N-doped graphene and TiO$_2$ supported manganese and cerium oxides on low-temperature selective catalytic reduction of NO$_x$ with NH$_3$

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Abstract: A series of N-doped graphene (NG) and TiO$_2$ supported MnO$_x$–CeO$_2$ catalysts were prepared by a hydrothermal method. The catalysts with different molar ratios of Mn/Ce (6 : 1, 10 : 1, 15 : 1) were investigated for the low-temperature selective catalytic reduction (SCR) of NO$_x$ with NH$_3$. The synthesized catalysts were characterized by HRTEM, SEM, XRD, BET, XPS, and NH$_3$-TPD technologies. The characterization results indicated that manganese and cerium oxide particles dispersed on the surface of the TiO$_2$–NG support uniformly, and that manganese and cerium oxides existed in different valences on the surface of the TiO$_2$–NG support. At Mn element loading of 8 wt%, MnO$_x$–CeO$_2$(10 : 1)/TiO$_2$–1%NG displayed superior activity and improved SO$_2$ resistance. On the basis of the catalyst characterization, excellent catalytic performance and SO$_2$ tolerance at low temperature were attributed to the high content of manganese with high oxidation valence, extensive oxidation of NO into NO$_2$ by CeO$_2$ and strong NO adsorption capacity, and electron transfer of N-doped graphene.

Keywords: low-temperature; selective catalytic reduction (SCR); N-doped graphene (NG); manganese and cerium oxides

1 Introduction

Nitrogen oxides (NO$_x$) are one of the main atmospheric pollutants, which have given rise to a variety of health-related and environmental issues [1–3]. The environmental effects of nitrogen oxides (NO$_x$) include formation of photochemical smog, acid precipitation, greenhouse effect, ozone depletion, and fine particles.

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Selective catalytic reduction (SCR) is most widely used in flue gas denitrification technology. The reaction mechanism of SCR technique is that the reducing agent (usually NH$_3$) selectively reduces NO$_x$ to N$_2$ under the action of the catalyst in an oxygen-containing atmosphere. In recent years, low-temperature selective catalytic reduction (SCR) with NH$_3$ is a promising method to remove NO$_x$ in flue gas because the catalyst unit can be located downstream of the particulate control device and desulfurization system, where the temperature is declined to 120–180 °C [4–6]. Mn-based catalysts
exhibit excellent DeNO_x activity at low temperature of 80–220 °C, such as MnO_x–CeO_2/TiO_2, MnO_x–FeO_2/TiO_2, and so on [7–11]. Because manganic oxides have a variety of different surface active oxygen, they can be used to complete the catalytic cycle. But SO_2 in the exhaust gas could easily lead to serious poisoning effect on SCR catalytic in the low-temperature range [12,13]. Ce-based NH_3-SCR catalysts have also been widely studied due to the high oxygen storage capacity and excellent redox properties of CeO_2 [14–16]. Therefore, low-temperature SCR catalysts with high activity and good SO_2 resistance have obtained wide concern [17,18].

In the past years, graphene has drawn an amount of attention as a promising candidate for wide applications in catalysis due to unique two-dimensional monolayer structure, and physical and chemical properties [19–22]. It has a large specific surface area, high electron mobility, and high stability, and is widely used in the study of heterogeneous catalyst support [23–28]. The graphene-supported catalytic system exhibits many special catalytic activities. By introducing graphene into the catalyst, the loading of the active component (MnO_x) is improved, and hence the catalytic activity is enhanced [6]. Some researches indicated that incorporation of nitrogen into the carbon structures enhances the SCR activity [29,30]. N element can be doped through post treatment of graphene or GO, such as hydrazine reduction, and thermal annealing in ammonia method [31–33]. It has been well established that the incorporation of N atoms into the graphene matrix can lead to three main types of N formats, including graphitic N with direct substitution structure, and pyridinic N and pyrrolic N structures [34]. Through the surface functionalization to form a controllable chemical defect, the special physical and chemical properties of N-doped graphene play a role in increasing the active site of the supported catalyst. The pyridine-like N is absorbing nitric oxide (NO) more easily than the graphite-like N [35]. It has been discovered and reported that N-doped graphene can be used as a new catalyst for the oxygen reduction reaction [36], C–H bond activation reaction [37], reduction of nitro compounds [38], oxidation of benzylic alcohols [39], and electrochemical biosensing [40]. However, there is few report about N-doped graphene for SCR reactions.

We recently found that the hydrothermal synthesis method has the advantages of simplicity, high efficiency, high purity, and good homogeneity. The Mn–Ce–Ti mixed oxide catalyst prepared by the hydrothermal method exhibited excellent NH_3-SCR activity and strong resistance against H_2O and SO_2 with a broad operating temperature window [41]. The purpose of this work is to study the effect of NH_3-SCR on the removal of NOx in flue gas at low temperature and to develop low-temperature SCR denitrification catalyst with high activity and high durability with MnO_x, CeO_2, N-doped graphene, and TiO_2 as main components. In this work, a series of MnO_x–CeO_2/TiO_2–1%NG catalysts were prepared by the hydrothermal method, which few researchers have concerned about. To fully examine the structure and catalytic mechanism, the catalysts were characterized by SEM, HRTEM, XRD, BET, NH_3-TPD, and XPS.

2 Experimental

Expandable graphite (50 mesh) was supplied by Qingdao Tianhe Graphite Co., Ltd. Manganous nitrate (50% solution), and cerium (III) nitrate hexahydrate (Ce(NO_3)_3·6H_2O, 99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Sodium nitrate (NaNO_3, 99.0%), urea (H_2NCONH_2, 99.0%), and ammonia solution (NH_3, 25%–28%) were purchased from Modern Oriental (Beijing) Technology Development CD., Ltd. Potassium permanganate (KMnO_4, 99.3%), hydrogenperoxide (H_2O_2, 30%), sulfuric acid (H_2SO_4, 97%), hydrochloricacid (HCl, 36.5%–38%), and titanium dioxide (TiO_2, 98.5%) were purchased from Beijing Chemical Reagent Company. All of the chemical reagents were of analytical grade and used as received without further purification. All aqueous solutions were prepared using deionized water.

2.1 Preparation of graphene oxide (GO)

GO is obtained by chemical oxidation treatment, which is synthesized by a pressurized oxidation [42]. Graphite, KMnO_4, sulphuric acid (98%), and a Teflon reactor were completely cooled in a refrigerator at 0–4 °C before use. The Teflon reactor was placed in a stainless steel autoclave. The cooled graphite (2 g) and KMnO_4 (8 g) were put into the reactor, and then, sulphuric acid (60 mL) was added. As soon as the sulphuric acid was added, the reactor and stainless steel autoclave were covered and fasten down. The autoclave was kept at 0–4 °C for 1.5 h and then heated at 100 °C in an oven for 1.5 h. The obtained mud was diluted with 1 L
water. With mechanical stirring, \( \text{H}_2\text{O}_2 \) (30%) was dripped into the suspension until the slurry turned golden yellow. The suspension was washed with hot HCl and deionized water until the pH reached 7, and humid graphite oxide was obtained. After drying, 1 g of GO was added under stirring to 1 L of deionized water. The suspension was placed in an ultrasonic bath for 3 h and then centrifuged at 4000 rpm. The supernatant, consisting of a dispersion of GO with a concentration of about 1 mg/mL, was finally recovered and used for the N-doped graphene preparation.

2.2 Preparation of N-doped graphene (NG)

0.9 g of urea was added to 60 mL of GO dispersion under magnetic stirring for 30 min. The mass ratio of GO to urea was 1 : 30 [43]. The suspension was placed in autoclave at 160 \(^\circ\)C for 3 h, and then washed several times. The precipitation was dried. Finally, the product was tagged as NG.

2.3 Synthesis of catalyst

The MnO\(_x\)-CeO\(_2\)/TiO\(_2\)–1%NG catalysts were prepared with different molar ratios of Mn/Ce by the hydrothermal method. Mn element accounted for 8 wt% of catalyst quality. Appropriate amounts of Mn(NO\(_3\))\(_2\), Ce(NO\(_3\))\(_3\)·6H\(_2\)O, NG, and TiO\(_2\) were dissolved in deionized water at room temperature and stirred for 20 min, and then ammonia solution (25 wt%, 20 mL) was slowly added to the above solution under vigorous stirring until pH = 11 was achieved. After stirring for 30 min, the obtained suspension was transferred to a 250 mL Teflon-sealed autoclave and allowed to react at 130 \(^\circ\)C for 12 h. The precipitate was separated by centrifugation and washed several times with deionized water and ethanol, respectively. The resulting powder was dried at 100 \(^\circ\)C for 12 h, and then calcined in a tubular furnace in a nitrogen atmosphere at 450 \(^\circ\)C for 3 h. For comparison, MnO\(_x\)-CeO\(_2\)/TiO\(_2\) and MnO\(_x\)/TiO\(_2\)–1%NG were also prepared by the same preparation method as described above.

2.4 Catalyst characterization

The morphology of the samples was characterized by scanning electron microscopy (SEM; Quanta 250 FEG, FEI, USA), and high-resolution transmission electron microscopy (HRTEM; JEM-2100, JEOL, Japan). The structure of the samples was determined by X-ray diffraction (XRD) performed on a Bruker D8 Advance diffractometer, running at 60 kV and 30 mA. The specific surface areas were calculated from adsorbed nitrogen volume by an automatic volumetric apparatus following standard Brunauer–Emmett–Teller (BET) theory, with a Micromeritics ASAP2020 equipment by N\(_2\) physisorption at 77 K. Temperature-programmed desorption of NH\(_3\) (NH\(_3\)-TPD) was conducted using a TPS080 auto-adsorption apparatus (XQ, Tianjin). The catalysts (150 mg) were pretreated at 300 \(^\circ\)C in a flow of N\(_2\) (30 mL/min) for 0.5 h and cooled to 100 \(^\circ\)C under N\(_2\) flow. Then the samples were exposed to a flow of NH\(_3\) at 100 \(^\circ\)C for 1 h, followed by N\(_2\) purging for 0.5 h. Finally, the reactor temperature was raised to 600 \(^\circ\)C under N\(_2\) flow at a constant rate of 10 \(^\circ\)C/min. The X-ray photoelectron spectroscopy (XPS) was carried out to analyze surface chemical composition and the valence state of the metal species on the surface of the catalysts on an Escalab 250 xi spectrometer (Thermo, USA) with Al K\(_\alpha\) radiation source, and the binding energy was corrected using the C 1s spectrum at 284.8 eV.

2.5 SCR performance test

SCR activity measurement was performed in a fixed-bed reactor using the catalyst of 40–60 mesh at 100–200 \(^\circ\)C by ZHKPR Instrument Co., Ltd. (Chengdu, China). The reactor was placed in an electrically heated furnace with the typical reaction gas consisted of 500 ppm NO, 500 ppm NH\(_3\), 6 vol% O\(_2\), 100 ppm SO\(_2\) (when used), balance N\(_2\) gas, and GHSV = 30000 h\(^{-1}\). The inlet and outlet concentrations of NO\(_x\) were continually measured by an analyzer (Testo 350, Germany). All the data were obtained after 20 min as the SCR reaction reached steady state. NO\(_x\) conversion was calculated according to the following formula:

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

where [NO\(_3\)]\(_{\text{in}}\) and [NO\(_3\)]\(_{\text{out}}\) represent the inlet and outlet concentrations of NO\(_x\) under steady-state status, respectively.

3 Results and discussion

3.1 Morphology and texture

The TEM image in Fig. 1(a) shows that N-doped graphene is transparent with some clearly visible wrinkles, suggesting that NG is mainly composed of few layers. Because the sheets have a high specific
surface area, in order to reduce the surface energy, there will be overlapping phenomenon. Figure 1(b) shows the TEM image of the MnO$_x$–CeO$_2$/TiO$_2$–1%NG catalyst at a Mn/Ce molar ratio of 10:1. It is clear that a large number of TiO$_2$ nanoparticles ranging from 100 to 200 nm with an average particle size of ca. 150 nm, are anchored onto the stacked and wrinkled NG sheets. The corresponding HRTEM image reveals clear lattice fringes. Figure 1(c) shows the fringe spacing is 0.352 nm, corresponding to the (101) plane of anatase TiO$_2$. The low-magnification SEM image in Fig. 1(d) indicates that MnO$_x$–CeO$_2$ and TiO$_2$ nanoparticles are anchored onto the surface of NG sheets and some particles aggregate together. A large amount of the catalyst nanoparticles uniformly disperse on the surface of the N-doped graphene carrier and the surface area of the MnO$_x$–CeO$_2$/TiO$_2$–1%NG catalyst is greatly increased.

3.2 GO and NG by XPS

In order to investigate the effect of urea on GO reduction and nitrogen doping in hydrothermal process, XPS was used to qualitatively and quantitatively analyze the samples. It can be seen from the XPS full spectra (Fig. 2(a)) that the intensity of the O 1s (531.3 eV) peak is significantly reduced after the hydrothermal reaction, indicating that GO is reduced. N 1s (~399.3 eV) peak of NG is also observed indicating that nitrogen element is doped into the sample, and N element content is up to 6.33% as shown in Table 1. C=C (284.6 eV), C–O/C–O–C (286.9 eV), and C=O (288.2 eV) are found in the C 1s XPS spectra of GO (Fig. 2(b)) and NG (Fig. 2(c)). After hydrothermal process, the content of C–O (286.9 eV) is significantly reduced in NG (Fig. 2(c))
compared to that in GO (Fig. 2(b)), which indicates GO is reduced with urea. A C–N peak (285.9 eV) is appeared (Fig. 2(c)). N atoms are divided into “pyridinic N” (398.2 eV), “pyrrolic N” (399.5 eV), and “graphitic N” (401.5 eV) as shown in Fig. 2(d), which replace the C atoms in the graphene lattice [43]. Nitrogen atoms of NG due to its basic nature should have affinity towards weakly acidic molecules like NO. The presence of nitrogen in the carbon matrix was reported to enhance adsorption of NO [29,35], which may cause an electron transfer from the support surface to the NO molecules. Table 1 lists the surface atomic concentrations of GO and NG. Consequently, GO is reduced with urea after the removal of a large number of oxygenated functional groups, and nitrogen element is doped into the graphene lattice.

3.3 XRD analysis of the catalysts

Figure 3 shows the XRD patterns of the MnO$_x$–CeO$_2$/TiO$_2$–1%NG, MnO$_x$–CeO$_2$/TiO$_2$, and TiO$_2$–1%NG. All diffraction peaks could be readily indexed to anatase TiO$_2$ (JCPDS Card No. 21-1272). Anatase TiO$_2$ presents an abundance of active sites, which can enhance the SCR activity of the catalyst. Peaks at 2θ values of 25.3°, 37.8°, 48.1°, 53.9°, 55.0°, 62.7°, 68.7°, 70.3°, and 75.1° are respectively indexed to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase TiO$_2$ [26]. The diffraction peaks of MnO$_x$ are characteristic of Mn$_2$O$_3$ (JCPDS Card No. 06-0540) in MnO$_x$–CeO$_2$/TiO$_2$–1%NG and MnO$_x$–CeO$_2$/TiO$_2$ peaks at 2θ values of 28.9°. The weak diffraction peaks at 33.1° can be attributed to ceria with a cubic fluorite structure (JCPDS Card No. 34-0394), and the weak diffraction peaks at 37.1° can be attributed to MnO$_2$ (JCPDS Card No. 30-0820) [6]. The above two peaks have only been found in MnO$_x$–CeO$_2$/TiO$_2$. Furthermore, the peak intensities of MnO$_x$–CeO$_2$/TiO$_2$–1%NG are lower than those of MnO$_x$–CeO$_2$/TiO$_2$, indicating that the addition of NG results in the lower crystallinity of MnO$_x$–CeO$_2$. However, characteristic diffraction peaks for MnO$_2$ and CeO$_2$ are not obvious in the MnO$_x$–CeO$_2$/TiO$_2$–1%NG and MnO$_x$–CeO$_2$/TiO$_2$ because of the amorphous nature [45].

3.4 BET surface area and pore size distribution

Detailed data of the specific surface area, pore volume, and pore size of MnO$_x$–CeO$_2$/TiO$_2$ and MnO$_x$–CeO$_2$/TiO$_2$–1%NG are listed in Table 2. Through adding NG, MnO$_x$–CeO$_2$/TiO$_2$–1%NG has a larger specific surface area than MnO$_x$–CeO$_2$/TiO$_2$, which leads to the high dispersion in the metal oxide composite with the support. The nitrogen adsorption–desorption isotherms are displayed in Fig. 4. According to the Brunauer–Deming–Deming–Teller (BDDT) classification, the majority of physisorption isotherms could be classified into six types. As shown in Fig. 4, MnO$_x$–CeO$_2$/TiO$_2$ and MnO$_x$–CeO$_2$/TiO$_2$–1%NG could both be classified into the representative type IV adsorption–desorption isotherm with an H3-type hysteresis loop [6]. The samples have mesoporous structure, which could be derived from the packing of the nanoparticles. MnO$_x$–CeO$_2$/TiO$_2$–1%NG presents larger pore volume than MnO$_x$–CeO$_2$/TiO$_2$. As illustrated in Table 2, the pore distribution of MnO$_x$–CeO$_2$/TiO$_2$ and MnO$_x$–CeO$_2$/TiO$_2$–1%NG shows an average pore size of 13.20 and 13.03 nm, respectively. In general, the larger specific surface area is expected to be beneficial to offer more active sites and increase the adsorption of reactants in

![Table 1: C, N, O surface atomic concentrations of GO and NG](image)

![Table 2: Porous structure parameters of MnO$_x$–CeO$_2$/TiO$_2$ and MnO$_x$–CeO$_2$/TiO$_2$–1%NG catalysts](image)
those in the fresh catalyst. N element content of the spent catalyst slightly reduces relative to the fresh catalyst. As shown in Fig. 5(a), peak-fitting deconvolution separates the Mn 2p3/2 spectra into three characteristic peaks attributed to Mn2+ (640.8 eV), Mn3+ (641.8 eV), and Mn4+ (643.4 eV). The Mn 2p1/2 spectra show two peaks at 653.88 eV (Mn4+) and 653.0 eV (MnOx/Mn) [26]. The presence of multiple-valence manganese oxides contributes to the oxidation–reduction reaction. Furthermore, the relative surface content of manganese oxides with different valences also changes, which plays an important role in improving the electron transfer and low-temperature SCR activity of MnOx–CeO2–TiO2–1%NG catalysts. It is noted that the relative surface content of Mn4+/Mn over MnOx–CeO2–TiO2–1%NG (37.9%) is much higher than that over MnOx–CeO2/TiO2 (32.6%). It is clear that much more Mn4+/Mn species are exposed on the surface of MnOx–CeO2/TiO2–1%NG, while the Mn4+ species and their redox cycle might be beneficial for the high activity in the NH3-SCR reaction at low temperature, attributed to the enhancement of NO reduction to N2. Active components are highly dispersed on the surface of the catalyst support by introduction of NG, which affects the surrounding electronic state of manganese species, may also explain the improvements in SCR activity observed in this work.

3.5 Chemical composition by XPS

To obtain the information on the atomic concentration and element chemical state of manganese or cerium species in the catalysts, the surface of samples was further investigated by XPS. Figure 5 illustrates the XPS spectra of Mn 2p, Ce 3d, and O 1s. The atomic surface compositions of MnOx–CeO2/TiO2, fresh and spent MnOx–CeO2/TiO2–1%NG have been summarized by XPS in Table 3. Results show that MnO2 and MnO/Mn contents of the spent catalyst increase relative to the catalytic reaction, resulting in the excellent catalytic performance of MnOx–CeO2/TiO2–1%NG.

Table 3 Atomic surface compositions of MnOx–CeO2/TiO2 and MnOx–CeO2/TiO2–1%NG (fresh, spent) obtained by XPS

| Sample                                | Atomic composition (%) |
|---------------------------------------|------------------------|
|                                       | C  | N  | Mn | Ce | Ti | Oα  | Oβ  | MnO/Mn | MnO2/Mn | MnO2/Mn | MnO3/Mn |
| MnOx–CeO2/TiO2                        | —  | —  | 4.2| 2.3| 39.5|54.0 |14.8 |0.151  |0.358    |0.326    |0.165    |
| MnOx–CeO2/TiO2–1%NG (fresh)           | 9.5| 0.5| 4.6| 2.5| 25.6|57.3 |16.3 |0.073  |0.352    |0.379    |0.196    |
| MnOx–CeO2/TiO2–1%NG (spent)           | 9.2| 0.4| 4.7| 2.4| 25.3|58.0 |16.7 |0.080  |0.350    |0.382    |0.188    |

Fig. 4 Nitrogen adsorption–desorption isotherms of the catalysts: (a) MnOx–CeO2/TiO2 and (b) MnOx–CeO2/TiO2–1%NG.

Fig. 5 XPS spectra for (a) Mn 2p, (b) Ce 3d, and (c) O 1s of the catalysts: (A) MnOx–CeO2/TiO2 and (B) MnOx–CeO2/TiO2–1%NG.
The Ce 3d spectrum is presented in Fig. 5(b). The peaks are attributed to 3d_{3/2} and 3d_{5/2} spin-orbit states. The peaks at the binding energy of 882.4 (v), 898.9 (v’), 900.5 (u), 907 (u”), 916.9 (u”’) eV are assigned to Ce^{4+}. The peaks at the binding energy of 885.4 (v’) and 904.5 (u’) are assigned to Ce^{3+} species [6]. Results imply that Ce^{4+} is the main valence state in MnO_x–CeO_2/TiO_2–1%NG catalyst. No obvious difference is observed from the Ce 3d XPS spectra of MnO_x–CeO_2/TiO_2 and MnO_x–CeO_2/TiO_2–1%NG samples.

The XPS patterns of O 1s (Fig. 5(c)) show the presence of two types of surface oxygen in the samples. The peak at 529.4–529.7 eV corresponds to lattice oxygen (O_{β}), while that at 531.6–532.0 eV is assigned to chemisorbed oxygen (O_{α}, surface-adsorbed oxygen), such as O_2^2– or O^–, in the form of OH^– and CO_3^2– [26]. According to the XPS analysis, the surface concentration of O_{α} species on MnO_x–CeO_2/TiO_2–1%NG is higher than that on MnO_x–CeO_2/TiO_2. It has been demonstrated that O_2 species are more active than O_{β} species, due to their higher mobility [46]. Hence, the higher concentration of O_{α} species is beneficial to the NH_3-SCR of NO, resulting in the promotion of the reduction of NO and the subsequent facilitation of the “fast SCR” reaction.

3. 6 Acidic properties

The adsorption and activation of NH_3 at active sites of the catalysts play an important role in the NH_3-SCR reaction. NH_3-TPD was performed to investigate the surface acid amount and strength of the catalysts, and the corresponding results are shown in Fig. 6(b). The area and position of these desorption peaks directly relate to the amounts of acidic sites and their acidic strength, respectively. One broad peak spanning the temperature range of 100–250 °C is observed for both samples, attributed to physisorbed NH_3 and NH_3 at weak acid sites. The NH_3-TPD physisorption is too weak to activate NH_3 molecules, while the adsorbed NH_3 species on strong acid sites are hardly to desorb, which make not much contribution to low-temperature NH_3-SCR reaction. Therefore, we focus on the adsorption of NH_3 molecules on medium-strong acid sites. The desorption peak at 306 °C of the MnO_x–CeO_2/TiO_2–1%NG is obviously higher than MnO_x–CeO_2/TiO_2 as shown in Fig. 6. It is considered that the peak area correlates with the acid amount. This indicates that MnO_x–CeO_2/TiO_2–1%NG catalysts have more acid sites than MnO_x–CeO_2/TiO_2, which may be due to the increase in specific surface area of MnO_x–CeO_2/TiO_2–1%NG and improve the dispersion of the catalyst nanoparticles. Therefore, MnO_x–CeO_2/TiO_2–1%NG has a stronger acid intensity due to the addition of NG. The difference in the strength and the number of acid sites on the two catalysts might lead to the distinction of their catalytic performances. In other word, MnO_x–CeO_2/TiO_2–1%NG catalyst possesses the largest amount of NH_3 molecules, and further promotes the enhancement of catalytic performance for NH_3-SCR reaction.

3. 7 Catalytic activity

Figure 7 shows the NH_3-SCR activity of these prepared catalysts with the variation in temperature. It can be seen that the NO_x conversion over all the catalysts increases with increasing temperature in 80–200 °C. The loading of manganese element is 8 wt%, together with different molar cerium supported on TiO_2–1%NG. When the Mn/Ce molar ratio is 10 : 1, the NO_x conversion is up to 99% at 160 °C. Further when the Mn/Ce molar ratio is 6 : 1, NO_x conversion decreases evidently. MnO_x–CeO_2(10 : 1)/TiO_2–1%NG samples have higher SCR activity compared to MnO_x–CeO_2(10 : 1)/TiO_2 in the temperature region. It also can be seen that the MnO_x–CeO_2(10 : 1)/TiO_2–1%NG samples have higher SCR activity compared to MnO_x–CeO_2 (10 : 1)/TiO_2 in the whole temperature region. The reaction mechanism may be gaseous NH_3 molecules are adsorbed onto the acid sites to form NH_4^+ ions, and then the formed molecules of NO_2 react with adjacent NH_4^+ ions to produce N_2 and H_2O [29]. Nitrogen atoms of NG as a basic center can adsorb acid gas NO and the increased adsorption may be associated with an electron transfer between the support surface to the NO molecule, which is oxidized NO_2. The reaction is probably the rate-determining step for SCR reaction of catalysts. This demonstrates that NG improves
interaction of the species, which possibly provides more effective contact with the reactants resulting in the process of NO adsorption oxidation.

3.8 Influence of SO2

The SO2 resistance effects of the catalysts on NOx conversion at 160 °C are investigated in Fig. 8. It is obvious that the NG in MnOx–CeO2/TiO2–1%NG plays a great role in the high catalytic activity. It shows that when 100 ppm SO2 is added to the system, the NOx conversion of MnOx–CeO2(10 : 1)/TiO2–1%NG decreases from an initial value of 99% to 55% in 2 h. And when SO2 is removed from the flue gas, the activity of MnOx–CeO2(10 : 1)/TiO2–1%NG reaches a stable level of about 49%. For MnOx–CeO2/TiO2 resistance to SO2, SCR reaction system was also studied and a similar phenomenon is observed. The NOx conversion markedly decreases to 50% in 2 h and is finally restored to 41%. For MnOx/TiO2–1%NG resistance to SO2, the NOx conversion markedly decreases to 32% in 2 h and is finally restored to 26%. These indicate that the NOx conversion of MnOx–CeO2/TiO2–1%NG obviously decreases but a relatively higher activity is still maintained compared with MnOx–CeO2/TiO2 and MnOx/TiO2–1%NG. The results indicate that introduction of NG and Ce enhances the resistance of Mn-based catalysts to SO2. A possible reason is that nitrogen functional group of NG due to its basic nature can absorb acid gas SO2. Consequently, NG can act as a SO2 trap to limit the sulfation of the main active phase when exposed to SO2. Introduction of Ce inhibits the formation of manganese sulfates, lowers the probability of surface active site poisoning by SO2, and decreases by-products, such as NH4SO3 and NH4HSO4, all of which could improve the resistance of the catalyst to SO2 poisoning during low-temperature SCR.

4 Conclusions

In summary, a series of MnOx–CeO2/TiO2–1%NG catalysts were successfully prepared with different molar ratios of Mn/Ce by the hydrothermal method. The obtained results of HRTEM images and XRD patterns showed the anatase TiO2 and several valences of amorphous manganese and cerium oxides were uniformly distributed on the surface of the catalysts. Among the catalysts prepared, MnOx–CeO2(10:1)/TiO2–1%NG catalyst exhibited the highest SCR activity (up to 99% at 160 °C). MnOx was observed as MnO, MnO2, Mn2O3, and non-stoichiometric MnOx/Mn in the samples by XPS. Redox reactions were likely to occur in the presence of manganese oxides with multiple valence states. The introduction of NG could be associated with the high specific surface areas, which provided more active sites to adsorb and activate reagents. In particular, active sites on the surface of NG adsorb NO molecular. Addition of Ce increased chemisorbed oxygen on the catalyst surface and promoted NO oxidation into NO2, thereby improving the redox performance of the catalyst. MnOx–CeO2(10:1)/TiO2–1%NG exhibited a large surface area, high activity, and improved resistance to SO2 at low temperatures. This work enhanced the low-temperature NH3-SCR performance and SO2 tolerance of catalysts by adding NG and promoted the practical application of these catalysts in low-temperature SCR.

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