al. 2015). Among them, spinel-type oxides have been widely studied because of their unique structure characteristics, and these oxide catalysts can simultaneously reduce NOₓ and soot at comparatively low temperatures (possibly within the range typical of diesel exhaust 150–380 °C) (Fino et al. 2008). Chen et al. (2009) had reported that the CuCoOₓ/TiO₂ catalyst exhibited a maximum of 98.9 % NO conversion at 200 °C. Du et al. (2014) had reported that Co₁₋ₓOₓ showed high performance on the removal of low-concentration (10 ppm) NO at room temperature.

Nickel cobaltite (NiCo₂O₄) is a mixed-metal oxide spinel that possesses interesting magnetic properties, rich redox chemistry, good electronic conductivity, and high electrochemical activity (Kim et al. 2000; Rui et al. 2013). In the recent research, NiCo₂O₄ is usually explored as an electrode material (Chi et al. 2006; Xu et al. 2014) and has rare reports about the catalytic reduction performance in the SCR reaction. Wang et al. (2015b) had reported that NiCo₂O₄ possessed the highest catalytic activity within 50–400 °C, with NOₓ conversion of more than 70 % at 150 °C and N₂ selectivity of more than 90 % at 100–400 °C. Therefore, we choose nickel cobaltite as a model catalyst.

Generally, doped noble metal can improve the catalytic activity and reduce the operating temperature. Palladium is less expensive and more abundant than platinum (Gaspar and Dieguez 2000), and Pd as an active component shows high activity for H₂-SCR and is highly active for H₂ activation (Li et al. 2012). The exceptional performance is due to the high dispersion of Pd in the catalyst that forms the Pd-NO intermediates, which adsorb more NO on the catalyst surface and are reduce to N₂ by hydrogen with high N₂ selectivity (Li et al. 2008). Rodriguez and Saruhan (2010) reported that the highly active centers could be formed by the interaction sites between Pd and supports and high NOₓ conversion and N₂ selectivities could be achieved by the synergistic effects of palladium and perovskites. Moreover, the synergistic effects efficiently enhance H₂ temperature-programmed reduction (H₂-TPR). Besides, Xu et al. (2015) had researched that doped Pd could make NiFe₁₀₉Pd₀₉O₄ increase acidity, reducibility, and catalytic activity.

NO was selected as a model nitrogen oxide in the simulated gas (Wang et al. 2009), because nitrogen monoxide accounts for 95–99 % of all nitrogen oxide emissions in flue gas (Fritz and Pitchon 1997). And the Pd-doped nickel cobaltite catalyst was successfully prepared through a sol-gel auto-ignition method and exhibited good catalytic performance for the selective catalytic reduction of NO by H₂ in the presence of oxygen at a low temperature. And we have considered the effects of the gas hourly space velocity (GHSV), NO/H₂ ratios, and O₂ feed concentration on the SCR activity. For practical consideration, we also investigated the durability of the catalyst and its tolerance to SO₂ and H₂O, respectively.

Materials and methods

Catalyst preparation

The catalyst used in this research was prepared via a sol-gel method using inorganic salts. All of the chemicals were of analytical grade and used without further purification. The compounds were weighed by analytical balance with the molar ratio of citric acid/Ni(NO₃)₃·6H₂O/Co(NO₃)₃·6H₂O/PdCl₂ = 3:1:1.95:0.05. Then, these compounds were dissolved in 50 mL deionized water with a concentration of 0.1 mol nitrate precursor (Jauhar et al. 2013). The pH of the mixture solution was additionally adjusted to 5–6 by slowly adding the ammonia solution, then the resulting solution was mixed together under stirring at room temperature for 3 h, and the sol was heated at 80 °C to form a wet gel; afterwards, the gel was dried at 130 °C. After drying, the obtained material was ground into fine powder. In order to obtain crystallized NiCo₁₋ₓPdₓO₄, the powder was calcinated in Muffle furnace at 400 °C for 4 h. Spinel NiCo₂O₄ was prepared in similar way with the only difference that merely the molar ratio of citric acid/Ni(NO₃)₃·6H₂O/Co(NO₃)₃·6H₂O/PdCl₂ was 3:1:2.
According to the drying and roasting process, the particles were easy to reunite and affect the catalyst activity, so about 5 mL polyethylene glycol (PEG) 400 was added to ensure high specific surface area and uniform particle size (Fan and Huang 2011).

**Catalyst characterization**

The as-prepared products were characterized by powder X-ray diffraction (XRD) using a Rigaku D/Max 2550 diffractometer (Japan) with Cu Kα radiation (λ = 1.54056 Å) operating at 40 kV and 100 mA. The elemental composition of the samples was characterized by energy-dispersive spectrometer (EDS) using a Falion 60s spectrometer. The Brunauer–Emmett–Teller (BET) surface area, average particle size, and pore size of the catalysts were measured with a nitrogen adsorption instrument (Micromeritics, TriStar II 3020) using N₂ gas as an adsorbant at the temperature of liquid nitrogen. Prior to BET analysis, the samples were degassed at 300 °C for 3 h.

The X-ray photoelectron spectroscopy (XPS) analysis was conducted in a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics). The instrument uses a focused monochromatic Al Kα X-ray (1486.7 eV) source operated at a 100 W and 100-μm-diameter beam. The binding energy scale was calibrated using the carbon C1s at 284.6 eV for known standards. The de-convolution of XPS peaks was performed with the CasaXPS program. The Raman spectroscopy experiments were carried out on an Iuvia microscope instrument (Iuvia Reflex) with a wavelength of 514.5 nm.

H₂-TPR and temperature-programmed desorption of ammonia (NH₃-TPD) were performed on AutoChem II 2920 equipped with a thermal conductivity detector (TCD) detector. Prior to the H₂-TPR or NH₃-TPD analysis, 50 mg of the oven-dried sample was pretreated in a He stream at 300 °C for 60 min to remove the adsorbed H₂O and other gases followed by cooling to room temperature. After that, the H₂-TPR analysis was performed using a 10 % H₂/Ar mixture at a flow rate of 40 mL/min with a heating rate of 10 °C/min to 800 °C, while the NH₃-TPD analysis was carried out by 10 % NH₃/He mixture with a total flow rate of 40 mL/min at 50 °C for 60 min. After NH₃ adsorption, the sample was purged by He (40 mL/min) for another 60 min. The desorption profile was recorded using a TCD by heating the sample to 600 °C at 10 °C/min under a flow of He (50 mL/min).

**Catalyst activity testing**

The selective catalytic reduction of NO by hydrogen was carried out in a fixed-bed flow micro-reactor, the catalyst bed temperature was controlled by thermocouple which was interpolated into the fixed-bed reactor, and reactor was heated through an AI-518/518P-type artificial intelligence temperature controller. A sample weighed 1 g, and the reactant gas composites consisted of 1071 ppm NO; 1071–10,710 ppm H₂ (the concentration was based on the ratio of NO to H₂); 0–6 % O₂; 2 %, 5 %, and 8 % H₂O (when used); 100, 300, and 500 ppm SO₂ (when used); and the balance N₂. These gases were fed from compressed cylinders provided by Jia Jie Specialty Gases (Shanghai, China) and adjusted with Brooks thermal mass flow controllers. The catalyst was fixed by silica pellets and quartz wool and placed in the constant temperature zone of the tubular reactor. The total flow of the inlet gas and the gas hourly space velocity were based on the change of gas conditions. The gas effluent stream from the reactor was analyzed by a Chemiluminescent NO–NO₂–NOX Analyzer (Thermo Scientific, model 42i), and the nitric oxide conversion was indicated using the following equation:

\[
X_{NO}^\text{inlet}(\%) = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\% \tag{1}
\]

Among them, \(X_{NO}^\text{inlet}\) represents the NO conversion and \([\text{NO}]_{\text{inlet}}\) and \([\text{NO}]_{\text{outlet}}\) show the inlet and outlet concentrations of NO in the gas mixture at steady state, respectively.

The Thermo Scientific NO–NO₂–NOX Analyzer revealed that the NOX was the sum of NO, NO₂, and less low-state nitrogen oxides, and the \(X_{NOX}^\text{inlet}\) represented the total NOX conversion rate.

\[
X_{NOX}^\text{inlet}(\%) = \frac{[\text{NOX}]_{\text{inlet}} - [\text{NOX}]_{\text{outlet}}}{[\text{NOX}]_{\text{inlet}}} \times 100\% \tag{2}
\]

where the \([\text{NOX}]_{\text{inlet}}\) and \([\text{NOX}]_{\text{outlet}}\) show the inlet and outlet concentrations of NO in the gas mixture at steady state, respectively. The N₂ selectivity was calculated as follows:

\[
S_{N_2}(\%) = \frac{X_{NOX}^\text{inlet} - [\text{NO}]_{\text{inlet}}}{X_{NOX}^\text{inlet} - [\text{NO}]_{\text{inlet}}} \times 100\% \tag{3}
\]

In this equation, the \(X_{NO}^\text{inlet}\) expresses the amount of nitric oxide in the transformation, while the \(X_{NOX}^\text{inlet} - [\text{NO}]_{\text{inlet}}\) expresses the amount of nitrogen from the transformation of nitric oxide.

**Results and discussion**

**Catalyst characterization**

**Structural and textural properties**

The XRD patterns of the samples used in this study are shown in Fig. 1a. The major peaks of the samples at ca. 2θ = 18.9°, 31.1°, 36.7°, 38.4°, 44.6°, 55.4°, 59.1°, and 65.1° could be indexed to (111), (220), (311), (222), (400), (422), (511), and (440) crystal planes of spinel NiCo₂O₄, respectively. It could be seen that the samples were a spinel cubic structure which...
were in good agreement with the standard pattern (JCPDS No. 73-1702) (Xu et al. 2014). While the XRD pattern of NiCo1.95Pd0.05O4 was similar to that of NiCo2O4, the diffraction angle theta of (440) crystal planes slightly shifted from 65.1° to 64.9°, which is shown in Fig. 1b. These results indicated that the heavier and larger Pd2+ ions substituted the Co2+ ions in the structure of the nickel cobaltite spinel, resulting in a small angle deviation of XRD peaks (Kavas et al. 2009). And the Pd doping did not cause a significant change in the crystallinity of the samples, possibly due to the palladium that replaced Co without distorting the spinel structure; therefore, the NiCo1.95Pd0.05O4 sample also maintained the spinel cubic structure.

The average crystalline size of NiCo2O4 and NiCo1.95Pd0.05O4 was estimated to be 32.2 and 26.7 nm using Scherrer’s formula based on the (422) peak, respectively (Lou et al. 2008). Scherrer’s formula is as follows:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

(4)

Among which, \(D\) is crystalline size, \(K\) is constant, \(\lambda\) is X-ray wavelength (0.154056 nm), \(\beta\) is peak half-high width, and \(\theta\) is the diffraction angle theta. Due to nickel cobaltite’s spinel cubic structure, \(K\) should be changed to 0.943 and a half-high width should be converted into a radian system, \([(\beta / 180) \times 3.14]\).

**BET and EDS analysis**

The BET surface areas, average particle size, and pore size of the studied NiCo2O4 and NiCo1.95Pd0.05O4 were summarized in Table 1. The surface areas of the NiCo2O4 and NiCo1.95Pd0.05O4 samples were 14.9956 and 12.6566 m² g⁻¹, respectively, while the average particle sizes were 14.0774 and 15.4802 nm, respectively, which had the reverse order compared to the surface area values. Generally, the larger the particle size, the smaller the BET area. The elemental composition of the samples was investigated using an EDS, as shown in Table 1. The Co/Ni atomic ratio (we chose Ni for comparison due to the stoichiometric amount being 1 in all of the studied samples) for NiCo2O4 was 2.03, which was consistent with the stoichiometric ratio. Due to the palladium doping, the Co/Ni atomic ratio of NiCo1.95Pd0.05O4 was 1.92, deviating slightly from the theoretical ratio of 1.95. The Pd/Ni atomic ratio was 0.049, which was consistent with the theoretical value of 0.05.

**H2-TPR and NH3-TPD analysis**

In order to investigate the reducibility and acidic properties of the NiCo2O4 and NiCo1.95Pd0.05O4, the as-prepared samples were characterized by H2 temperature-programmed reduction (H2-TPR) and temperature-programmed desorption of ammonia (NH3-TPD) analysis, respectively. As shown in Fig. 2a, there were three distinct reduction peaks in NiCo2O4, and the peaks appeared at 253 and 360 °C, corresponding to the reduction steps of Co3+ to Co2+ and Co2+ to Co0, respectively (Gou et al. 2013; Lim et al. 2015), while the peak appeared at 315 °C, which was attributed to the reduction of Ni2+ to Ni0. However, in comparison to NiCo2O4, the H2-TPR profile of the NiCo1.95Pd0.05O4 catalyst showed one slight peak and one strong broad peak. The slight peak at 129 °C was assigned to the reduction of Pd2+ to Pd0 (Giraudon et al. 2007; Linge et al. 2015), which was observed in pure Ni-Co spinel. And the strong broad peak within the range of 200–350 °C was formed by three reduction peaks fully overlapped, which corresponded to the reductions of Co3+ to Co2+ at 223 °C, Ni2+ to Ni0 at 286 °C, and Co2+ to Co0 at 316 °C. Compared to NiCo2O4, the reduction peaks of NiCo1.95Pd0.05O4 shifted to low temperature, which indicated that the H2 consumption was raised, enhancing the redox properties of catalysts. In addition, the TPR peak areas were an indicator to determine the reducibility of catalyst; the greater the peak area, the stronger the reducibility. The peak areas
of H$_2$-TPR were provided in Table 2. It could be seen that the Pd-containing nickel cobaltate exhibited relatively higher TPR areas than NiCo$_2$O$_4$, indicating that the palladium doping could improve the catalyst reducibility.

The acidic properties of the as-prepared samples were shown in Fig. 2b. The NH$_3$ adsorbed on the acid sites and then desorbed at different temperature regions, which was determined by the strength of acid sites and the amount of acid, respectively. The NH$_3$ desorption below 400 °C corresponded to the weak- and medium-strength acid sites (Imran et al. 2013). Nevertheless, the TPD profile of NiCo$_2$O$_4$ showed a broad NH$_3$ desorption peak from 100 to 350 °C, which was assigned to the NH$_3$ desorbed by weak- and medium-strength acid sites. Moreover, the acid amount could be determined by the TPD peak areas and the size of peak area corresponded to the amount of acid. Table 2 showed the NH$_3$-TPD peak areas. Compared to NiCo$_2$O$_4$, NiCo$_{1.95}$Pd$_{0.05}$O$_4$ slightly increased the peak areas from 100 to 350 °C, indicating that NiCo$_{1.95}$Pd$_{0.05}$O$_4$ showed a relatively more acidic amount than NiCo$_2$O$_4$.

Raman analysis

NiCo$_2$O$_4$ is an inverse spinel with tetragonal (A site) positions occupied by mostly Co$^{3+}$ and octahedral (B site) positions occupied by nearly equal concentrations of Ni$^{2+}$ and Co$^{3+}$ (Iliev et al. 2013). In order to further understand the composition and structural features of the NiCo$_2$O$_4$ and NiCo$_{1.95}$Pd$_{0.05}$O$_4$, the samples were characterized with Raman spectroscopy. The typical Raman spectrum was shown in Fig. 3; the peaks of NiCo$_2$O$_4$ at 183, 465, 509, and 651 cm$^{-1}$ corresponded to F$_{2g}$, E$_{1g}$, F$_{2g}$, and A$_{1g}$ models of NiCo$_2$O$_4$, respectively, and the Co–O and Ni–O stretching vibrations could be detected in the Raman spectrum. These results were well consistent with previously reported literatures (Babu et al. 2014; Li et al. 2015; Liu et al. 2013). Moreover, the peaks at 181, 418, 501, and 644 cm$^{-1}$ corresponded to F$_{2g}$, E$_{1g}$, F$_{2g}$, and A$_{1g}$ models of NiCo$_{1.95}$Pd$_{0.05}$O$_4$, respectively. Compared with that of NiCo$_2$O$_4$, the Raman spectra of the Pd-substituted nickel cobaltate (NiCo$_{1.95}$Pd$_{0.05}$O$_4$) exhibited a shift toward lower wave number, which was the result of the heavier and larger Pd$^{2+}$ ions substituting the Co$^{2+}$ ions in the structure of the nickel cobaltite spinel.

XPS analysis

In order to investigate the chemical bonding states and compositions of surface elements of as-synthesized NiCo$_2$O$_4$ and NiCo$_{1.95}$Pd$_{0.05}$O$_4$, the samples were studied by X-ray photoelectron spectroscopy (XPS), and the results were shown in Fig. 4a–d. The Ni, Co, O, and Pd elements were detected for the prepared samples.

The high-resolution spectrum for the O1s region in Fig. 4a showed two peaks at binding energies of around 529.1 and 530.8 eV, respectively, which had been denoted as O1

| Catalysts         | $S_{BET}$ (m$^2$ g$^{-1}$) | $D_{\text{particle}}$ (nm) | $D_{\text{pore}}$ (nm) | Elemental composition (at.%) |
|-------------------|---------------------------|----------------------------|------------------------|-----------------------------|
| NiCo$_2$O$_4$     | 14.9956                   | 400.1164                   | 14.0774                | Ni 18.78 Co 38.26 Pd 0.00  Pd/Ni 0.000 Ni/Co 2.037 |
| NiCo$_{1.95}$Pd$_{0.05}$O$_4$ | 12.6566                   | 474.0594                   | 15.4802                | Ni 20.29 Co 38.97 Pd 1.00 Ni/Co 0.0493 Ni/Co 1.921 |

Fig. 2  H$_2$-TPR and NH$_3$-TPD profiles of NiCo$_2$O$_4$ and NiCo$_{1.95}$Pd$_{0.05}$O$_4$ used in this study. a H$_2$-TPR. b NH$_3$-TPD
(529.1 eV) and O2 (530.8 eV). The O1 at the low energy of 529.1 eV was typical of the O atoms in the O–Co/Ni bonding. And the O2 at 530.8 eV was a characteristic of the as-prepared NiCo2O4 samples, which corresponded to a number of defect sites with low-oxygen coordination in the material with small particle size (Kim et al. 2000; Liu et al. 2013; Rui et al. 2013). The Co2p binding energies and peak shape were similar for the two preparations (Fig. 4b) and yield binding energies of 779.8 and 794.7 eV for the 2p3/2 and 2p1/2 transitions, respectively (Kim et al. 2000). XPS spectra of Co2p3/2 in the two preparations showed two main peaks of binding energies at 779.4 and 781.4 eV, which were assigned to the surface Co3+ and Co2+ species, respectively (Wang et al. 2015b). And this indicated that there were only a few Co2+ species in the octahedral sites and most of the low-spin Co3+ species occupied the octahedral sites (Babu et al. 2014; Kim et al. 2000).

The Ni2p spectra given in Fig. 4c were fitted considering two spin-orbit doublets as a characteristic of Ni2+ and Ni3+ and two shake-up satellites. The fitting peaks at the binding energy of 854.4 and 871.6 eV were indexed to Ni2+, while the fitting peaks at the binding energy of 856.43 and 873.8 eV were ascribed to Ni3+, respectively (Li et al. 2015, 2010a; Yu et al. 2016). The Pd3d spectra, as presented in Fig. 4d, showed two peaks at the binding energy of 337.1 eV for 3d5/2 and 342.5 eV for 3d3/2, respectively. The Pd5/2 binding energy was closed to the value of 336.9 which is a characteristic of Pd2+, indicating that the Pd doped in the as-prepared NiCo1.95Pd0.05O4 sample (Giraudon et al. 2007; Hu et al. 2011; Ling et al. 2015). These results exhibited that the surface of the as-synthesized NiCo2O4 that contained Ni2+, Ni3+, Co2+, and Co3+ (Moni et al. 2014), while the NiCo1.95Pd0.05O4 also contained Pd2+ except the common elements.

### Catalyst performance

**SCR activity of the NiCo2O4 and NiCo1.95Pd0.05O4 catalysts**

Figure 5 shows the results of the NO conversion and N2 selectivity over the NiCo2O4 and NiCo1.95Pd0.05O4 in the temperature range of 50–350 °C with a GHSV of 4800 mL g−1 h−1 in the presence of 2 % O2. As shown in Fig. 5a, as the reaction temperature increased, the NO conversion firstly increased then decreased over the NiCo1.95Pd0.05O4 catalyst. While the SCR activity over the NiCo2O4 catalyst was always increasing until it reached the maximum NO conversion. The highest NO conversion of the NiCo2O4 catalyst was approximately 40.05 % at 350 °C; yet, the N2 selectivity over the NiCo2O4 catalyst was only 60–80 %, which is illustrated in Fig. 5b. The NO conversion over the NiCo1.95Pd0.05O4 catalyst was higher than 90 % at a suitable temperature of 200–250 °C with the maximum of 94.65 % at 230 °C. And the N2 selectivity was higher than 90 % in the whole 130–350 °C range, with the maximum closed to 100 % at the 200–270 °C range.

Moreover, a previous study showed that the content of O2 was a crucial parameter for the H2-SCR reaction (Yang et al. 2011; Yuan et al. 2013). The combustion of fuel was not sufficient in the old burners, which resulted in the high oxygen content of 6~12 %. However, the new type of circulating fluidized bed burns the fuel more efficiently, resulting in the low oxygen content of 4~6 % (Huilin et al. 2000). Hence, in our study, the highest oxygen content was chosen to be 6 %. In general, oxygen can inhibit NO removal efficiency by oxidizing H2 to H2O, but it also oxidizes NO into adsorbed nitrite/nitrate on the surface to enhance the reduction reaction by hydrogen in the H2-SCR process (Machida et al. 2001; Wei

---

**Table 2** The peak areas of H2-TPR and NH3-TPD

| Catalysts          | H2-TPR |                      |                      |                      | NH3-TPD |                      |                      |
|--------------------|--------|----------------------|----------------------|----------------------|---------|----------------------|----------------------|
|                    | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Total | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak |
| NiCo2O4            | 253    | 3.1764 | 315    | 11.5537 | 360    | 17.7736 | 0     | 0.0000 | 32.5037 | 186   | 0.2000 |
| NiCo1.95Pd0.05O4   | 129    | 11.1585 | 223    | 4.3780 | 286    | 26.4388 | 316    | 3.5521 | 45.5274 | 206   | 0.3189 |

The unit of the peak area was defined as 1. The dosage of the samples was the same in the measurement of H2-TPR and NH3-TPD.

---

**Fig. 3** Raman profiles of NiCo2O4 and NiCo1.95Pd0.05O4 used in this study
et al. 2012). Hence, the effect of the oxygen concentration ([O\textsubscript{2}] = 0 %, 2 %, 4 %, and 6 %) in the feed gas over the NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} and NiCo\textsubscript{2}O\textsubscript{4} catalysts was investigated, which also consisted of 1070 ppm NO/10,700 ppm H\textsubscript{2}/x % O\textsubscript{2}/N\textsubscript{2} at a temperature range of 50–350 °C with a GHSV of 4800 mL g\textsuperscript{-1} h\textsuperscript{-1}.

The oxygen content in the flue gas from the circulating fluidized bed boiler is generally 4–6 % (Huilin et al. 2000). Therefore, experiments were performed to examine the O\textsubscript{2} tolerance of the prepared catalysts. As illustrated in Fig. 5c, under O\textsubscript{2}-free reaction conditions, a higher removal efficiency of NO was achieved and an efficiency of 100 % over the NiCo\textsubscript{2}O\textsubscript{4} catalysts was stabilized within a temperature range of 250–350 °C. As the O\textsubscript{2} content increased from 0 % to 6 %, the deNO\textsubscript{X} performance rapidly decreased and the maximum NO conversion decreased from 100 to 30.77 % at the 350 °C. As shown in Fig. 5d, the high NO conversion of 100 % over NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} was stabilized within a wider temperature range of 150–350 °C in the absence of oxygen, indicating that the doped Pd improved the catalytic activity and shifted the reaction temperature of the maximum removal efficiency from 250 to 150 °C. When the O\textsubscript{2} content increased to 2 %, the maximum NO conversion over NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} only changed to 94 % at the 230 °C; as the O\textsubscript{2} content increased, the SCR still exhibited good activity for NO reduction, with the maximum NO conversion of 81.16 % with 4 % O\textsubscript{2} at 230 °C and 61 % in the presence of 6 % O\textsubscript{2} at 230 °C, proving that Pd incorporation not only significantly improves the catalytic activity but also increases the O\textsubscript{2} tolerance ability (Wei et al. 2012).

To sum up, the NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} catalyst showed higher catalytic performance as well as greatly reduced the reaction temperature of the maximum removal efficiency. Hence, the NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} catalyst was suitable for the selective catalytic reduction of NO by H\textsubscript{2} in the presence of oxygen at a low temperature. Therefore, Pd played a very important role in the nickel cobaltite catalyst in the H\textsubscript{2}-SCR reaction. In addition, palladium did not destroy the spinel structure of NiCo\textsubscript{2}O\textsubscript{4} when it doped in nickel cobaltite, which was consistent with the XRD results. And from the H\textsubscript{2}-TPR and NH\textsubscript{3}-TPD activity tests, the NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} exhibited relatively high TPR areas, reduction level, and slightly larger acidity than NiCo\textsubscript{2}O\textsubscript{4}. All these factors resulted in the better catalytic performance of NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4}.

**Effect of GHSV and NO/H\textsubscript{2} ratio**

In general, GHSV could significantly affect the NO conversion rate at low temperature, and it was believed that it has less effect on the conversion rate at high temperature (Qi et al. 2006). Consequently, the H\textsubscript{2}-SCR activity of the NiCo\textsubscript{2}O\textsubscript{4} and NiCo\textsubscript{1.95}Pd\textsubscript{0.05}O\textsubscript{4} catalysts at different GHSVs (from 4800 to 9300 mL h\textsuperscript{-1} g\textsuperscript{-1}) and NO and H\textsubscript{2} feed concentration ratios (NO/H\textsubscript{2} = 1:10–1:1) were investigated at a temperature...
range of 50–350 °C in the presence of 2 % O₂, and the results are shown in Fig. 6.

As shown in Fig. 6a, the NO conversion over the NiCo₂O₄ catalyst decreased with the increasing GHSV. When the GHSV was 4800 mL h⁻¹ g⁻¹, the maximum NO conversion was up to 40.5 % at 350 °C, while when the GHSV increased to 6960 and 9300 mL h⁻¹ g⁻¹, the maximum conversion decreased to 35 % and 31 %, respectively. However, in contrast with NiCo₂O₄, the NO conversion faintly decreased over the NiCo₁.₉₅Pd₀.₀₅O₄ catalyst with the increase of the GHSV from 4800 to 9600 mL h⁻¹ g⁻¹ at the reaction temperature of 125–350 °C, which was shown in Fig. 6b. When the GHSV was 4800 mL h⁻¹ g⁻¹, the maximum NO conversion was up to 94 % at 230 °C, and when the GHSV was 9300 mL h⁻¹ g⁻¹, the maximum conversion was approximately 92 % at 230 °C.

These results demonstrated that the GHSV was a crucial parameter for the H₂-SCR reaction and the space velocity determined the residence time of the gas in the catalyst. As GHSV increased, the residence time of feed gas decreased. The NiCo₁.₉₅Pd₀.₀₅O₄ catalyst showed high NO conversion with the increasing GHSV, due to the Pd addition, which enhanced the redox properties of the active catalyst component. And this was consistent with H₂-TPR. Although the increase of GHSV resulted in the decrease of the reaction gas residence time in the catalyst, the activity of the active component was enhanced in the Pd-doped catalyst, resulting in more reduction reaction sites for NO and only a slight decrease of NO conversion. Therefore, the Pd-doped NiCo₁.₉₅Pd₀.₀₅O₄ catalyst showed better catalytic performance than the NiCo₂O₄ catalyst at different GHSVs (from 4800 to 9300 mL h⁻¹ g⁻¹).

The variation trend of NO conversion over the sample catalysts was roughly similar as the increase of reaction temperature at different NO/H₂ ratios, the NO conversion firstly increased then decreased over the NiCo₁.₉₅Pd₀.₀₅O₄ catalyst with the increasing reaction temperature, but the removal of NO over the NiCo₂O₄ catalyst increased as the temperature increased. As shown in Fig. 6c, the NO conversion over the NiCo₂O₄ catalyst decreased as the NO and H₂ feed concentration ratio increased within a temperature range of 170–350 °C in the presence of 2 % O₂. When the NO/H₂ ratio was 1:10, the maximum NO conversion was 41 %. When the NO/H₂ ratio was changed to 1:5 and 1:1, the NO conversion was 34 % and 31 %, respectively, exhibiting that higher H₂ concentration that resulted in higher NO conversion. Nevertheless, compared with the NiCo₂O₄ catalyst, the NiCo₁.₉₅Pd₀.₀₅O₄ catalyst showed higher catalytic activity at different NO and H₂ ratios, which is shown in Fig. 6d. When the NO/H₂ ratio was 1:10, the maximum NO conversion was...
more than 95\% at a reaction temperature of 230 °C. Actually, the economic factors must be considered. Industrially, the lower NO/H_2 ratio was used to obtain a relatively high NO conversion. When the NO/H_2 ratio was changed to 1:5 and 1:1, the NO conversion rate was 76\% and 37\%, respectively. Therefore, the doped Pd largely improved the catalytic activity and NiCo_{1.95}Pd_{0.05}O_4 exhibited higher catalytic performance than NiCo_{2}O_4 in the common reaction condition.

Effect of the presence of H_2O and SO_2

H_2O and SO_2 were usually contained in the industrial flue gases, which could cause a deactivation on SCR catalysts, and the general content of water was 2–10\%. At the same time, the SCR catalysts are sensitive to sulfur poisoning since sulfur compounds could deposit on the active sites of catalysts and deactivate them irreversibly (Chang et al. 2013; Lee et al. 2013; Yin et al. 2015). Therefore, it was important to investigate the effect of H_2O and SO_2 on NO conversion over selected catalysts.

The effect of H_2O and SO_2 on the selective catalytic reduction of nitric oxide with hydrogen over the NiCo_{2}O_4 and NiCo_{1.95}Pd_{0.05}O_4 catalyst was demonstrated in Fig. 7. As shown in Fig. 7a, when 2\%, 5\%, and 8\% H_2O was introduced to feed gas, the NO conversion of NiCo_{2}O_4 decreased rapidly from 36.8\%, 36.5\%, and 36.3\% to 33.2\%, 32.5\%, and 31.8\%, respectively, and then the NO conversion recovered slowly to 34.2\%, 33.4\%, and 32.6\% after the removal of H_2O, respectively. Compared with the initial value, the decrement of NO conversion was 7.07\%, 8.49\%, and 12.95\%, respectively. It could be seen that the conversion decreased more as the content of H_2O increased, which was due to the water-irreversible dissociative adsorption on the active sites of the catalyst (Burch and Coleman 1999; Leicht et al. 2012). And the NO conversion recovered a little, which was due to the reversible competitive adsorption by water. Hence, the influence of water on the catalyst was both reversible and irreversible.

However, the behavior of H_2O poisoning of the NiCo_{1.95}Pd_{0.05}O_4 catalyst was quite different. As shown in Fig. 7b, after 2\%, 5\%, and 8\% H_2O was introduced into the inlet gas, the NO conversion showed a slight decrease approximately from 87.2\% to 86.5\%, 84.5\%, and 80.5\%, respectively, which probably was due to the H_2O competitive adsorption with NO as well as with H_2. The water on the
catalyst could form the additional surface hydroxyls because of the dissociative adsorption of water (Kijlstra et al. 1996), and the surface hydroxyls would neutralize the acid sites, resulting in the reduction of SCR activity. For the Pd-doped catalyst, the surface acidity was enhanced. The multi-acid neutralized the hydroxyls and decreased the water poisoning on active sites of the catalyst. Therefore, the NiCo_{1.95}Pd_{0.05}O_4 catalyst has a better H_2O tolerance than NiCo_{2}O_4.

Furthermore, the influence of surface hydroxyls neutralizing the acid sites was irreversible; when the H_2O was off, the acidity of acid sites could not recover, and hence, the NO conversion over the NiCo_{1.95}Pd_{0.05}O_4 catalyst could not restore to the original level, which was consistent with Fig. 7b.

Moreover, the SO_2 tolerance and regenerability of NiCo_{2}O_4 and NiCo_{1.95}Pd_{0.05}O_4 catalysts were also examined. As shown in Fig. 7c, when the 100 ppm SO_2 was added to the reactant gas, the NO conversion of NiCo_{2}O_4 at 350 °C decreased rapidly from 35.8 % to 31.6 % in 150 min and only recovered to 32.6 % after the removal of SO_2, manifesting the inhibition effect of SO_2 on the SCR activity over NiCo_{2}O_4 (Chang et al. 2013; Yin et al. 2015). When the SO_2 increased to 300 and 500 ppm, the NO conversion decreased rapidly to lower than 27.5 % and 14.5 % and only recovered to 30.6 % and 21.6 % after the removal of SO_2, respectively. The decrease of NO conversion was mainly due to the blocking of the active sites by the formation of metal sulfates and/or sulfites (Li et al. 2011). The sulfated species formed on the catalytic center inhibited the SCR activity, which resulted in the decrease of NO conversion. After the supply of SO_2 was cut off, the NO conversion recovered slowly in a certain amount, which was mainly due to the regeneration of the part of sulfated catalysts by the hydrogen (Wang et al. 2015a).

The SO_2 poisoning behavior to the NiCo_{1.95}Pd_{0.05}O_4 catalyst at 230 °C was quite similar. As shown in Fig. 7d, after 100, 300, and 500 ppm SO_2 was introduced to the inlet gas, the NO conversion of NiCo_{1.95}Pd_{0.05}O_4 decreased steadily.
from 88.1 % to 83.8 %, 80.5 %, and 51.6 % in 130 min, respectively. The decrement of NO conversion was 4.88 %, 8.63 %, and 41.43 % compared to the initial value; however, the decrement value of NiCo2O4 was 11.73 %, 23.18 %, and 59.50 %, respectively. This was attributed to the improvement of catalytic activity by enhanced surface acidities and redox properties, which was consistent with NH3-TPD and redox properties, which was consistent with NH3-TPD and H2-TPR. After 100, 300, and 500 ppm SO2 was off, the NO and the N2 selectivity of 100 %. Moreover, the prepared catalyst possesses better SO2 tolerance than NiCo2O4. In this study, the NiCo2O4 and NiCo1.95Pd0.05O4 catalysts were investigated for NO selective reduction by hydrogen in the presence of O2. The results showed that the NiCo2O4 catalyst had a certain effect for NO removal, while the Pd-containing NiCo1.95Pd0.05O4 catalyst exhibited higher SCR activity with the maximum NO conversion of 94.65 % at 230 °C and the N2 selectivity of 100 %. Moreover, the prepared NiCo1.95Pd0.05O4 exhibited higher H2O and SO2 tolerance than NiCo2O4.

Conclusions

In this study, the NiCo2O4 and NiCo1.95Pd0.05O4 catalysts were investigated for NO selective reduction by hydrogen in the presence of O2. The results showed that the NiCo2O4 catalyst had a certain effect for NO removal, while the Pd-containing NiCo1.95Pd0.05O4 catalyst exhibited better SCR activity with the maximum NO conversion of 94.65 % at 230 °C and the N2 selectivity of 100 %. Moreover, the prepared NiCo1.95Pd0.05O4 exhibited higher H2O and SO2 tolerance than NiCo2O4.

Acknowledgments

This research is based on the work supported by the National Natural Science Foundation of China (21277045). Thanks to Zhenhua Zhou and Baosheng Tu for providing solutions to the experimental process and writing assistance.

Open Access

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

Auxilia FM, Ishihara S, Mandal S, Tanabe T, Saravanan G, Ramesh GV, Umerawawa N, Hara T, Xu Y, Hishita S (2014) Low-temperature remediation of NO catalyzed by interleaved CuO nanoparticles. Adv Mater 26:4481–4485

Babu GA, Ravi G, Hayakawa Y (2014) Surfactant assisted growth and optical studies of NiCo2O4 nanostructures through microwave heating method. Int J Sci Eng Appl 1:17–20

Burch R, Coleman MD (1999) An investigation of the NO/H2/O2 reaction on noble-metal catalysts at low temperatures under lean-burn conditions. Appl Catal B Environ 23:115–121

Chang H, Li J, Yuan J, Chen L, Dai Y, Arandiyi H, Xu J, Hao J (2013) Ge, Mn-doped CeO2–WO3 catalysts for NH3–SCR of NOx: effects of SO2 and H2 regeneration. Catal Today 201:139–144

Chen X, Zhang JF, Huang Y, Tong ZQ, Huang M (2009) Catalytic reduction of nitric oxide with carbon monoxide on copper-cobalt oxides supported on nano-titanium dioxide. J Environ Sci 21:1296–1301

Chi B, Lin H, Li J, Wang N, Yang J (2006) Comparison of three preparation methods of NiCo2O4 electrodes. Int J Hydrog Energy 31:1210–1214

Chiarello GL, Ferri D, Grunwaldt JD, Formi L, Baiker A (2007) Flame-synthesized LaCoO3-supported Pt: 2. Catalytic behavior in the reduction of NO by H2 under lean conditions. J Catal 252:137–147

Chiu CH, Hsi HC, Lin HP (2015) Multipollutant control of Hg/SO2/NO from coal-combustion flue gases using transition metal oxide-impregnated SCR catalysts. Catal Today 245:2–9

Costa CN, Efstatthiou AM (2007a) Low-temperature H2-SCR of NO on a novel Pt/MgO-CoO catalyst. Appl Catal B Environ 72:240–252

Costa CN, Efstatthiou AM (2007b) Mechanistic aspects of the H2-SCR of NO on a novel Pt/MgO-CoO catalyst. J Phys Chem C 111:3010–3020

Du Y, Huang W, Hua Z, Wang Y, Cai X, Wu M, Shu Z, Zhang L, Wang J, Chen H (2014) A facile ultrasonic process for the preparation of Co3O4 nanoflowers for room-temperature removal of low-concentration NOx. Catal Commun 57:73–77

Fan J, Huang W (2011) Preparation of Cu-Zn-Al bifunctional catalyst by sol-gel method with the assistance of PEG and its catalytic performance. Chin J Catal 32:139–143

Fino D, Russo N, Saracco G, Specchia V (2008) Removal of NOx and diesel soot over catalytic traps based on spinel-type oxides. Powder Technol 180:74–78

Fritz A, Pitchon V (1997) The current state of research on automotive lean NOx catalysis. Appl Catal B Environ 13:1–25

Gaspar AB, Dieguez LC (2000) Dispersion stability and methylicyclopentane hydrogenolysis in Pt/Al2 O3 catalysts. Appl Catal A Gen 201:241–251

Giraudon JM, Elhachimi A, Wyrwalski F, Siffert S, Aboukaïs A, Lamonier JF, Leclercq G (2007) Studies of the activation process over Pd perovskite-type oxides used for catalytic oxidation of toluene. Appl Catal B Environ 75:157–166

Gou Y, Liang X, Chen B (2013) Porous Ni-Co bimetal oxides nanosheets and catalytic properties for CO oxidation. J Alloys Compd 574:181–187

Grossaile A, Nova I, Tronconi E (2008) Study of a Fe–zeolite-based system as NH3–SCR catalyst for diesel exhaust after treatment. Catal Today 136:18–27

Hu L, Peng Q, Li Y (2011) Low-temperature CH4 catalytic combustion over Pd catalyst supported on Co3O4 nanocrystals with well-defined crystal planes. ChemCatChem 3:868–874

Huiling L, Guanbo Z, Rushan B, Yongjin C, Gidaspow D (2000) A coal combustion model for circulating fluidized bed boilers. Fuel 79:165–172

Iliev MN, Silwal P, Loukya B, Datta R, Kim DH, Todorov ND, Pachauri R, Khanna N, Gupta A (2013) Raman studies of cation distribution and thermal stability of epitaxial spinnel NiCo2O4 films. J Alloys Compd 531:3020–3027

Imran M, Kim DH, Al-Masry WA, Mahmood A, Hassain A, Haider S, Ramay SM (2013) Manganese-, cobalt-, and zinc-based mixed-oxide spinels as novel catalysts for the chemical recycling of poly(ethylene terephthalate) via glycolysis. Polym Degrad Stab 98:904–915

Jauhar S, Goyal A, Lakshmi N, Chandra K, Singhal S (2013) Doping effect of Cr3+ ions on the structural, magnetic and electrical properties of Co–Cd ferrites: a study on the redistribution of cations in CoCo6.0Fe1.6–0.8Ce1.4–0.6O4–1.0 ceramics. J Mater Chem 23:3793–3802

Jin Yub L, Bum KS, Sung Chang H (2003) Characterization and reactivity of natural manganese ore catalysts in the selective catalytic oxidation of ammonia to nitrogen. Chemosphere 50:1115–1122

Kavas H, Baykal A, Toprak MS, Köseoğlu Y, Sertkol M, Aktas B (2009) Cation distribution and magnetic properties of Zn doped NiFe2O4 nanoparticles synthesized by PEG-assisted hydrothermal route. J Alloys Compd 479:49–55

Kılıçstra WS, Daamen JCM, Graaf JMVD, Linden BVD, Poels EK, Bliedtner A (1996) Inhibiting and deactivating effects of water on the selective catalytic reduction of nitric oxide with ammonia over MnOx/Al2O3. Appl Catal B Environ 7:337–357
Kim SS, Hong SC (2010) Relationship between the surface characteristics of Pt catalyst and catalytic performance on the H$_2$-SCR. J Ind Eng Chem 16:992–996

Kim JG, Pugmire DL, Battaglia D, Langell MA (2000) Analysis of the NiCo$_2$O$_4$ spinel surface with Auger and X-ray photoelectron spectroscopy. Surf Sci 455:70–84

Koebel M, Elsener M, Madia G (2001) Reaction pathways in the selective catalytic reduction process with NO and NO$_2$ at low temperatures. Ind Eng Chem Res 40:52–59

Lee KJ, Maqbool MS, Kumar PA, Song KH, Ha HP (2013) Enhanced activity of ceria loaded Sn$_2$O$_3$/TiO$_2$ catalysts for NO reduction with ammonia. Catal Lett 143:988–995

Leicht M, Schott FJP, Brum M, Kureti S (2012) NOx reduction by H$_2$ on WO$_x$/ZrO$_2$-supported Pd catalysts under lean conditions. Appl Catal B Environ 117–118:275–282

Li L, Zhang F, Guan N, Schreier E, Richter M (2008) NO selective reduction by hydrogen on potassium titanate supported palladium catalyst. Catal Commun 9:1827–1832

Li JH, Wang CC, Huang CJ, Sun YF, Weng WZ, Wan HL (2010a) Mesoporous nickel oxides as effective catalysts for oxidative dehydrogenation of propane to propene. Appl Catal A Gen 382:99–105

Li L, Wu P, Yu Q, Wu G, Guan N (2010b) Low temperature H$_2$-SCR over platinum catalysts supported on Ti-containing MCM-41. Appl Catal B Environ 94:254–262

Li J, Chang H, Ma L, Hao J, Yang RT (2011) Low-temperature selective catalytic reduction of NOx with NH$_3$ over metal oxide and zeolite catalysts—a review. Catal Today 175:147–156

Li J, Wu G, Guan N, Li L (2012) NO selective reduction by hydrogen over bimetallic Pd–Ir/TiO$_2$ catalyst. Catal Commun 24:38–43

Li D, Gong Y, Zhang Y, Luo C, Li W, Fu Q, Pan C (2015) Facile synthesis of carbon nanoparticle/NiCo$_2$O$_4$ core-shell sub-microspheres with visible light. Int J Hydrogen Energy

Liu ZQ, Xiao K, Xu QZ, Li N, Su YZ, Wang HJ, Chen S (2013) Fabrication of hierarchical flower-like super-structures consisting of porous NiCo$_2$O$_4$ nanosheets and their electrochemical and magnetic properties. RSC Adv 3:4372–4380

Lou XW, Deng D, Lee JY, Archer LA (2008) Thermal formation of mesoporous single-crystal Co$_3$O$_4$ nano-needles and their lithium storage properties. J Mater Chem 18:4397–4401

Machida M, Ikeda S, Kurogi D, Kijima T (2001) Low temperature catalytic NOx–H$_2$ reactions over Pt/TiO$_2$-ZrO$_2$ in an excess oxygen. Appl Catal B Environ 35:107–116

Moni P, Kriangsak K, Sangaraju S (2014) Hierarchical nanostructured NiCo$_2$O$_4$ as an efficient bifunctional non-precious metal catalyst for rechargeable zinc-air batteries. Nanoscale 6:3173–3181

Olympiou GG, Estathiou AM (2011) Industrial NOx control via H$_2$-SCR on a novel supported-Pt nanocatalyst. Chem Eng J 170:424–432

Qi G, Yang RT, Rinaldi FC (2006) Selective catalytic reduction of nitric oxide with hydrogen over Pd-based catalysts. J Catal 237:381–392

Qing YU, Kong F, Landong LI, Guangjun WU (2010) Fast catalytic reduction of NOx by H$_2$ over Pd-based catalysts. Chin J Catal 31: 261–263

Rodriguez GCM, Saruhan B (2010) Effect of Fe/Co ratio on the phase composition of Pd-integrated perovskites and its H$_2$-SCR of NOx performance. Appl Catal B Environ 93:304–313

Rui D, Li Q, Jia M, Wang H (2013) Facile and large-scale chemical synthesis of highly porous secondary submicron-micron-sized NiCo$_2$O$_4$ materials for high-performance aqueous hybrid AC-NiCo$_2$O$_4$ electrochemical capacitors. Electrochim Acta 107:494–502

Schott FJP, Balle P, Adler J, Kureti S (2009) Reduction of NOx by H$_2$ on Pt/WO$_3$/ZrO$_2$ catalysts in oxygen-rich exhaust. Appl Catal B Environ 87:18–29

Wang Z, Dong Y, Chunyuan, Sun S (2009) Influence of temperature change on conversion characteristics of NOx in the reburning zone. Int Conf En Env Technol 707–710

Wang X, Jiang L, Wang J, Wang R (2015a) Ag/bauxite catalysts: improved low-temperature activity and SO$_2$ tolerance for H$_2$-promoted NH$_3$-SCR of NOx. Appl Catal B Environ 165:700–705

Wang X, Wen W, Mi J, Li X, Wang R (2015b) The ordered mesoporous transition metal oxides for selective catalytic reduction of NOx at low temperature. Appl Catal B Environ 176–177:454–463

Wei Y, Runduo Z, Biaohua C, Daniel D, Sébastien R (2012) New aspects on the mechanism of CuO:H$_2$ selective catalytic reduction of NO in the presence of O$_2$ over LaFe$_{1-x}$(Cu, Pd)$_x$O$_3$ perovskites. Environ Sci Technol 46:11280–11288

Weirong GU, Zhou M, Wei MA, Wang Y (2012) Research progress on selective catalytic reduction de-NOx catalysts. Chem Ind Eng Process 31:1493–1500

Xiaoling M, Bingsen Z, Yong L, Lide Y, Xuejiao W, Dang Sheng, Wenjie S (2012) Rod-shaped Fe$_3$O$_4$ as an efficient catalyst for the selective reduction of nitrogen oxide by ammonia. Angew Chem 51: 2989–2993

Xu J, He L, Xu W, Tang H, Liu H, Han T, Zhang C, Zhang Y (2014) Facile synthesis of porous NiCo204 microflowers as high-performance anode materials for advanced lithium-ion batteries. Electrochim Acta 145:185–192

Xu C, Sun W, Cao L, Yang J (2015) Selective catalytic reduction of nitric oxide by hydrogen over NiFe$_2$Pd$_4$O$_{23}$ catalysts at low temperature. Chem Eng J 283

Yang JH, Jung H (2009) The effect of temperature on NOx reduction by H$_2$ in the presence of excess oxygen on a Pt/Al$_2$O$_3$ monolithic catalyst. Chem Eng J 146:11–15

Yang S, Wang X, Chu W, Song Z, Zhao S (2011) An investigation of the surface intermediates of H$_2$-SCR of NOx over Pt/H-FER. Catal B Environ 3:380–385

Yin C, Wang L, Rivillon S, Shih AJ, Yang RT (2015) SCR of nitric oxide by hydrogen over Pd and Ir based catalysts with different supports. Catal Lett 145:1491–1499

Yu Z, Li H, Zhang X, Liu N, Tan W, Zhang X, Zhang L (2016) Facile synthesis of NiCo$_2$O$_4$@polyaniline core-shell nanocomposite for sensitive determination of glucose. Biosens Bioelectron 75:161–165

Yuan L, Zheng X, Duan K, Hu H, Wang J, Woo SI, Liu Z (2013) The effect of preparation conditions of Pt/Al$_2$O$_3$ on its catalytic performance for the H$_2$-SCR in the presence of oxygen. Fron Env Sci Eng 7:457–463