Facile preparation of high-performance Fe-doped Ce–Mn/TiO2 catalysts for the low-temperature selective catalytic reduction of NOx with NH3†

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A Ce–Mn–Fe/TiO2 catalyst has been successfully prepared using a single impregnation method, and excellent low-temperature NH3-SCR activity was demonstrated in comparison with other typical SCR catalysts including Mn–Ce/TiO2 and metal-doped Mn–Ce/TiO2. The crystal structure, morphology, and textural properties of the novel catalyst were investigated comprehensively by X-ray diffraction (XRD), N2 adsorption and desorption analysis, X-ray photoelectron spectroscopy (XPS), NH3-temperature-programmed desorption (NH3-TPD), and H2-temperature-programmed reduction (H2-TPR). The Fe-doped Ce–Mn/TiO2 catalyst boosted the low-temperature NH3-SCR activity effectively under a broad temperature range (100–280 °C) with a superior NO conversion rate at low temperatures (100 °C, 96%; 120–160 °C, ~100%). Fe doping caused this improvement by enlarging the catalyst pore volume, improving the redox properties, and increasing the amount of acid sites. These properties enhanced the ability of the catalyst to adsorb NH3 and improved the low-temperature SCR performance, especially at temperatures lower than 150 °C. Moreover, redox cycles of Ce, Mn, and Ti (Mn4+ + Ce3+ ↔ Mn3+ + Ce4+, Mn4+ + Ti3+ ↔ Mn3+ + Ti4+) also played an important role in enhancing the low-temperature SCR efficiency by accelerating the electron transfer. The excellent NH3-SCR result is promising for developing environmentally-friendly and more effective industrial catalysts in the future.

Introduction

Nitrogen oxides (NO, NO2, N2O) are mainly emitted from power plants and vehicles from the combustion of N-containing fossil fuels.1–3 These nitrogen oxides cause severe pollution to the environment and negative human health effects.4–7 Technology involving the selective catalytic reduction (SCR) of NOx with NH3 (NH3-SCR) has grown in recognition as the most effective and the most widely used method.8–10 SCR technology applied to upstream processes where ash arrangements are present (SO2, alkali metal ions, etc.) poison and deactivate catalysts quickly. In contrast, using catalysts after a desulfurization scrubber in the presence of lower dust and sulfur concentrations has been shown to be a significantly superior method. This method increases the catalyst lifetime because a majority of the SO2 and dust have been removed so that the deactivation of the catalyst does not readily take place.19 The fundamental goal for downstream denitrification technology is to develop a SCR catalyst that possesses a high activity within lower-temperature ranges, possesses a strong anti-sulfur performance, and is vanadium-free to be environmentally friendly.

Metal oxide catalyst groups Mn-based11–13 and Ce-based16–18 have high efficiencies for low-temperature activity. The reduction of Mn5+ to Mn3+ in the Mn phase, and the large oxygen storage capacity and redox properties of CeO2 cause this high efficiency. Smirniotis’ group20–21 applied the advanced instruments to full characterize the catalysts to reveal the mechanism of the NH3-SCR reaction in the presence of Mn-based catalysts. Moreover, previous studies have proven that the co-doped Mn–Ce catalysts22–25 have better SCR activity at low-temperature ranges because of the synergistic effect between Ce, Mn, and their supports. Qi et al.26 prepared a non-load-type MnO2–CeO2, low-temperature SCR catalyst using a co-precipitation method. The removal of NO was furthered by improving the ability of the redox catalyst to perform such that the Mn permeated the CeO2 lattice, and this generated a large number of oxygen vacancies.
Lee et al.27 prepared a MnO2/CeO2–TiO2 catalyst, and Ce doping of this catalyst enhanced the catalytic activity by increasing the surface area of the catalyst while improving the Mn4+ concentration. Shen et al.28 prepared a Mn/Ce–ZrO2 catalyst using an impregnation method, and NO conversion reached 98.6% at a temperature of 180 °C. Moreover, the Mn/Ce–ZrO2 catalyst exhibited a resistance to water and sulfur with a NO conversion rate of 87% in the presence of 100 ppm SO2 and 3% H2O. Liu et al.29 proved that the environmentally benign Mn–Ce–Ti catalyst had a high affinity for NOx removal because of the dual redox properties and the amorphous structure of the catalyst. Moreover, the Mn–Ce–Ti catalyst displayed a high resistance toward H2O and SO2. The Co-doped Mn–Ce catalysts exhibited a high NOx removal efficiency and sulfur resistance in the SCR at a low-temperature range of 150–300 °C; however, NOx removal efficiency at temperatures lower than 150 °C still need to be improved to meet industry requirements.

The aim of this work is to further improve the low-temperature SCR co-doped Ce–Mn/TiO2 catalyst activity by modifying the catalyst with Fe,19,29 Cu7,28 or Co31. A series of Ce–Mn–X/TiO2 catalysts (where X = Fe, Cu, or Co) were prepared using a single impregnation method and investigated for the low-temperature SCR of NOx with NH3. The possible mechanism of the best performing low-temperature SCR catalyst in this work is discussed in detail using various characterization methods.

Experimental section

Materials

Cerium nitrate (100% purity), acetic acid manganese (100% purity), iron nitrate (100% purity), and copper nitrate (100% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nitric acid cobalt (100% purity) was purchased from the Tianjin Guangfu Technology Development. Nano TiO2 was obtained from Tianjin Guangfu Fine Chemical Co., Ltd. Deionized water was prepared in the lab. All the chemicals were used without further purification.

Catalyst preparation

The catalysts were prepared using a previously defined impregnation method.32 First, 2.5 g of cerium nitrate, 1.46 g of acetic acid manganese and 2.15 g of iron nitrate (or 1.46 g copper nitrate or 1.55 g cobalt nitrate) were dissolved in deionized water, followed by stirring for 1 h to dissolve the solute completely. Five grams of nano TiO2 was added to the solution and stirred for 2 h. Subsequently, water was removed using a rotary evaporation instrument at 60 °C. The remaining solid was dried at 105 °C in an oven for 24 h, and then calcined at 500 °C for 2 h in an air environment with a tube furnace at atmospheric conditions. The calcined samples were ground into a powder and sieved through a 20–40 mesh to perform catalytic activity evaluations. The mass ratios of Ce/TiO2, Mn/TiO2 and X (Cu/Fe/Co)/TiO2 catalysts were 0.2, 0.06, and 0.1, respectively.

Catalyst activity measurement

SCR activity evaluation of all the catalysts were carried out in a fixed bed stainless steel tube reactor with an inner diameter of 11 mm and an outer diameter of 14 mm. Laboratory gas was purchased which contained specific concentrations of components to simulate flue gas in the experiment. The feed gas mixture consisted of 500 ppm NH3, 500 ppm NO, 3% O2 (volume fraction), 100 ppm SO2 and a balance of N2. The simulated gas flow rate was 1000 mL min−1. The nitrogen oxide concentrations were monitored in real-time by a gas analyzer (Testo 340). Six millilitres of each catalyst (20–40 mesh) was loaded for each reaction, and the experiment was performed between 100 and 300 °C at a heating rate of 3 °C min−1 with a gas hourly space velocity (GHSV) of 10 000 h−1. The concentrations of NO were measured at the inlet and outlet with a flue gas analyzer to calculate the conversion rate using eqn (1). Eqn (1) describes the NO to NO2 conversion.

\[
\text{NO conversion (\%) = } \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)
\]

where [NO]in and [NO]out refer to the NO concentration at the reactor inlet [in] and outlet [out], respectively. The measurements were recorded in ppm. The concentration was measured when the reaction reached a steady state condition (about 20–40 min) at each temperature which reduced measurement errors caused by instability.

Catalyst characterization

The powder X-ray diffraction (XRD) characterization of the samples was performed using a Bruker D8-Advance X-ray powder diffractometer with a Cu Kα radiation source (λ = 1.5406 Å), a pulverized sample with scattering angles (2θ) of 5–85°, and a 0.0197 step size operated at 50 kV and 50 mA. The diffraction lines were identified by matching them with reference patterns from the Joint Committee on Powder Diffraction Standards (JCPDS) database.

A ThermoFisher Escalab 250Xi X-ray powder photoelectron spectrometer was used to qualitatively analyze the X-ray photoelectron spectroscopy (XPS) characterization of the sample surface composition using an Al Kα radiation source with a scattering of 0–5000 eV. The binding energy was calibrated using the C 1s peak contaminant carbon (BE = 284.6 eV) as an internal standard.

N2 adsorption and desorption of each sample was measured at −196 °C using the ASAP 2020 automatic rapid surface area and mesopore/microporous analyzer with a N2 adsorption gas. The samples were degassed at 200 °C for 12 h before the analysis occurred. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The total pore volume was determined based on the amount of the adsorbed N2 volume at a relative pressure of approximately \( p/p^0 = 0.99 \).

Temperature programmed reduction with H2 (H2-TPR) was performed using a MICROMERITICS Autochem 2920 fully automatic chemistry-adsorption-tester. A sample with a mass of 0.1 g was pretreated under a He atmosphere with a heating rate...
of 10 °C min⁻¹ until reaching at 300 °C and then cooled to 40 °C. Subsequently, 10% H₂-Ar flowed through the catalyst bed while the temperature was ramped from 40 °C to 900 °C at a heating rate of 10 °C min⁻¹. The hydrogen consumption signal was measured by a thermal conductivity detector (TCD).

Temperature programmed desorption of ammonia (NH₃-TPD) was performed using a MICROMERITICS Autochem 2920 fully automatic chemistry-adsorption-tester. A sample with a mass of 0.1 g was pretreated under a He atmosphere at 600 °C for 1 h and then saturated with high purity ammonia at 40 °C for 1 h. Subsequently, helium was flowed through the sample at the same temperature for 1 h to remove ammonia. TCD desorption was performed from 100 to 500 °C at a heating rate of 10 °C min⁻¹, and the ammonia was detected by the TCD.

Results and discussion

NH₃-SCR performance at low-temperatures

The NH₃-SCR activities of Ce/TiO₂, Mn/TiO₂, co-doped Ce–Mn/TiO₂, and X (Fe, Co, Cu) modified Ce–Mn/TiO₂ catalyst were determined between 100 and 300 °C, and the results are shown in Fig. 1. Both Ce/TiO₂ and Mn/TiO₂ have a certain low-temperature NH₃-SCR activity, while Mn/TiO₂ showed a higher NO conversion than Ce/TiO₂ below 200 °C. However, the NO conversion was lower than 40% in the presence of the Ce/TiO₂ and Mn/TiO₂ catalysts. In contrast, co-doped Ce–Mn/TiO₂ catalysts afforded highly remarkable catalytic activity. The co-doped catalysts demonstrated catalytic activity under a wide temperature operation window. A NO conversion of 90% was obtained from 140 to 280 °C, and nearly 100% NO conversion was obtained at 160 °C. This improvement has also been demonstrated in another study; however, high NH₃-SCR activities at low-temperature have not been determined in the co-doped Ce–Mn/TiO₂ catalysts.

To enhance NH₃-SCR activities below 150 °C, the Ce–Mn/ TiO₂ catalyst was modified using Fe, Co or Cu. Fe addition has been demonstrated to greatly improve NH₃-SCR activity with a conversion of 96.8% at 180 °C in the presence of Fe–Ce–Mn/ TiO₂ catalysts prepared via a sol–gel method. In this study, the Fe-doped, Ce–Mn/TiO₂ catalyst prepared by an impregnation method improved the low-temperature NH₃-SCR by increasing the NO conversion from 43.2% to 96.3% at 100 °C. The NO conversion below 200 °C was improved to greater than 90% within the temperature range 100–260 °C. Nearly 100% NO conversion occurred between 120–160 °C, indicating Fe–Ce–Mn/TiO₂ was very active and selective for NH₃-SCR of NO at temperatures lower than 150 °C. This catalyst was shown to have the highest NO conversion concerning the SCR reaction at temperatures lower than 150 °C when compared to other studies thus far. The catalyst preparation approach played a vital role in NH₃-SCR process efficiency. However, the Co-doped catalyst had a minuscule impact on the Ce–Mn/TiO₂ catalytic performance, and the Cu-doped catalyst had a substantially negative effect on the low-temperature activity; the NO conversion was reduced from 43.2% to 13.6% at 100 °C after using Cu to dope the catalyst. The comparisons of the NH₃-SCR activities with the reported results in recent studies are summarized in Table S1.† The Fe–Ce–Mn/TiO₂ catalyst was the only catalyst selected for further study and characterization because of the excellent NH₃-SCR activity at temperatures below 150 °C.

Effect of Fe doped Ce–Mn/TiO₂ catalysts on NO oxidation

The effects of Ce, Mn and Fe doped TiO₂ catalysts on NO oxidation were investigated under the conditions of 500 ppm NO and 3% O₂ at a temperature range of 100–300 °C. The results in Fig. 2 show that NO oxidation rates in the presence of Ce/TiO₂ and Mn/TiO₂ catalysts were below 35% at 100–300 °C. Co-doping Ce and Mn improved the NO oxidation at higher temperatures ranging from 160 to 300 °C. The oxidation rate reached approximately 80% at 300 °C. The NO oxidation rate in the presence of Fe modified Ce–Mn/TiO₂ catalysts was much higher than the single Ce/TiO₂ or Mn/TiO₂ catalyst. The NO...
oxidation rate of the Fe modified catalysts was only slightly reduced when compared with the Ce–Mn/TiO2 catalyst at higher temperatures of 200–280 °C.

The Fe modified Ce–Mn/TiO2 catalysts reduced the oxidation properties of NO to NO2 when compared to non-Fe modified catalysts. Moreover, Fe modified Ce–Mn/TiO2 catalysts showed a much lower NO oxidation level at low temperatures than the single Mn/TiO2 catalyst. Currently, most studies suggest that rapid SCR reactions (2NH3 + NO + NO2 → N2 + 3H2) with faster reaction rates occur at low temperatures when using Ce and Mn doped catalysts due to their superior low-temperature denitrification properties.33 This study has shown that Ce–Mn/TiO2 and Ce–Mn–Fe/TiO2 catalysts improved the NO oxidation reaction to produce NO2, which would promote a rapid SCR reaction at high temperatures above 200 °C while decreasing the NO oxidation rate at temperatures less than 200 °C. Therefore, the high NH3-SCR activity of the Ce–Mn–Fe/TiO2 catalyst (96% NO conversion at 100 °C and nearly 100% between 120–160 °C) was not realized by enhancing the NO oxidation.

Resistance to SO2 poisoning on Fe doped Ce–Mn/TiO2 catalysts

The effect of SO2 on the SCR activity of Ce–Mn/TiO2 and Ce–Mn–Fe/TiO2 catalysts was investigated at a temperature of 160 °C, and the results are shown in Fig. 3.

In the absence of SO2, both Ce–Mn/TiO2 and Ce–Mn–Fe/TiO2 catalysts had excellent stability for 7 h, and the NO conversion was approximately 100%. After adding 100 ppm of SO2, the SCR activity of Ce–Mn/TiO2 decreased rapidly to a NO conversion of 83% in 50 min. This NO conversion remained constant at 80% throughout the test. After the SO2 was removed from the stream, the SCR activity increased to approximately 92%, but it did not recover completely. After 100 ppm of SO2 was added to the stream, the NO conversion of the Ce–Mn–Fe/TiO2 catalyst decreased to 40% after 5 h. After the SO2 was removed from the stream, the SCR activity continued to decline with no recovery for another 1 h. After the catalyst was doped with Fe, the sulfur resistance performance severely decreased. The loss of catalyst activity was possibly due to competing reactant adsorption mechanisms occurring on the catalyst surface.18 Furthermore, the active component Fe2O3 of the catalyst easily reacts with SO2 and O2 to produce the component Fe2(SO4)3, which leads to poisoning and deactivation of catalysts.24

Resistance to H2O poisoning on Fe doped Ce–Mn/TiO2 catalysts

At low temperatures, water vapor (H2O) in the flue gas is a key factor that can lead to the deactivation of a SCR catalyst. The resistance of the catalyst under these H2O conditions at low temperatures was investigated. Fig. 4 shows the comparison of NO conversion using Ce–Mn/TiO2 and Ce–Mn–Fe/TiO2 catalysts in the presence of 1 vol% H2O. Before the addition of H2O, the SCR reaction was stabilized at 200 °C for 3 h, and the NO conversion was 91.9% and 97.3% in the presence of the Ce–Mn/TiO2 and Ce–Mn–Fe/TiO2 catalysts, respectively. When 1 vol% of H2O was added into the flue gas, the NO conversion immediately decreased to 76.3% and 81.5% for the Ce–Mn/TiO2 and the Ce–Mn–Fe/TiO2 catalysts in 6 h, respectively. After undergoing 6 h in the presence of 1 vol% H2O, the H2O was removed from the flue gas, and after 4 h the NO conversion was 78.5% and 80.4% for the Ce–Mn/TiO2 and Ce–Mn–Fe/TiO2 catalysts, respectively. The H2O exhibited a largely irreversible effect on the activities of these catalysts. The presence of water vapor in the flue gas inhibited the reactant adsorption over the catalyst surface, and the reduced adsorption of the reactant was found to have an irreversible effect on the activity of the catalysts. However, the addition of Fe improved the resistance of H2O poisoning on Ce–Mn/TiO2 catalyst.

Catalyst characterization

X-ray powder diffraction patterns of different catalysts are shown in Fig. 5. The diffraction peaks of anatase titanium dioxide were observed in all four catalysts, and no diffraction
 peaks of the brookite and rutile phases were observed. The diffraction peak of manganese oxide was not observed. This observation suggests the distribution of manganese oxides on the catalyst surface was uniform, and no large MnO₂ grains were produced. The XRD pattern of Ce/TiO₂ showed sharp diffraction peaks of CeO₂ at 2θ = [28.6°, 33.1°, 47.6° and 56.5°]. XRD patterns of the Ce–Mn/TiO₂ catalyst showed a diffraction peak of CeO₂ at 2θ = 28.6°, and a lower peak intensity than that of the Ce/TiO₂ catalyst. This indicated that Ce and Mn doping can promote the dispersion of CeO₂ on the catalyst surface and reduce the degree of crystallization. The diffraction peaks of CeO₂ and TiO₂ were similar to the Ce–Mn/TiO₂ catalyst, and no FeO₂ peak was observed in the XRD pattern of the Ce–Mn–Fe/TiO₂ catalyst. This indicated that Fe possibly existed in an amorphous or highly dispersed phase on the surface of the catalyst. After Fe doping, the active components of the catalyst remained well dispersed. This is also one of the reasons for the excellent catalytic activity of Ce–Mn–Fe/TiO₂ at low temperatures.²⁴ SEM images of the Ce–Mn–Fe/TiO₂ catalyst were captured at four scales (500 nm, 1.0 μm, 2.0 μm and 5 μm) and are shown in Fig. 6(a–d). These images clearly confirmed that the Mn–Ce–Fe metal oxides were highly dispersed on the catalyst surface. The images also prove that the catalyst had homogenous particle sizes and shapes.

Table 1 shows the effects of Ce, Mn, and Fe doping on the BET surface area and pore structure of the catalysts investigated with N₂ adsorption–desorption experiments. After Ce and Mn co-doping, the specific surface area and pore volume of the Ce–Mn/TiO₂ catalyst increased substantially more than the Ce/TiO₂ and Mn/TiO₂ catalysts. Fe doping on the Ce–Mn/TiO₂ catalyst enlarged the specific surface area, the pore volume, and pore size. This improvement is possibly due to the synergy of the Mn and Fe, which facilitated the dispersion of the active components on the catalyst and improved the low temperature activity.²⁴,3⁴

Fig. 7 shows the effect of Fe doping on the redox properties of the catalysts investigated by hydrogen temperature-programmed reduction (H₂-TPR) experiments. The hydrogen reduction peak at T₁ (352 °C) and T₂ (435 °C) were attributed to the transformation of MnO₂ → Mn₂O₃ and Mn₂O₃ → Mn₃O₄, respectively.¹¹ The hydrogen reduction peaks at T₃ (596 °C) and T₄ (726 °C) were attributed to transformations of surface CeO₂ → Ce₂O₃ and crystal lattice CeO₂ → Ce₂O₃, respectively.³⁵ After the catalyst was doped with Fe, the reduction peak area of hydrogen increased significantly, indicating that Fe doping increased the oxidation–reduction capacity of the catalyst. Moreover, the reduction temperature of the crystal lattice transformation of CeO₂ → Ce₂O₃ was decreased. This indicated that the ceria oxide became more reducible, and can be ascribed to the synergetic effect between Ce and Fe. NH₃-SCR reactions consume active oxygen on the catalyst surface and undergo several redox reactions.³⁴ This may be another reason for the high NH₃-SCR activity of Ce–Mn–Fe/TiO₂ at low temperatures.

Fig. 8 shows the effect of Fe doping on the surface acidity of Ce–Mn/TiO₂ catalysts using ammonia temperature-programmed desorption (NH₃-TPD). The NH₃ desorption peak in the temperature range of 80–200 °C was caused by desorption of NH₃ at the weak acidic sites. The NH₃ desorption peak at 200–350 °C was due to desorption of NH₃ on the medium strength acidic sites. The Ce–Mn/TiO₂ catalyst only had weak acid sites, while the Ce–Mn–Fe/TiO₂ catalyst had both weak and medium strength acidic sites.²⁷ The adsorption of NH₃ on the catalyst surface was a key step in the SCR reaction, regardless of the reaction in the Langmuir–H or Eideal–Rley pathway.²⁷,²⁶,²⁷ Fe doping not only increased the number of weak acidic sites on the catalyst but also produced medium acidic sites. The enhancement of the surface acidity of the catalyst contributed to the adsorption and activation of NH₃. This was an important

<table>
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<th>Catalyst</th>
<th>S_BET/m² g⁻¹</th>
<th>V_p/cm³ g⁻¹</th>
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</table>
reason for the low temperature activity of Ce–Mn–Fe/TiO₂ catalysts. This is especially applicable to the increased quantity of the weak acidic sites, where unstable or metastable nitrates species were produced at low-temperatures. These species did not occupy the active sites for extended periods of time and therefore improved the low-temperature SCR performance.²⁷

The XPS spectra of the Ce, Mn, Ti, Fe, and O of the Ce–Mn–TiO₂ and Ce–Mn–Fe/TiO₂ catalysts are shown in Fig. 9(a–e). XPS spectra of Ce 3d of the Ce–Mn–TiO₂ and Ce–Mn–Fe/TiO₂ catalyst are shown in Fig. 9(a). The spectrum of Ce 3d contained eight peaks, six of which are the characteristic peaks of Ce³⁺ and two of which are the characteristic peaks of Ce⁴⁺. The relative surface concentration of the element valence was calculated by the peak area shown in Table 2. The ratio of Ce³⁺/Ce⁴⁺ decreased from 84.0% to 86.2% after Fe was doped onto the Ce–Mn/TiO₂ catalyst. The catalytic effect of MnO₂ was related to its valence state, where MnO₂ > Mn₃O₄ > MnO₃²⁻ this has also been demonstrated by Boningari et al.³⁸ indicating that MnO₂ was the most active among a series comprising MnO₂, Mn₃O₄, Mn₂O₃ and MnO₄.

The XPS spectra of Ti 2p of the Ce–Mn/TiO₂ and Ce–Mn–Fe/TiO₂ catalysts are shown in Fig. 9(c). The spectrum peaks of Ti 2p₁/₂ and Ti 2p₃/₂ at the binding energy of 458.6 eV and 464.3 eV, respectively, are attributable to the characteristic peak of Ti⁴⁺ and Ti³⁺.²⁹ Compared to Ce–Mn/TiO₂ catalyst, the Ti 2p peak position of the Ce–Mn–Fe/TiO₂ catalyst was shifted to the right by approximately 0.3 eV, indicating some of the Ti⁴⁺ ions were reduced to Ti³⁺ ions. The Ti⁴⁺/Ti³⁺ ratio increased from 36.8% to 49.6% after the addition of Fe as shown in Table 2. The high reducibility of Ti contributes to the improvement of the NH₃-SCR efficiency. The redox cycle of Ti⁴⁺/Ti³⁺ is hypothesized to be another reason for the high SCR performance at low-temperature conditions.

The XPS spectra of Fe 2p of the Ce–Mn/TiO₂ and Ce–Mn–Fe/TiO₂ catalysts are shown in Fig. 9(d). The spectrum peaks of Fe 2p₁/₂ and Fe 2p₃/₂ are at the binding energy of 710.4 eV and 724.0 eV respectively, which are mainly assigned to Fe³⁺ and Fe²⁺.³⁰ However, the Fe 2p₃/₂ peak is obviously an asymmetrical distribution and the peak is broad, indicating the existence of Fe⁵⁺. Moreover, compared to the standard spectrum of Fe, the binding energy of Fe 2p₃/₂ was shifted to a higher energy. This is because of the strong interaction between Fe and Mn or Ce led to the change of the electron cloud of Fe. The ratio of Fe⁵⁺/Fe³⁺ was 8.28 as shown in Table 2. The Fe element mainly existed in the form of Fe³⁺ in the catalyst, which can be reduced to Fe²⁺. The Fe redox cycles Fe⁵⁺/Fe³⁺ is hypothesized to be another reason for the high SCR performance at low-temperature conditions.

The XPS spectra of O 1s of the Ce–Mn/TiO₂ and Ce–Mn–Fe/TiO₂ catalysts are shown in Fig. 9(e). The spectrum of O 1s contains characteristic peaks of O₂ and Oₐ, where O₂ belongs to the characteristic peak of lattice oxygen at a binding energy of 529.5–529.8 eV, and Oₐ belongs to the surface adsorption characteristic peaks of oxygen at a binding energy of 531.8–532.5 eV.³⁴ The relative surface concentration of the element valence calculated by the peak area is shown in Table 2. The surface adsoption of the oxygen concentration on the Ce–Mn/TiO₂ catalyst was 43.6% and remained unchanged after Fe was doped onto the Ce–Mn/TiO₂ catalyst. The high concentration of the surface adsoption oxygen had a strong oxidation effect, which not only completed the oxidation and reduction cycle, but also enhanced the oxidation process of NO to NO₂. This promoted a rapid response to the SCR reaction.⁴¹ Eqn (2)

\[
\text{Mn}^{4+} + \text{Ce}^{3+} \leftrightarrow \text{Mn}^{3+}/\text{Mn}^{2+} + \text{Ce}^{4+}
\]
In summary, the Fe-doped Ce–Mn/TiO₂ catalyst increased the number of weak and medium strength acidic sites, and properties of the catalyst were analyzed using XRD, BET, XPS, H₂-TPR, and NH₃-TPD. Doping the catalyst with Fe also increased the surface area, which increased NH₃ adsorption on the catalyst to boost the low-temperature SCR activity. Moreover, the addition of Fe enhanced the redox performance of the catalyst which accelerated the electron transfer.

Based on the XPS analysis results, the high ratios of Mn⁴⁺/Mn³⁺ or Mn³⁺, Ce⁴⁺/Ce³⁺, and Ti⁴⁺/Ti³⁺ could form dual redox cycles as shown in eqn (2) and (3), which accelerated the electron transfer and improved the NH₃-SCR performance.⁸

\[
\text{Mn}^{4+} + \text{Ti}^{3+} \rightarrow \text{Mn}^{3+}/\text{Mn}^{2+} + \text{Ti}^{4+} \tag{3}
\]

In summary, the Fe-doped Ce–Mn/TiO₂ catalyst increased the number of weak and medium strength acidic sites, and properties of the catalyst were analyzed using XRD, BET, XPS, H₂-TPR, and NH₃-TPD. Doping the catalyst with Fe also increased the surface area, which increased NH₃ adsorption on the catalyst to boost the low-temperature SCR activity. Moreover, the addition of Fe enhanced the redox properties of the catalyst which accelerated the electron transfer.⁸ Based on the XPS analysis results, the high ratios of Mn⁴⁺/Mn³⁺ or Mn³⁺, Ce⁴⁺/Ce³⁺, and Ti⁴⁺/Ti³⁺ could form dual redox cycles as shown in eqn (2) and (3), which accelerated the electron transfer and improved the NH₃-SCR performance.⁸

Conclusions

The modification of Ce–Mn/TiO₂ catalysts by doping Fe, Cu, or Co revealed that Cu doping significantly decreased the low-temperature NH₃-SCR activity. Co doping had little obvious effect on NH₃-SCR low-temperature activity. Fe doping effectively improved the low-temperature NH₃-SCR activity. The NO conversion rate in the presence of the Ce–Mn–Fe/TiO₂ catalyst achieved 96% at the low temperature of 100 °C. The NO conversion was maintained at 90% between 100 and 280 °C. Fe doping also reduced the sulfur-poisoning resistance for SCR. In the presence of 100 ppm SO₂, the catalytic activity continued to decline and the NO conversion dropped to approximately 40% after 5 h at 160 °C. The SO₂ poisoning was the main reason for the decrease in catalytic activity. XRD, BET, H₂-TPR, NH₃-TPD and XPS characterization results demonstrated that Fe₂O₃ was dispersed and well-proportioned on the surface of the catalyst. Fe-doping Ce–Mn/TiO₂ catalysts increased the specific surface area, enhanced the redox performance, and increased the surface acidity, especially to the medium strength acidic sites. Fe-doping had little impact on the valence states of other elements on the surface which still maintained a high proportion of Ce⁴⁺/Ce³⁺, Mn⁴⁺/Mn³⁺, Ti⁴⁺/Ti³⁺ and O₂/O₃, respectively. The redox cycles between Mn, Ce, Fe, and Ti were one reason for the excellent low-temperature NH₃-SCR efficiency. In summary, Fe-doped Ce–Mn/TiO₂ catalysts were observed to be environmentally friendly, effective, and an attractive catalyst for low-temperature SCR, especially at temperature ranges of less than 150 °C.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We would like to thank the Beijing Nova Program (No. Z171100001117058), Beijing Municipal Science and Technology Project (No. Z16110000136010, D141100002814001), National Key Research and Development Plan (No. 2016YFC0303701) and the Science Foundation of China University of Petroleum-Beijing (No. C201604, 2462014YJRC) for the support. This material is also supported by the National Institute of Food and Agriculture, U.S. Department of Agriculture, and McIntire Stennis under accession number 1009735.
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