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Article

Effects of cerium on the selective catalytic reduction activity and structural properties of manganese oxides supported on multi-walled carbon nanotubes catalysts

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ABSTRACT

A series of manganese and cerium oxides supported on multi-walled carbon nanotubes (MWCNTs) catalysts for low-temperature NH_3 selective catalytic reduction (SCR) of NO_x were prepared by the pore volume impregnation method. The SCR activity of Mn-Ce/MWCNTs catalysts was compared with that of Mn/MWCNTs catalyst. The effects of Ce were characterized by transmission electron microscopy, N_2 adsorption-desorption, H_2 temperature-programmed reduction, X-ray photoelectron spectroscopy and X-ray powder diffraction. The results show that the addition of cerium oxides could improve the SCR activity of Mn/MWCNTs catalysts. Mn-Ce/MWCNTs catalyst with a Ce/Mn ratio of 0.6 was found to have the highest activity. The addition of cerium oxides enhanced the dispersion of metal oxides on the MWCNTs. It could also increase the specific surface area and total pore volume, and decrease the average pore size of the catalysts. Ce would improve the concentration of oxygen and the valence of manganese. Furthermore, from the XRD results, it was obvious that the crystalline MnO_x disappeared because of the introduction of Ce to the catalyst. MnO_x mainly existed in an amorphous state or microcrystal structure in the Mn-Ce/MWCNTs catalysts. CeO_2 was found to be the main phase for CeO_x .

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1. Introduction

Selective catalytic reduction (SCR) of NO_x with NH_3 is one of the most effective flue gas cleaning technologies for stationary sources. The catalyst is the most important part of the SCR technology, and it determines the efficiency of the SCR system. However, commercial catalysts ($\text{V}_2\text{O}_5\text{--WO}_3$ (MoO_3)/ TiO_2) for these processes are active within a narrow temperature window of 300–400 °C, and they will be deactivated by high concentrations of SO_2 or dust [1,2]. Therefore, developing

low-temperature SCR processes and catalysts, which can be installed after the desulfurizer and particulate removal device (below 200 °C), is of significant importance to prevent catalysts from being poisoned.

In the last decade, much of the literature focused on developing efficient SCR catalysts. A majority of the papers looked at active components and supports for low-temperature NH_3 SCR [3]. The $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{TiO}_x$ catalyst [4] has been reported to have high low-temperature SCR activity because of its high specific surface area, proper structure, high oxidizability, and high

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transfer capability of lattice oxygen. This catalyst allows for NO_x conversion of higher than 90% at reaction temperature of 200 °C. Zamudio et al. [2] prepared the Mn_{0.95}Ca_{0.05}Cr₂O₄ catalyst via gel combustion synthesis, and the catalyst showed that the highest NO conversion was at a reaction temperature of 125 °C. Yao et al. [5] found that the SCR activity of the γ-Fe₂O₃ catalyst was higher than 90% at 250 °C, which was attributed to the magnetism of γ-Fe₂O₃. Shen et al. [6] prepared a series of Ce-doped Mn/TiO₂-pillared clay catalysts and evaluated the effect of Ce on their performance in SCR reactions with H₂O and SO₂. The results show that Ce could improve SCR activity and catalyst resistance to SO₂.

Many transition metals and their oxides can be used as active components for the SCR catalysts, such as Mn, Ce, Fe, Pt, and Cr. Mn and Ce are among the most active transition metals because of their unique characteristics [2,5–8]. Manganese oxides exhibit strong redox abilities as there are many unstable lattice oxygen atoms on their surfaces [1,9–12]. Kang et al. [13] reported that the unloaded manganese oxide catalysts prepared by precipitation methods gave higher than 90% NO_x conversion at reaction temperature of 100 °C. It has been reported that CeO₂ presents excellent oxygen storage capacity because it can release and store oxygen according to the transformation between Ce⁴⁺ and Ce³⁺ [14]. Huang et al. [15] and Wu et al. [16] mentioned that the addition of Ce to SCR catalysts improved low-temperature SCR activity.

TiO₂, Al₂O₃, zeolite, and carbon materials have been widely studied for use as SCR catalyst supports [9,17–19]. Carbon materials have been reported to be excellent catalyst supports because of their high specific surface area, particular pore structure and high adsorptive properties. Carbon nanotubes (CNTs), as a special orderly carbon materials, have been widely reported as successful catalyst supports based on their unique electronic properties and structure, such as strong mechanical strength, good thermal stability, quantum confinement effect and good conductivity [24–26].

Based on previous investigation of Mn/MWCNTs catalysts, a series of Mn-Ce/MWCNTs catalysts were prepared for this study by the pore volume impregnation method. The effects of Ce on the catalyst structure and SCR activity were studied using transmission electron microscopy (TEM), nitrogen adsorption, X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), and SCR activity tests.

2. Experimental

2.1. Catalyst preparation

MWCNTs with outer diameters of 60–100 nm were purchased from Shenzhen Nanotech Port Co. Ltd and were purified with 3 mol/L HNO₃ solution for 4 h at 100 °C, then washed with distilled water and dried in a convection oven at 80 °C overnight. MWCNTs were then pretreated in oxygen dielectric barrier discharge (DBD) plasma at a discharge power of 15 W for 40 min. The purpose of the DBD plasma process is to introduce oxygen containing functional groups to the surfaces of the

MWCNTs, which improves the dispersion stability of MWCNTs in water. As a result, the introduction of active components to MWCNTs can be performed in water [27].

A series of Mn-Ce/MWCNTs catalysts were prepared by the pore volume impregnation method. Mixed solutions of manganese acetate and cerous nitrate were made with certain molar ratios of Ce/Mn and a constant Mn loading of 10 wt%. The mixed solution was then added to the beaker containing MWCNTs. This mixture was sonicated for 1 h for better dispersion of MWCNTs in the solution. After impregnation, the samples were dried in air at 100 °C for 12 h, then calcined in a tubular furnace in atmospheric conditions of air at the desired temperatures for 2 h. The catalysts were denoted as Mn-Ce(*x*)/MWCNTs, where *x* represents the molar ratio of Ce to Mn. When the manganese acetate or cerous nitrate was not added, the catalyst was denoted as Ce/MWCNTs or Mn/MWCNTs.

2.2. Catalyst activity test

The steady state SCR reaction was performed in a quartz tube (inner diameter was 12 mm) fixed-bed continuous flow reactor using 180 mg catalyst of 40–60 mesh. The typical reactant gas composition was NH₃ (0.1%), NO (0.1%), O₂ (5%), and the balance of Ar. Mass flow controllers controlled the gas flow rates. The gas hourly space velocity (GHSV) was fixed at 40000 h⁻¹. The inlet and outlet concentrations of NO_x were monitored by a NO_x analyzer (42i-HL, Thermo Ins.).

The NO_x removal efficiency was determined by the following equation: $X(\text{NO}_x) = (C_{\text{NO}_x}^{\text{in}} - C_{\text{NO}_x}^{\text{out}}) / C_{\text{NO}_x}^{\text{in}} \times 100\%$. Where $C_{\text{NO}_x}^{\text{in}}$ and $C_{\text{NO}_x}^{\text{out}}$ correspond to the inlet and outlet concentrations of NO_x, respectively.

2.3. Catalyst characterization

The morphologies of Mn-Ce/MWCNTs catalysts were investigated by a JEOL JEM-2100HR transmission electron microscope at an accelerating voltage of 200 kV. The point resolution was 0.23 nm, the enlargement factor was 50–1500000, and the acceleration voltage was 100–200 kV. The specific surface area, pore volume and pore size of the samples were determined by nitrogen adsorption on an ASAP 2020 M (Micromeritics, USA). Before testing, 0.1 g of the sample was pretreated for 1 h at 350 °C to remove any adsorbed gases. The measurement was performed at -196 °C (liquid nitrogen temperature) using a static-volumetric method. H₂-TPR experiments were performed with an Auto Chem II (Micromeritics, USA). The samples were pretreated in Ar at 350 °C for 1 h. Samples were then treated from 60 to 700 °C at a heating rate of 10 °C/min in 10% H₂/Ar (30 ml/min). The H₂ consumption was determined by a TCD detector. XPS (Axis Ultra DLD, Kratos, UK) was used to analyze the chemical state and surface composition of samples. All spectra were acquired at a basic pressure of 25×10^{-9} Torr with Al K_α radiation ($h\nu = 1486.6$ eV) at 15 kV. The binding energy calibration was performed using the C 1s peak in the background as the reference energy (284.6 eV). XRD measure-

ments were taken on a D8 Advance Diffractometer (Bruker, Germany) with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm, 40 kV, 40 mA) in the 2θ range of 5° – 90° . The XRD phases were identified by comparison with reference data files from the Joint Committee on Power Diffraction Standards (JCPDS).

3. Results and discussion

3.1. SCR activity of the catalysts

Patterns of the catalytic activity of Mn-Ce/MWCNTs catalysts are presented in Fig. 1. The results show that the NO_x conversions for all samples were within 20%–40% at reaction temperatures below 120°C . With increased reaction temperature, obvious differences in NO_x conversion appeared for all the samples, with most of the samples showing higher SCR activity. NO_x conversion reduced when the reaction temperature increased above 240°C . This was attributed to a competitive reaction with the SCR reaction. NH_3 was oxidized by oxygen in high temperature conditions, which has also been observed for some other catalysts [28–30].

For the Mn/MWCNTs catalyst, NO conversion was below 60% when the reaction temperature was lower than 180°C . The NO conversion sharply increased to 97.9% when the reaction temperature increased to 210°C . The conversion efficiency also remained above 90% at higher reaction temperatures. The active temperature window was large for this catalyst (210 – 300°C). In the case of Ce/MWCNTs catalyst, the NO_x conversion increased with an increase in the reaction temperature (60 – 300°C). However, the NO_x conversion efficiency was low, at 73.6% with reaction temperature of 300°C . Compared with the active temperature windows of the catalysts above, Mn-Ce/MWCNTs catalysts are active at lower temperatures. With an increased Ce/Mn ratio from 0.2 to 1.8, the active tem-

Fig. 1. SCR activity of various Mn-Ce(x)/MWCNTs catalysts. (1) Mn/MWCNTs; (2) Mn-Ce(0.2)/MWCNTs; (3) Mn-Ce(0.6)/MWCNTs; (4) Mn-Ce(1.2)/MWCNTs; (5) Mn-Ce(1.8)/MWCNTs; (6) Ce/MWCNTs.

perature window of the catalyst grew and then narrowed. With a Ce/Mn ratio of 0.6, the catalyst showed the highest catalytic activity and the largest active temperature window. Its NO_x conversion remained above 90% when the reaction temperature was within the range of 190 – 270°C .

To investigate the effects of Ce modification on the SCR activity of Mn/MWCNTs catalysts and the dispersion of Mn in MWCNTs, several catalysts listed below were selected to be further characterized, including Mn/MWCNTs, Ce/MWCNTs, Mn-Ce(0.6)/MWCNTs, and Mn-Ce(1.8)/MWCNTs catalysts.

3.2. Characterization of the catalysts

3.2.1. TEM results

The TEM images of the samples are shown in Fig. 2. From

Fig. 2. TEM images of various catalysts. (a) Mn/MWCNTs; (b) Ce/MWCNTs; (c) Mn-Ce(0.6)/MWCNTs; (d) Mn-Ce(1.8)/MWCNTs.

the image showing Mn/MWCNTs (Fig. 2(a)), it was found that MnO_x particles were uniformly dispersed on the surface of the MWCNTs with diameters between 10 and 40 nm. In Fig. 2(b), CeO_x particles agglomerated on the surface of the nanotubes. The diameters of the particles were from 50 to 100 nm. When both Ce and Mn were supported on MWCNTs (Figs. 2(c) and (d)), the dispersion of the metal oxide particles improved and the particle diameters were reduced to less than 10 nm. Reaction gases easily make good contact with the active sites on the surface of the Mn-Ce/MWCNTs catalysts, enhancing the SCR activity. When the Ce/Mn ratio reached 1.8 (Fig. 2(d)), the metal oxide particles aggregated together and some active sites became hidden. This kind of metal oxide agglomeration is loosened rather than pyknotic.

3.2.2. Nitrogen adsorption

Detailed textural data of the catalysts are summarized in Table 1. It was shown that for most of the catalysts except for the Ce/MWCNTs catalyst, the specific surface area was enlarged while the total pore volume and average pore size decreased after supporting the metal oxides. For the Ce/MWCNTs catalyst, because of the agglomeration of CeO_x particles, the specific surface area and total pore volume were reduced while the average pore size increased after loading with CeO_x . Comparing the four catalysts, it was observed that the addition of Ce increased the specific surface area and total pore volume while reducing the average pore size. After introducing Ce to the Mn/MWCNTs catalyst (Ce/Mn = 0.6), the average pore size decreased, but the specific surface area and the total pore volume increased by 24% and 18%, respectively. It was believed that metal oxide particles dispersed well on the surface of MWCNTs in an amorphous state or microcrystal structure based on the interactions between Ce and Mn atoms. A large number of tiny tunnels were formed and the metal oxides exposed enough to improve the specific surface area (TEM and XRD results). As the value of the Ce/Mn ratio continued increasing (1.8), the A_{BET} nearly doubled that of the Mn-Ce(0.6)/MWCNTs catalyst, and the total pore volume also continued to increase. The excess metal oxides aggregated together to form loosened particles after dispersing on the surface of the MWCNTs. However, the average pore volume is reduced sharply because of excess loading (Mn was 10 wt% and Ce was 45 wt%). The average pore size of the Mn-Ce(1.8)/MWCNTs catalyst was similar to that of the unloaded MnO_x - CeO_2 catalysts reported by Gong et al. [31] and Qi et al. [14], which had Ce/Mn ratios of 2.3 and 2.5, respectively. Considering the SCR activity, it is suggested that when the

Ce/Mn ratio is 0.6, the large specific surface area and proper pore structure would improve the SCR activity. However, the specific surface area and SCR activity did not always correlate well with each other. When the value of Ce/Mn was increased to 1.8, the SCR activity decreased with the larger specific surface area.

Tang et al. [1] reported that the catalytic activity variations of the different Mn-based catalysts could be attributed to the specific surface areas, phases and structures. A larger specific surface area enhances the adsorption of the reagent, and provides more reaction space to the catalytic reaction. This then improves the NO_x conversion efficiency [10]. Reactant gases could easily adsorb on the surface of catalysts and promote the SCR reaction at low temperatures. In Table 1, it was noted that the specific surface areas of different catalysts were quite different to others. However, their NO_x conversions were similar at reaction temperatures lower than 120 °C. It is indicated that the number of active sites on different Mn-Ce/MWCNTs catalysts varies significantly at low reaction temperatures. With an increased reaction temperature and desorption of reactant gases, the SCR activity did not reduce as expected, but increased. Therefore, it is believed that the effect of specific surface area on catalytic activity is weakened at higher temperatures. The phases and structures of the catalysts dominate the SCR activity.

3.2.3. XRD results

The XRD patterns of various catalysts are shown in Fig. 3. The pattern of Mn/MWCNTs catalyst exhibited the typical peaks corresponding to graphite ($2\theta = 26.2^\circ, 42.6^\circ, 44.7^\circ, 54.8^\circ$, and 77.6°). The peaks attributed to crystalline MnO_x (MnO_2 , Mn_3O_4 , MnO) were observed and mainly assigned to Mn_3O_4 . From Fig. 3(4), it was shown that CeO_2 ($2\theta = 28.5^\circ, 33.0^\circ, 47.5^\circ$, and 56.3°) was the dominant phase for CeO_x in Ce/MWCNTs catalyst. The peaks of graphite for this catalyst were noticeably lower than those for the Mn/MWCNTs catalyst. With the introduction of Ce to the Mn/MWCNTs catalysts, the peaks of MnO_x declined (Ce/Mn = 0.6) or even disappeared (Ce/Mn = 1.8). Manganese oxide interacts with the cerium oxide in these catalysts. This reaction would disturb the MnO_x crystal struc-

Table 1

The surface area, pore volume, and average pore diameter of different catalysts.

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{Total}}/(\text{cm}^3/\text{g})$	Average pore size (nm)
MWCNTs	35	0.138	15.9
Mn/MWCNTs	37	0.109	11.7
Mn-Ce(0.6)/MWCNTs	46	0.129	11.3
Mn-Ce(1.8)/MWCNTs	75	0.134	7.1
Ce/MWCNTs	26	0.111	16.8

Fig. 3. XRD patterns of various catalysts. (1) Mn/MWCNTs; (2) Mn-Ce(0.6)/MWCNTs; (3) Mn-Ce(1.8)/MWCNTs; (4) Ce/MWCNTs.

ture and diminish the volume of MnO_x crystal particles [33]. The tiny crystal particles uniformly disperse on the MWCNTs and enlarge the effective interface, improving the catalytic activity. By contrast, the typical peaks of CeO_2 for the Mn-Ce/MWCNTs catalysts were clearly observed but were slightly broader than those of the Ce/MWCNTs catalyst. It indicates that their CeO_2 crystallinity was lower than that of the Ce/MWCNTs. Ce modification also broadens the typical peaks of graphite. This is mainly because: (i) Ce modification disturbs the crystal structure and diminishes the volume of the crystal particles. The tiny crystal particles uniformly adsorb on the MWCNTs and weaken the detection of graphite in the XRD characterization, and (ii) A mass of metal oxide particles inside the MWCNTs disturb the structure of the graphite.

3.2.4. H_2 -TPR results

Figure 4 shows the H_2 -TPR curves of various catalysts. The Mn/MWCNTs catalysts present two redox peaks at 290 °C and 410 °C, which correspond to the reduction of MnO_2 or Mn_2O_3 to Mn_3O_4 , and Mn_3O_4 to MnO, respectively. A weak peak at 230 °C is also attributed to the reduction of MnO_2 to Mn_3O_4 [17,32]. The H_2 consumption of the Mn/MWCNTs catalyst was 0.99 mmol/g. For catalysts with MWCNTs support, the hydrogen consumption peaks of MnO_x and CeO_2 are located at lower temperatures than those for catalysts with no support [35] or with other supports, such as TiO_2 [16,31], Al_2O_3 [36], zeolite NaY [37], or TiO_2 -pillared clays [6]. This indicated that MWCNTs would improve the oxidizability of the metal oxides.

In the case of Mn-Ce/MWCNTs catalysts, the H_2 consumption peaks of Mn_3O_4 and CeO_2 overlap each other. The H_2 -TPR patterns for the Mn-Ce/MWCNTs catalysts were similar to that of the Mn/MWCNTs catalyst, but with some apparent changes. First, the peaks are moved towards lower or higher temperatures. Compared with the reduction peak of MnO_2 or Mn_2O_3 to Mn_3O_4 of Mn/MWCNTs catalyst, the peak for Mn-Ce(0.6)/MWCNTs catalyst was shifted by 40 °C towards the lower temperature side. With increased Ce loading (Ce/Mn = 1.8), this peak turns to move to a higher temperature side. This might be due to the crystalline CeO_2 structure of Mn-Ce(1.8)/MWCNTs being more apparent than for Mn-Ce(0.6)/MWCNTs in the XRD results. For the Mn-Ce(1.8)/MWCNTs catalyst, excess CeO_x aggregated together and formed more crystalline CeO_x , reducing mobility of the lattice oxygen. Naturally, the valence and oxidizability of manganese decreased. Considering the SCR activity, it was found that the movement of the reduction peak of MnO_2 or Mn_2O_3 to Mn_3O_4 was in accordance with the SCR activity. Second, the addition of Ce to Mn/MWCNTs catalyst increased the consumption of H_2 . When the values of the Ce/Mn ratios were 0.6

Fig. 4. H_2 -TPR profiles of various catalysts. (1) Mn/MWCNTs; (2) Mn-Ce(0.6)/MWCNTs; (3) Mn-Ce(1.8)/MWCNTs; (4) Ce/MWCNTs.

and 1.8, the H_2 consumption was 1.52 and 1.87 mmol/g, respectively. These values were much larger than those of the Mn/MWCNTs and Ce/MWCNTs catalysts. This indicates that Ce could improve the oxidizability and oxygen storage capacity of the catalysts. Jin et al. [18] have investigated the NH_3 -SCR reaction mechanism for catalysts of Mn-Ce oxide supported on two supports (TiO_2 and Al_2O_3). They found that with catalyst support of TiO_2 , NO was oxidized to NO_2 by lattice oxygen and then participated into the reaction. With Al_2O_3 as a catalyst support, NO was oxidized to NO_2 by O_2 . It has been suggested that the improvement of oxidizability of Mn-Ce based catalysts would enhance SCR activity as well as the oxidation of NO. It should be specified that there was no apparent variation in the location of the Mn reduction peaks at higher temperatures (Mn_3O_4 to MnO) for all Mn-based samples. It can be concluded that the active sites on MnO_2 and Mn_2O_3 were dominant factors for SCR activity. By contrast, Mn_3O_4 and MnO appear to have little effect on SCR activity.

3.2.5. XPS results

To further investigate the effects of Ce on the chemical state and surface composition in the near-surface region of Mn/MWCNTs catalyst, XPS analysis was conducted. The atomic surface compositions are given in Table 2. After adding Ce to the Mn/MWCNTs catalyst, the amounts of surface carbon and manganese were varied. It was shown that the amount of surface carbon declined with addition of Ce. This was due to the enhanced dispersion of the metal oxides. The covered areas of the MWCNTs were enlarged by the well-dispersed metal oxides. Meanwhile, the amount of surface manganese declined by more than 30%. This has been attributed to two reasons: (i)

Table 2

Atomic surface compositions of the catalysts obtained with XPS.

Sample	Surface composition (x%)				$\text{MnO}_2/\text{MnO}_x$	$\text{Mn}_2\text{O}_3/\text{MnO}_x$	$\text{Mn}_3\text{O}_4/\text{MnO}_x$	MnO/MnO_x	$\text{Ce}^{4+}/\text{Ce}^{3+}$	$\text{O}_{\text{lattice}}/\text{O}_{\text{ads}}$
	C	O	Mn	Ce						
Mn/MWCNTs	92.77	4.95	2.28	—	0.51	—	0.48	0.01	—	0.68
Mn-Ce(0.6)/MWCNTs	87.25	9.15	1.47	2.13	0.57	—	0.43	—	4.67	0.88
Mn-Ce(1.8)/MWCNTs	84.92	9.86	1.53	3.69	0.52	0.48	—	—	6.37	1.46
Ce/MWCNTs	89.81	9.70	—	0.49	—	—	—	—	11.32	0.10

Fig. 5. XPS profiles of various catalysts. (a) Mn $2p_{3/2}$; (b) Ce $3d$; (c) O $1s$. (1) Mn/MWCNTs; (2) Mn-Ce(0.6)/MWCNTs; (3) Mn-Ce(1.8)/MWCNTs; (4) Ce/MWCNTs.

The interaction between Mn and Ce causes some tiny metal oxides particles to form and are introduced into the inner MWCNTs, where some metal atoms were unable to be detected under the XPS measurement. (ii) The semi-diameters of Mn^{n+} (Mn^{4+} , Mn^{3+} , and Mn^{2+} are 0.053, 0.058, and 0.080 nm, respectively) were lower than that of Ce^{4+} (0.094 nm) in CeO_2 . This allows Mn^{n+} to enter into the CeO_2 lattices but avoid being detected. In contrast, the surface Ce on the Mn-Ce/MWCNTs catalyst was greater than that of the Ce/MWCNTs. This is expected to be because of CeO_x particles on the Ce/MWCNTs aggregating together, causing some Ce atoms to be hidden. For the Mn-Ce/MWCNTs catalyst, more Ce atoms were unfolded because of the tiny metal oxide particles. The detected ratio of surface Ce to Mn was larger than the mixed ratio of Ce/Mn in the catalyst preparation. This was mainly because of the hidden Mn^{n+} ions in the CeO_2 lattices [31,32].

The characteristic peaks for Mn $2p_{3/2}$, Ce $3d$ and O $1s$ core level spectra are shown in Fig. 5. The peaks at 642.8, 641.3–641.4, 641.6–641.7, and 640.4 eV represent MnO_2 , Mn_2O_3 , Mn_3O_4 , and MnO , respectively [19,38]. MnO_2 was the predominant phase of Mn for all the samples. The ratio of MnO_2 to MnO_x increased with the addition of Ce, in accordance with the SCR activity. CeO_2 would improve the oxygen storage capacity and the valence of manganese [15]. In the case of the valence of cerium (Fig. 5(b)), characteristic peaks u, u'', u''', v, v'', and v''' attributed to Ce^{4+} , and peaks u' and v' corresponded to Ce^{3+} [6,33]. It was shown that Ce mainly exists as Ce^{4+} . The ratio of Ce^{4+} to Ce^{3+} is shown in Table 2.

It was noted that surface oxygen on the Mn/MWCNTs catalysts was 4.95% and increased by 4%–5% with the addition of Ce. This is in agreement with the conclusion found in the H_2 -TPR study that Ce improves the oxygen storage capacity of the catalysts. From the XPS patterns of O $1s$ (Fig. (c)), it is shown that there were two kinds of surface oxygen for these catalysts, including lattice oxygen and chemisorption oxygen. The XPS results show that -OH and -COOH were the main species of chemisorption oxygen. For Mn/MWCNTs catalyst, the predominant species of oxygen was of surface chemisorption oxygen. With increased Ce loading, the amount of surface lat-

tice oxygen exceeded the amount of surface chemisorption oxygen. Jin et al. [18] found that NO was oxidized to NO_2 and then participated in the SCR reaction for Mn-Ce/ TiO_2 catalysts. Lattice oxygen could also oxidize NH_3 to NH_2 , which then reacts with nitro-oxidized species [33,39]. It could be concluded that lattice oxygen of these catalysts could improve the SCR activity. The ratio of surface lattice oxygen to surface chemisorption oxygen was denoted as $O_{lattice}/O_{ads}$ in Table 2. According to the SCR activity test results, it was found that the NO_x conversion was the highest with an $O_{lattice}/O_{ads}$ ratio of 4.67. It was reported [11,40] that oxygen was important for the SCR reaction of Mn-based catalysts. It improves the process of NH_3 dehydrogenation (initiation of the SCR reaction) and the oxidation of NO to higher oxidation states. The SCR activity was subsequently improved. In conclusion, the amount of oxygen in the Mn-Ce/MWCNTs catalysts was found to dominate SCR activity.

4. Conclusions

Mn-Ce/MWCNTs catalysts had higher SCR activity than Mn/MWCNTs catalyst when prepared by a pore volume method. The addition of cerium enhances the dispersion of metal oxides on the surface of the MWCNTs and enlarges the specific surface area of the Mn/MWCNTs catalyst. Phase and structure are the dominant influencing factors on SCR activity for Mn-Ce/MWCNTs acting as catalysts. The addition of Ce increases the valence of Mn and forms MnO_2 and Mn_2O_3 , offering more active sites for reaction. Ce also improves the oxygen storage capacity and the amount of surface oxygen on the catalyst, and enhances the dehydrogenation of NH_3 and the oxidation of NO. In addition, Ce reduces the crystallinity of the Mn-Ce/MWCNTs catalysts. MnO_x mainly exists in an amorphous state or microcrystal structure for these catalysts.

References

- [1] Tang X L, Hao J M, Xu W G, Li J H. *Chin J Catal* (唐晓龙, 郝吉明, 徐文国, 李俊华. 催化学报), 2006, 27: 843
- [2] Zamudio M A, Russo N, Fino D. *Ind Eng Chem Res*, 2011, 50: 6668

Graphical Abstract

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Effects of cerium on the selective catalytic reduction activity and structural properties of manganese oxides supported on multi-walled carbon nanotubes catalysts

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This study examines the effects of cerium on the selective catalytic reduction (SCR) activity and the structure of Mn/MWCNTs by comparing SCR activity, specific surface area, crystallization, oxidizability, and superficial species and elements.

- [3] Liu F D, Shan W P, Shi X Y, Zhang C B, He H. *Chin J Catal* (刘福东, 单文坡, 石晓燕, 张长斌, 贺泓. 催化学报), 2011, 32: 1113
- [4] Liu F D, He H, Ding Y, Zhang C B. *Appl Catal B*, 2009, 93: 194
- [5] Yao G-H, Gui K-T, Wang F. *Chem Eng Technol*, 2010, 33: 1093
- [6] Shen B X, Yao Y, Ma H Q, Liu T. *Chin J Catal* (沈伯雄, 姚燕, 马宏卿, 刘宁. 催化学报), 2011, 32: 1803
- [7] Costa C N, Efstathiou A M. *Appl Catal B*, 2007, 72: 240
- [8] Liu X Y, Jiang Z, Chen M X, Shi J W, Zhang Z X, Shangguan W F. *Ind Eng Chem Res*, 2011, 50: 7866
- [9] Tang X L, Hao J M, Yi H H, Li J H. *Catal Today*, 2007, 126: 406
- [10] Liu W, Tong Z Q, Luo J. *Acta Sci Circumstant* (刘炜, 童志权, 罗婕. 环境科学学报), 2006, 26: 1240
- [11] Wu Z B, Jiang B Q, Liu Y, Wang H Q, Jin R B. *Environ Sci Technol*, 2007, 41: 5812
- [12] Wu Z B, Jiang B Q, Liu Y, Zhao W R, Guan B H. *J Hazard Mater*, 2007, 145: 488
- [13] Kang M, Park E D, Kim J M, Yie J E. *Appl Catal A*, 2007, 327: 261
- [14] Qi G, Yang R T, Chang R. *Appl Catal B*, 2004, 51: 93
- [15] Huang Y, Tong Z Q, Wu B, Zhang J F. *J Fuel Chem Technol* (黄妍, 童志权, 伍斌, 张俊丰. 燃料化学学报), 2008, 36: 616
- [16] Wu Z B, Jin R B, Liu Y, Wang H Q. *Catal Commun*, 2008, 9: 2217
- [17] Fan X Y, Qiu F M, Yang H S, Tian W, Hou T F, Zhang X B. *Catal Commun*, 2011, 12: 1298
- [18] Jin R B, Liu Y, Wu Z B, Wang H Q, Gu T T. *Chemosphere*, 2010, 78: 1160
- [19] Lin Q, Li J, Ma L, Hao J. *Catal Today*, 2010, 151: 251
- [20] Bao X H. *Sci China, Ser B* (包信和. 中国科学B辑), 2009, 39: 1125
- [21] Lambin P, Fonseca A, Vigneron J P, Nagy J B, Lucas A A. *Chem Phys Lett*, 1995, 245: 85
- [22] Long R Q, Yang R T. *Ind Eng Chem Res*, 2001, 40: 4288
- [23] Ajayan P M. *Chem Rev*, 1999, 99: 1787
- [24] Li Q, Yang H, Qiu F, Zhang X. *J Hazard Mater*, 2011, 192: 915
- [25] Huang B, Huang R, Jin D, Ye D. *Catal Today*, 2007, 126: 279
- [26] Luo Y, Li C T, Lu P, Li Q, Ke Q, Tian L H. *Chin J Environ Eng* (罗瑶, 李彩亭, 路培, 李群, 柯琪, 田立辉. 环境工程学报), 2009, 3: 1844
- [27] Wang W H, Huang B C, Wang L S, Ye D Q. *Surf Coat Technol*, 2011, 205: 4896
- [28] Zhou G, Zhong B, Wang W, Guan X, Huang B, Ye D, Wu H. *Catal Today*, 2011, 175: 157
- [29] Grossale A, Nova I, Tronconi E. *Catal Today*, 2008, 136: 18
- [30] Zhang Y P, Wang X L, Sun K Q, Shen K, Xu H T, Zhou C C. *J Fuel Chem Technol* (张亚平, 汪小蕾, 孙克勤, 沈凯, 徐海涛, 周长城. 燃料化学学报), 2011, 39: 782
- [31] Gong L, Luo L T, Wang R, Ao Z Y, Zhang N. *J Chin Rare Earth Soc* (龚磊, 罗来涛, 王瑞, 敖志勇, 张宁. 中国稀土学报), 2011, 29: 41
- [32] Kijlstra W S, Brands D S, Poels E K, Blik A. *J Catal*, 1997, 171: 208
- [33] Wu X, Si Z, Li G, Weng D, Ma Z. *J Rare Earths*, 2011, 29: 64
- [34] Huang Q, Xue X, Zhou R. *J Hazard Mater*, 2010, 183: 694
- [35] Liu X, Lu J, Qian K, Huang W, Luo M. *J Rare Earths*, 2009, 27: 418
- [36] Smirniotis P G, Srekanth P M, Peña D A, Jenkins R G. *Ind Eng Chem Res*, 2006, 45: 6436
- [37] Richter M, Trunschke A, Bentrup U, Brzezinka K-W, Schreier E, Schneider M, Pohl M-M, Fricke R. *J Catal*, 2002, 206: 98
- [38] National Institute of Standards and Technology (NIST). X-ray Photoelectron Spectroscopy Database. Accessed on March 10, 2012, <http://srdata.nist.gov/xps>
- [39] Kijlstra W S, Brands D S, Smit H I, Poels E K, Blik A. *J Catal*, 1997, 171: 219
- [40] Wu D W, Zhang Q L, Lin T, Gong M C, Chen Y Q. *Chin J Inorg Chem* (吴大旺, 张秋林, 林涛, 龚茂初, 陈耀强. 无机化学学报), 2011, 27: 5

Ce掺杂对碳纳米管负载Mn催化剂结构及SCR反应性能的影响

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摘要: 采用等体积浸渍法制备多壁碳纳米管(MWCNTs)负载Ce-Mn的催化剂, 考察了Ce掺杂对Mn/MWCNTs催化剂上NH₃选择性催化还原(SCR)NO_x反应活性的影响. 并运用透射电镜扫描、N₂吸附-脱附、程序升温还原、X射线光电子能谱、X射线衍射等手段, 重点考察了Ce掺杂对Mn/MWCNTs催化剂结构性质的影响. 结果表明, Ce掺杂能显著提高催化剂的SCR活性, 其活性增量随着Ce含量的增加先增大后减小; 当Ce/Mn为0.6时, 催化剂活性最佳. 表征结果显示, Mn/MWCNTs中添加Ce后, 金属氧化物在MWCNTs上的分散程度提高; 催化剂的比表面积和孔体积增大, 平均孔径减小; 氧化能力提高; 表面氧含量增加, Mn化合价升高; 结晶度降低, Mn主要以无定形或微晶形式存在, Ce主要以CeO₂物相存在.

关键词: 选择性催化还原; 氮氧化物; 铈; 锰; 多壁碳纳米管

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1. 前言

选择性催化还原(SCR)是目前用于固定源氮氧化物(NO_x)排放控制的主要技术. SCR技术的核心是催化剂, 其性能直接影响到SCR系统的整体脱硝效果. 然而, 目前常用的商业催化剂V₂O₅-WO₃(MoO₃)/TiO₂活性温度窗口高(300~400 °C), 易受SO₂和粉尘的影响而发生催化剂中毒^[1,2]. 开发低温SCR催化剂, 让脱硝系统置于除尘脱硫装置之后(< 200 °C)是解决这些问题的重要途径.

近年来, 高效低温SCR催化剂的开发成为该领域的研究热点. 目前有关不同活性组分和载体的低温(< 200 °C)NH₃-SCR脱硝催化剂的报道较多^[3]. Liu等^[4]制备的Fe_{0.9}Mn_{0.1}TiO_x催化剂因具有较大的比表面积、合适的结构、较强的氧化性能、较高的晶格氧迁移能力而表现出较高的低温催化活性, 在200 °C附近NO_x转化率达到90%以上. Zamudio等^[2]采用凝胶燃烧合成法制得的Mn_{0.95}Ca_{0.05}Cr₂O₄催化剂在125 °C时即可达到最高的NO转化率. Yao等^[5]研究γ-Fe₂O₃催化剂时发现, 250 °C时NO_x转化率即达到90%以上, 这与γ-Fe₂O₃的磁性有关. Shen等^[6]采用浸渍法制备Mn/钛基层柱粘催化剂后, 考察了Ce的添加对该催化剂在SCR反应中抗水抗硫性能的影响. 研究发现, 添加Ce后其活性以及抗硫能力均有所提高, 200 °C时NO去除率达到95%, 同时SO₂的存在使得失活速率降低.

在众多用作低温SCR催化剂活性组分的过渡金属及其氧化物中^[2,5-8], Mn, Ce及其氧化物因其自身独特的化学性质而表现出良好的低温SCR活性. 锰氧化物表面具有较多不稳定晶格氧原子, 因而有较强的氧化还原能力^[1,9-12]. Kang等^[13]采用沉淀法制备了非负载型MnO_x催

化剂, 100 °C时NO_x转化率达到90%以上. CeO₂可通过Ce⁴⁺和Ce³⁺间的转化, 实现氧的释放和储存^[14]. 黄妍等^[15]和Wu等^[16]的研究表明, Ce的掺杂可提高SCR催化剂的低温催化活性.

TiO₂, Al₂O₃, 分子筛和碳材料等广泛用作低温SCR催化剂载体^[9,17-19]. 其中, 碳材料具有大比表面积、特殊孔道结构、强吸附性能, 因而其负载的催化剂表现出优异的性能. 作为一种特殊的碳材料的碳纳米管, 具有机械强度高、热稳定性高、限域效应, 以及良好的导电性等^[20-23], 因而广泛用作催化剂载体^[24-26].

因此, 本文以MWCNTs为载体, 采用等体积浸渍法负载Ce-Mn双组分, 运用透射电子显微镜(TEM)、N₂吸附-脱附、X射线光电子能谱(XPS)、X射线衍射(XRD)、H₂程序升温还原(H₂-TPR), 以及SCR反应活性测试, 探讨Ce的掺杂对Mn/MWCNTs催化剂结构及其SCR反应活性的影响.

2. 实验部分

2.1. 催化剂的制备

将碳纳米管(深圳市纳米港有限公司, 管径为60~100 nm)置于100 °C的硝酸水溶液(3 mol/L)中水浴4 h后, 用去离子水洗涤至中性, 经80 °C烘干, 研磨后, 于O₂中用等离子体(15 W)放电40 min. 碳纳米管的HNO₃纯化和氧等离子体预处理, 目的是在碳纳米管表面接枝含氧官能团, 提高其在水中的分散性, 使催化剂制备过程中活性组分的负载能在水相中进行^[27].

采用等体积浸渍法制备系列Mn-Ce/MWCNTs催化剂. 按照一定Ce/Mn摩尔比配制乙酸锰和硝酸铈的各种溶液, 分别加入经预处理的MWCNTs超声分散1 h, 室温

浸渍5 h. 混合物于100 °C干燥后,在管式炉中空气气氛下于400 °C焙烧2 h. 所得催化剂记为Mn-Ce(x)/MWCNTs,其中x为Ce/Mn摩尔比. 同法制得Ce/MWCNTs催化剂,其中Ce含量同Mn-Ce(0.6)/MWCNTs. 上述所有样品中Mn的质量分数为10%.

2.2. 催化剂的活性评价

催化剂的活性评价在石英玻璃连续流动固定床反应器(内径 $d = 12$ mm)中进行,催化剂用量180 mg. 各种反应气体的流量由质量流量计控制,其中0.1% NH_3 , 0.1% NO , 5% O_2 , Ar为平衡气,气体空速 40000 h^{-1} . 尾气中 NO_x 浓度由美国Thermo Scientific公司的42i-HL型 NO_x 烟气分析仪测得, N_2 由气相色谱仪(GC9560型)测得. 在稳定状态下, NO_x 转化率 $X(\text{NO}_x) = (C_{\text{NO}_x}^{\text{in}} - C_{\text{NO}_x}^{\text{out}}) / C_{\text{NO}_x}^{\text{in}} \times 100\%$,其中 $C_{\text{NO}_x}^{\text{in}}$ 和 $C_{\text{NO}_x}^{\text{out}}$ 分别为进口和出口处 NO_x 浓度.

2.3. 催化剂的表征

采用日本JEOL公司的JEM-2100HR型TEM观察催化剂微观形貌,点分辨率0.23 nm,放大倍数50~1500000,加速电压100~200 kV.

采用美国Micromeritics公司的ASAP 2020 M型全自动比表面积及微孔孔隙分析仪测定催化剂的比表面积和孔结构参数. 样品用量0.1 g,样品先在100 °C脱气1 h, 350 °C脱气4 h,然后以 N_2 为吸附质,于-196 °C下进行 N_2 吸附-脱附实验.

H_2 -TPR实验在美国Micromeritics公司的Auto Chem II型全自动化学吸附仪中进行,样品用量0.1 g,气体流速30 ml/min,在Ar吹扫下,以10 °C/min升至350 °C并吹扫1 h,降至60 °C,通入10% H_2 -90% Ar混合气,以10 °C/min升至700 °C,TCD记录耗 H_2 量.

XPS分析在英国Kratos公司的Axis Ultra DLD型X射线光电子能谱仪上进行. 真空度为 25×10^{-4} Pa, Al K_{α} 射线($h\nu = 1486.6$ eV),C 1s校准结合能为284.6 eV.

XRD分析在德国Bruker公司的D8 Advance型X射线衍射仪上进行,Cu K_{α} 射线($\lambda = 0.15418$ nm),电压40 kV,电流40 mA,扫描范围 $2\theta = 5^\circ \sim 90^\circ$ (步长 0.02°). XRD结果通过与JCPDS卡片对照进行分析.

3. 结果与讨论

3.1. 催化剂的SCR活性

图1为各催化剂上SCR反应活性. 由图可见,当反应温度低于120 °C时,各催化剂活性比较接近,且在20%~40%范围;随着温度的上升,各催化剂活性逐渐出

现显著的差异;当高于240 °C时,各催化剂活性均普遍下降. 高温时,催化剂活性下降是因为发生了SCR的竞争反应, NH_3 直接被 O_2 氧化^[28–30].

对于Mn/MWCNTs催化剂,当反应温度低于180 °C时, NO_x 转化率低于60%;当升至210 °C时,迅速升至97.9%. 可见,该催化剂的活化温度区间为180~210 °C. 当温度为200~300 °C时, NO_x 转化率保持在90%以上,活性温度窗口较宽. Ce/MWCNTs催化剂的SCR活性在60~300 °C区间内随着温度的上升而增加,但表现出较低的活性:300 °C时 NO_x 转化率仅为73.6%. 另外,Ce的添加使得Mn/MWCNTs催化剂的高活性温度区间向低温偏移;随着催化剂中Ce/Mn由0.2升至1.8,催化剂活性及活性温度窗口范围均是先增后减;Ce/Mn为0.6时,催化剂活性最佳,活性温度窗口也最宽:在190~270 °C反应温度区间内, NO_x 转化率保持在90%以上.

为了探讨Ce掺杂对Mn/MWCNTs催化剂脱硝性能改善的原因及其对Mn在碳纳米管上的分散行为的影响,下文选择Mn/MWCNTs, Ce/MWCNTs, 以及SCR活性较为典型的Mn-Ce(0.6)/MWCNTs与Mn-Ce(1.8)/MWCNTs催化剂,对其作了系列的表征.

3.2. 催化剂表征结果

3.2.1. TEM

图2为不同催化剂的TEM照片. 由图可见,在Mn/MWCNTs样品中 MnO_x 颗粒均匀附着在MWCNTs管壁上,粒径约为20~40 nm;而 CeO_x 在MWCNTs上的分散性较差,且团聚成大的颗粒物(50~100 nm)附着在MWCNTs管壁上. 当Ce和Mn同时负载在MWCNTs上时,金属氧化物在MWCNTs上的分散显著改善,氧化物颗粒的粒径降低到10 nm以下,有利于反应气体与金属氧化物上的催化活性位充分接触,从而提高催化剂的活性. 若Ce的添加量超过其在MWCNTs上的分散容量,就会出现金属氧化物的团聚,使得催化活性位重叠相互掩盖而降低催化活性. 还可以看出,这种金属氧化物团聚物是以疏松的絮状颗粒团形式存在的,而并非像单一金属负载时所观察到的较紧密的颗粒团.

3.2.2. N_2 吸附-脱附

表1列出了MWCNTs及其负载的催化剂的比表面积、孔体积和孔径. 由表可见,除Ce/MWCNTs样品外,金属氧化物的负载使得MWCNTs比表面积增加,总孔体积和平均孔径减小;而单独负载Ce使MWCNTs比表面积和总孔体积减小,平均孔径则增加,这主要是 CeO_x 在碳管外堆积形成较致密的大颗粒所致. 比较而言,单金属

负载时,催化剂的比表面积和孔体积均较小,而平均孔径较大.当Mn/MWCNTs催化剂中掺杂Ce(Ce/Mn = 0.6)后,其比表面积和总孔体积分别增加了24%和18%,平均孔径则有所减小.这是因为Ce掺杂后,Ce和Mn的相互作用,金属氧化物颗粒以无定形或微晶细小颗粒的形式高度分散在碳纳米管上,并形成许多细小的孔道,金属颗粒物充分裸露在外从而增加了催化剂的比表面积.随着Ce掺杂量的增加(Ce/Mn = 1.8), A_{BET} 增加了近一倍,总孔体积继续增加,这是因为Ce和Mn的氧化物除了负载在MWCNTs上,其中大于碳纳米管分散容量的部分形成了疏松的絮状颗粒团.然而,当Ce/Mn为1.8时,催化剂的平均孔径大幅度降低,与龚磊等^[31]和Qi等^[14]报道的非负载型 MnO_x - CeO_2 催化剂(Ce/Mn分别为2.3和2.5)的比较接近.结合催化剂的活性可知,当Ce/Mn = 0.6时,所制催化剂大的比表面积和合适的孔道结构使其活性增加,但催化剂的比表面积与其活性并非呈线性关系:当Ce/Mn为1.8时,虽然样品有更大的比表面积,但其催化活性却反而下降.

唐晓龙等^[1]研究指出,Mn基催化剂的活性主要取决于其比表面积和物相结构.较大的比表面积有利于反应物在催化剂的表面吸附,为催化反应提供更多的反应空间,从而提高 NO_x 的转化率^[10].低温时,反应气体容易吸附于催化剂上,有利于反应进行.如表1所示,各催化剂的比表面积相差较大,而较低温度(< 120 °C)时活性相当.由此可见,对于该Mn-Ce/MWCNTs系列催化剂,在较低的温度下,其单位表面积的金属氧化物活性位数量相差较大.随着温度的上升,各催化剂的SCR活性没有因为反应气体在高温下脱附而降低,反而提高.由此推测,在较高反应温度下,该催化剂活性受其比表面积的影响减弱,而更多地取决于催化剂上金属氧化物的物相结构(晶相、价态等).

3.2.3. XRD

图3为各催化剂的XRD谱.由图可见,Mn/MWCNTs样品出现尖锐的石墨特征峰($2\theta = 26.2^\circ, 42.6^\circ, 44.7^\circ, 54.8^\circ$ 和 77.6°),并可看到多种 MnO_x 物相(MnO_2 , Mn_3O_4 , MnO),其中以 Mn_3O_4 物相为主;而在Ce/MWCNTs催化剂上, CeO_2 是 CeO_x 的主要存在物相($2\theta = 28.5^\circ, 33.0^\circ, 47.5^\circ$ 和 56.3°),其石墨的特征峰明显较Mn/MWCNTs催化剂的宽化.当Ce掺杂Mn(Ce/Mn为0.6)负载在MWCNTs上时, MnO_x 各物相的特征峰减弱,当Ce/Mn为1.8时甚至消失.Ce与Mn相互作用,使 MnO_x 的晶体结构由有序向无序转变,混乱度提高,阻碍了 MnO_x 的聚集和结晶,使其晶粒变

小^[32].细小晶粒高度分散于载体上,使催化剂有效界面增大,有利于其活性的提高.相比之下, CeO_2 物相的特征峰仍可明显分辨,峰位置不变,但出现了宽化,可见 CeO_2 的结晶度也较单一负载时低.此外,当Ce掺杂后,催化剂的石墨特征峰较单独负载Mn或Ce时宽化.这可能有两种原因:(1)Ce掺杂使金属氧化物颗粒变得细小,大量微小金属颗粒高度附着在MWCNTs的外部,阻碍XRD测试时石墨层的探测;(2)许多颗粒进入到内管壁间,使得MWCNTs中的石墨片层结构受到扰乱.

3.2.4. H_2 -TPR

图4为各催化剂的 H_2 -TPR谱.Mn/MWCNTs催化剂在290和410 °C附近出现了两个还原峰,分别归属于Mn物种的分步还原 $\text{MnO}_2/\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$;另外,在230 °C处有一个微弱的肩峰,可归属于 MnO_2 还原为 Mn_2O_3 ^[17,33];该催化剂 H_2 耗量为0.75 mmol/g. Ce/MWCNTs催化剂主要有两个还原峰(250和450 °C),分别归属于表面氧和晶格氧的还原(CeO_2 还原为 Ce_2O_3)^[6,34],其 H_2 耗量为0.99 mmol/g.值得注意的是,MWCNTs负载的 MnO_x 和 CeO_2 的还原峰温度比一些非负载型^[35]和其它材料负载^[6,16,31,36,37]的Ce基催化剂的低.由此可知,以MWCNTs为载体时更有利于催化剂的还原,从而提高了金属氧化物的氧化性能.

当Mn/MWCNTs催化剂中掺入Ce时, Mn_3O_4 和 CeO_2 的还原峰在350~500 °C区间内发生重叠.其还原峰整体形状与Mn/MWCNTs的大致相同,但还原峰位置发生偏移,如Mn-Ce(0.6)/MWCNTs催化剂的 $\text{MnO}_2/\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ 还原峰向低温偏移了约40 °C;随着Ce含量的提高,该还原峰却向高温移动,可能与Mn-Ce(1.8)/MWCNTs催化剂中 CeO_2 的XRD衍射峰明显有关,即过量 CeO_x 在发生聚集的过程中形成了较多的 CeO_2 结晶物相,一定程度上减弱了晶格氧的流动性,导致Mn化学价降低和氧化性能减弱.结合活性评价结果发现, MnO_2 或 Mn_2O_3 转化为 Mn_3O_4 的还原峰偏移情况与催化剂活性一致.另外,Ce的掺杂使得催化剂还原峰面积增大,当Ce/Mn为0.6和1.8时, H_2 消耗量分别是1.52和1.87 mmol/g,比单负载时的大得多.这说明适量Ce的添加可提高催化剂的氧化性能和储氧能力.Jin等^[18]研究了Mn-Ce氧化物分别负载在 TiO_2 和 Al_2O_3 上的 NH_3 -SCR反应机理发现,催化剂表面上NO均以其更高价的氧化物参与反应.当 TiO_2 为载体时,NO被表面晶格氧氧化为 NO_2 物种参与反应; Al_2O_3 为载体时,NO被 O_2 氧化为 NO_2 后吸附于催化剂上参与反应.由此推测,以Mn-Ce氧化物为活性组分的催

化剂的氧化性能的增强有利于NO在催化剂表面的氧化,使得催化剂SCR活性增加. 需要指出的是,各含Mn催化剂中高温还原峰($\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$)的位置没有明显差异. 综上可见, MnO_2 和 Mn_2O_3 上的活性位是影响该系列催化剂SCR反应的主要因素,而 Mn_3O_4 和 MnO 的影响不大.

3.2.5. XPS

为了进一步研究Ce掺杂对Mn/MWCNTs催化剂表面氧含量的影响,以及催化剂表面各元素含量和价态分布,对各催化剂进行了XPS表征. 所得催化剂表面各元素含量列于表2. 可以看出,催化剂表面碳含量随着Ce的掺入而下降,是因为Ce促进了金属氧化物在MWCNTs表面的均匀分散,增大了碳管外表面被金属氧化物覆盖的面积. Ce掺杂后表面Mn含量下降30%以上,这可能有两方面的原因: (1)Ce与Mn的相互作用下形成颗粒细小的金属氧化物,可能进入到碳纳米管内部,不能被XPS探测到; (2)离子半径较小的 Mn^{n+} (Mn^{4+} (0.053 nm), Mn^{3+} (0.058 nm), Mn^{2+} (0.080 nm))进入到离子半径较大(0.094 nm)的 CeO_x 晶格中,导致Mn没能探测出来. 与此相反,Mn-Ce/MWCNTs催化剂表面Ce含量较单金属负载时高,这是因为在Ce/MWCNTs中 CeO_x 主要以大颗粒团聚物形式存在,导致大部分Ce包裹在大颗粒中,使得表面Ce含量偏低;而当Ce与Mn作用后,形成了细小的颗粒,内部的Ce向催化剂表面迁移. 另外,在两种Mn-Ce/MWCNTs催化剂中,表面Ce/Mn值均大于设定值,这可能是因为在催化剂制备过程中,离子半径较小的 Mn^{n+} 进入到离子半径较大的 CeO_x 晶格中,导致表面的Mn/Ce值比设定值低^[31,33].

XPS谱图拟合结果见图5. Mn $2p_{3/2}$ 的电子结合能谱峰中 MnO_2 , Mn_2O_3 , Mn_3O_4 和 MnO 的结合能分别是642.8, 641.3~641.4, 641.6~641.7和640.4 eV^[19,38]. 由图5(a)可见,各样品中Mn主要是以 MnO_2 形式存在, $\text{MnO}_2/\text{MnO}_x$ 值随着Ce掺入及其含量的增加而增大,并与催化剂活性变化一致. CeO_2 提高了催化剂中氧的储存和转移能力,促进Mn由低价态氧化为高价态^[15]. Ce 3d轨道的XPS谱如图5(b)所示,其中u, u', u''和v, v', v''峰归属于 Ce^{4+} ,而u'和v'

两个峰归属于 Ce^{3+} ^[6,32]. 可见,Ce主要以 Ce^{4+} 的形式存在(各样品中 $\text{Ce}^{4+}/\text{Ce}^{3+}$ 的比见表2).

由表2可见,Mn/MWCNTs催化剂中氧含量为4.95%,Ce的掺入使得催化剂中氧含量增加了4%~5%,即Ce使催化剂的储氧能力提高,这与 H_2 -TPR结果一致. 由图5(c)可知,催化剂中氧原子包括了表面晶格氧和表面化学吸附氧;分峰拟合结果显示,该系列催化剂的表面化学吸附氧主要以-OH和-COOH两种形式存在. 表面晶格氧与表面化学吸附氧的比值记为 $\text{O}_{\text{lattice}}/\text{O}_{\text{ads}}$. MWCNTs单独负载Mn时,催化剂中的氧主要以表面化学吸附氧为主;随着掺入Ce量增多,Mn-Ce(x)/MWCNTs催化剂表面晶格氧含量超过了表面吸附氧. Jin等^[18]研究发现,Mn-Ce/ TiO_2 催化剂上SCR反应过程是NO被表面晶格氧氧化为 NO_2 物种参与反应. 另外,晶格氧亦可将 NH_3 氧化为 NH_2 ,并与NO氧化后的物种反应生成中间物种^[32,39]. 可见,该系列催化剂晶格氧含量的增加有利于SCR反应的进行. 结合活性评价结果可知,当 $\text{O}_{\text{lattice}}/\text{O}_{\text{ads}}$ 为4.67时,Mn-Ce/MWCNTs催化剂的SCR活性最佳. 在Mn基催化剂中,氧对催化剂的活性起着重要的作用,它可促进SCR反应过程中 NH_3 的脱氢氧化(SCR反应的起始步骤)和NO氧化为反应中间物种硝酸根或者亚硝酸根等,从而提高催化剂的SCR活性^[11,40]. 可见,催化剂氧含量的增加对于催化剂的SCR活性提高起着本质的作用.

4. 结论

采用等体积浸渍法制备的Mn-Ce/MWCNTs催化剂上SCR反应活性高于Mn/MWCNTs催化剂. Ce的掺杂促进了金属氧化物在载体MWCNTs上的分散,增加了催化剂的比表面积. Mn-Ce/MWCNTs催化剂的物相结构是影响其SCR活性的主要因素. Ce提高了Mn的价态,形成更多 MnO_2 和 Mn_2O_3 ,为SCR反应提供更多活性位;同时提高了催化剂的储氧能力,增加了催化剂的表面氧含量,促进了SCR反应过程中 NH_3 的脱氢氧化和NO的氧化. 另外,Ce降低了催化剂的结晶度,使 MnO_x 主要以无定形或微晶形式存在.