

Article

Preparation, characterization, and catalytic performance of high efficient CeO₂-MnO_x-Al₂O₃ catalysts for NO elimination

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ARTICLE INFO

Article history: Received 16 February 2016 Accepted 20 March 2016 Published 5 August 2016

Keywords: Ceria-based mixed oxide Incorporation Electron interaction Adsorption property NO elimination

ABSTRACT

A series of CeO₂-MnO_x-Al₂O₃ mixed oxide catalysts (Ce:Mn:Al mole ratio = 6:4:*x*, *x* = 0.25, 0.5, 1, 2) were prepared by a simple one-step inverse co-precipitation method to investigate the influence of the incorporation of Al³⁺ into CeO₂-MnO_x mixed oxides. CeO₂-MnO_x, CeO₂-Al₂O₃, and MnO_x-Al₂O₃ mixed oxides, and CeO₂ were prepared by the same method for comparison. The samples were characterized by XRD, Raman, N₂ physisorption, H₂-TPR, XPS, and *in situ* DRIFTS. The catalytic reduction of NO by CO was chosen as a model reaction to evaluate the catalytic performance. The incorporation of a small amount of Al³⁺ into CeO₂-MnO_x mixed oxides resulted in a decrease of crystallite size, with the increase of the BET specific surface area and pore volume, as well as the increase of Ce³⁺ and Mn⁴⁺. The former benefits good contact between catalyst and reactants, and the latter promotes the adsorption of CO and the desorption, conversion and dissociation of adsorbed NO. All these enhanced the catalytic performance for the NO+CO model reaction. A reaction mechanism was proposed to explain the excellent catalytic performance of CeO₂-MnO_x-Al₂O₃ catalysts for NO reduction by CO.

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1. Introduction

Motor vehicles bring great convenience to people, but they also cause serious atmospheric pollution [1]. Nitric oxide (NO),

carbon monoxide (CO), and hydrocarbons (HCs) are the main pollutants in motor vehicle exhaust. They can be efficiently eliminated by three-way catalysis (TWC) technology [2–5]. There are several important reactions in this technology, in

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This work was supported by the National Natural Science Foundation of China (21507130), the Open Project Program of Chongqing Key Laboratory of Environmental Materials and Remediation Technology from Chongqing University of Arts and Sciences (CEK1405), the Open Project Program of Beijing National Laboratory for Molecular Sciences (20140142), the Open Project Program of Jiangsu Key Laboratory of Vehicle Emissions Control (OVEC001), the Open Project Program of Chongqing Key Laboratory of Catalysis and Functional Organic Molecules from Chongqing Technology and Business University (1456029), and the Chongqing Science & Technology Commission (cstc2014pt-gc20002)

DOI: 10.1016/S1872-2067(15)61098-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 8, August 2016

which the catalytic reduction of NO by CO (NO+CO model reaction) attracts more attention due to the simultaneous elimination of NO and CO pollutants [6,7]. In the past decades, supported noble metal catalysts were widely applied for this reaction, and they exhibited excellent catalytic performance [8–10]. However, the high cost, resource scarcity, and poor stability of noble metals prompted researchers to look for substitutes. For this purpose, low cost and efficient transition metal oxide catalysts have become the focus in recent years [11,12].

The rare earth metal oxide ceria (CeO₂) was widely used for the NO+CO model reaction due to its good redox property, high oxygen storage and release capacity, and abundant surface oxygen vacancies [13-17]. Some research results indicated that the incorporation of transition metal ions (such as Zr4+) into the lattice of CeO2 to form a ceria-based mixed oxide can increase the specific surface area of CeO2 and further improve its redox property and oxygen storage and release capacity [18-20]. Moreover, CeO₂-ZrO₂ mixed oxides have been practically applied for the purification of motor vehicle exhaust. In our previous study, we found that doping with ions with variable valence states (such as Sn^{4+}/Sn^{2+} and Ti^{4+}/Ti^{3+}) was beneficial to improve CeO₂ because of the electron transfer between Ce4+/Ce3+ and the doped ions [21,22]. Furthermore, manganese oxide (MnO_x) easily generates the $Mn^{n+}/Mn^{(n-1)+}$ redox couple, and thereby exhibits excellent catalytic performance in some redox reactions [23-25].

Recently, a CeO_2 -MnO_x mixed oxide was widely used in many important reactions (such as NO elimination, soot combustion, VOCs oxidation, etc.) due to its good physicochemical property and excellent catalytic performance [26-28]. Usually, the specific surface area of a two-component ceria-based mixed oxide is still too small to satisfy the practical application requirement. Gamma alumina $(\gamma - Al_2O_3)$ is one of the most commonly used catalyst support due to its large specific surface area and high thermal stability [29]. Therefore, γ -Al₂O₃ was widely used as a support to load ceria-based mixed oxides for the purpose of satisfying the practical application in the purification of motor vehicle exhaust. We found that the incorporation of Al3+ into the lattice of a ceria-based mixed oxide by a co-precipitation method was more conducive to improve the physicochemical property and catalytic performance in our previous work [12].

In the present work, we prepared a series of $CeO_2-MnO_x-Al_2O_3$ mixed oxide catalysts by a simple one-step inverse co-precipitation method. The samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, N₂ physisorption, H₂ temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS), and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS). The NO+CO model reaction was chosen to evaluate the catalytic performance of the samples. This study is mainly focused on: (1) exploring the influence of the doped amount of Al^{3+} on the catalytic performance of $CeO_2-MnO_x-Al_2O_3$ mixed oxide catalysts, and (2) investigating the interaction of CO or/and NO with these catalysts by *in situ* DRIFTS in the temperature range of 25–450 °C to discuss the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

A series of CeO₂-MnO_x-Al₂O₃ mixed oxide catalysts (Ce:Mn:Al mole ratio = 6:4:x, x = 0.25, 0.5, 1, 2) were prepared from their salt solutions as precursors by a simple one-step inverse co-precipitation method. The desired quantities of cerium nitrate, manganese nitrate (50%), and aluminum nitrate were dissolved in distilled water separately and mixed together by magnetic stirring for 1 h, and then slowly added into the excess ammonia (25%) with vigorously stirring until the pH = 10. The resulting suspension was kept stirred for another 3 h, aged for 24 h, and then filtered, washed several times with distilled water until the pH = 7. The obtained cake was dried at 110 °C for 12 h and finally calcined at 500 °C in flowing air for 5 h. In addition, CeO2-MnOx, CeO2-Al2O3, MnOx-Al2O3 mixed oxides, and CeO₂ were prepared by the same way for comparison. These samples are denoted as C₆M₄A_x. For example, C₆M₄A_{0.5} represents that the mole ratio of Ce:Mn:Al is 6:4:0.5.

2.2. Catalyst characterization

XRD patterns were recorded on a Philips X'Pert3 Powder diffractometer using Ni-filtered Cu K_{α} radiation ($\lambda = 0.15418$ nm). The X-ray tube was operated at 40 kV and 40 mA. The data were collected over a 2θ range of 10° – 90° . The scan speed was set at 10° /min with a step size of 0.02° . The mean crystallite size (D_{β}) from the strongest peak of these samples was determined by $D_{\beta} = K\lambda/\beta\cos\theta$ (Debye-Scherrer equation), where *K* is the particle shape factor, usually taken as 0.89, λ is the X-ray wavelength, β is the full width at half maximum height (FWHM) in radians, and θ is the diffraction angle.

Raman spectra were collected on a Renishaw inVia Reflex Laser Raman spectrometer using a Ar^+ laser beam. The Raman spectra were recorded with an excitation wavelength of 532 nm and the laser power of 5 mW.

Textural characteristics of the samples were obtained by N_2 physisorption at –196 °C on a Belsorp-max analyzer, using the Brunauer-Emmet-Teller (BET) method for the specific surface area and the Barrett-Joyner-Halenda (BJH) method for the pore distribution. Prior to each analysis, the catalyst was degassed under vacuum at 300 °C for 4 h.

H₂-TPR experiments were performed in a quartz reactor connected to a thermal conductivity detector (TCD) with an Ar-H₂ mixture (7.0% of H₂ by volume, 30 mL/min) as reductant. Prior to the reduction, the sample (50 mg) was pretreated in a highly purified N₂ stream at 300 °C for 1 h and then cooled to room temperature. After that, the TPR started from 50 °C to the target temperature at a rate of 10 °C/min.

XPS analysis was performed on a PHI 5000 VersaProbe system using monochromatic Al K_{α} radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the sample was outgassed at room temperature in a UHV chamber (< 5 × 10⁻⁷ Pa). Sample charging effects were compensated by calibrating binding energies (BE) with the adventitious C 1*s* peak at 284.6 eV. This reference gave BE values with an accuracy of ± 0.1 eV.

In situ DRIFTS were collected from 650 to 4000 cm-1 at a spectral resolution of 4 cm⁻¹ (number of scans, 32) on a Nicolet 5700 FT-IR spectrometer equipped with a high sensitivity MCT detector cooled by liquid N₂. The DRIFTS cell (Harrick) was fitted with a ZnSe window and a heating cartridge that allowed the sample to be heated to 450 °C. The fine catalyst powder placed on a sample holder was carefully flattened to enhance IR reflection. The sample was pretreated with a highly purified N₂ stream at 450 °C for 1 h to eliminate physisorbed water and other impurities. The sample background at each target temperature was collected during the cooling process. At ambient temperature, the sample was exposed to a controlled stream of CO-Ar (10% of CO by volume) or/and NO-Ar (5% of NO by volume) at a rate of 5.0 mL/min for 1 h for adsorption saturation. Desorption and reaction studies were performed by heating the adsorbed species and the spectra were recorded at various target temperatures at a rate of 10 °C/min from room temperature to 450 °C by subtraction of the corresponding background reference.

2.3. Catalytic performance

The catalytic performance of these catalysts for the NO+CO model reaction was determined under steady state conditions using a feed stream with a fixed composition, 5% NO, 10% CO and 85% He by volume as diluent. The sample (50 mg) was fitted into a quartz tube and pretreated in a highly purified N₂ stream at 300 °C for 1 h and then cooled to room temperature. After that, the mixed gases were switched on. The reactions were carried out at different temperatures with a space velocity of 12000 mL g⁻¹ h⁻¹. A gas chromatograph (GC-9860) with two columns (length, 1.75 m; diameter, 3 mm) and two thermal conductivity detectors (T = 100 °C) was used for analyzing the products. Column A with Paropak Q was chosen for separating CO2 and N2O and column B packed with 5A and 13X molecule sieve (40-60 mesh) was used for separating N₂, NO and CO. The NO conversion and N_2 selectivity were calculated by the following equations:

NO conversion = $([NO]_{in} - [NO]_{out})/[NO]_{in} \times 100\%$ (1)

 N_2 selectivity = $[N_2]_{out}/([N_2]_{out} + [N_2O]_{out}) \times 100\%$ (2) where $[NO]_{in}$, $[NO]_{out}$, $[N_2]_{out}$, and $[N_2O]_{out}$ are the inlet concentration of NO and outlet concentration of NO, N₂, and N₂O, respectively.

3. Results and discussion

3.1. Catalytic activity and selectivity (NO+CO model reaction)

The catalytic reduction of NO by CO was chosen as the model reaction to evaluate the catalytic performance of the samples. N₂O (byproduct), N₂, and CO₂ were the main reaction products. The catalytic activity and N2 selectivity as a function of reaction temperature are exhibited in Fig. 1. With regard to C₆M₄ mixed oxide, when the reaction temperature was not higher than 250 °C, both NO conversion and N2 selectivity are negligible (less than 20%). At high temperature (>250 °C), the values were dependent on the increase of reaction temperature. Full NO conversion and 100% N₂ selectivity were obtained at 450 °C. Some interesting phenomena are observed in the Al-containing C6M4A0.25, C6M4A0.5, C6M4A1, and C6M4A2 mixed oxides. We found that the introduction of a small amount of Al^{3+} into C_6M_4 mixed oxide resulted in the enhancement of catalytic performance. The catalytic performance was proportional to the amount of Al3+. However, further increasing the amount of Al3+ led to a negative effect on the catalytic performance, which indicated that the addition of Al3+ has an optimal amount, i.e., the C₆M₄A_{0.5} mixed oxide exhibited the best NO conversion and N₂ selectivity among these samples. Moreover, C₆A_{0.5} and $M_4A_{0.5}$ mixed oxides were prepared by the same inverse co-precipitation method for comparison. The NO conversion and N₂ selectivity of the C₆A_{0.5} and M₄A_{0.5} mixed oxides are also presented in Fig. 1. The catalytic performance of the C₆A_{0.5} and M₄A_{0.5} mixed oxides was obviously lower than that of the Mn-containing ceria-based mixed oxides. In order to get a thorough understanding for the reason for different catalytic performance, a series of characterizations were performed on these samples. The results are displayed and discussed in the



Fig. 1. Catalytic performance of the samples for NO+CO model reaction. (a) NO conversion; (b) N₂ selectivity.

following sections.

3.2. Structural characteristics (XRD and Raman)

The XRD patterns of the samples are shown in Fig. 2(a). For facilitating comparison, the result of CeO₂ is also given in this figure. We can find that CeO2 showed several characteristic diffraction peaks corresponded to the (111), (200), (220), (311), (222), (400), (331), (420), (422) crystal planes of the cubic fluorite structure [PDF-ICDD 34-0394]. The M₄A_{0.5} sample exhibited a series of characteristic diffraction peaks assigned to hausmannite Mn₃O₄ [PDF-ICDD 24-0734], while only the broad diffraction peaks attributed to cubic fluorite CeO₂ can be observed in the XRD patterns of the C₆A_{0.5}, C₆M₄, C₆M₄A_{0.25}, C₆M₄A_{0.5}, C₆M₄A₁, and C₆M₄A₂ mixed oxides. The characteristic lines of alumina and manganese oxide were absent, and the diffraction peaks of these ceria-based mixed oxides shifted to the high angle direction slightly compared with CeO₂. This suggested that Mnⁿ⁺ and Al³⁺ have been successfully incorporated into the lattice of CeO₂ to form a uniform solid solution maintaining the cubic fluorite structure and/or highly dispersed on the surface of these samples [21,22,27,28,30]. The diffraction peaks of these ceria-based mixed oxides were broader and weaker than those of CeO2 due to the decrease of crystallite size (Table 1), which indicated that the introduction of Mn^{n+} and Al³⁺ into the lattice of CeO₂ inhibited its grain growth effectively [27,31]. Especially, the crystallite size of the Al-containing C₆M₄A_{0.25}, C₆M₄A_{0.5}, C₆M₄A₁, and C₆M₄A₂ mixed oxides was obviously smaller than that of the C₆M₄ sample. Furthermore, Table 1 shows that the lattice parameter of these ceria-based mixed oxides is smaller than that of CeO₂. This was mainly because the ionic radius of Mn⁴⁺ (0.54 Å), Mn³⁺ (0.66 Å), Mn²⁺ (0.80 Å), and Al³⁺ (0.50 Å) are smaller than that of Ce⁴⁺ (0.92 Å), and the incorporation of Mn4+, Mn3+, Mn2+, and Al3+ into the lattice of CeO₂ resulted in the shrinkage and distortion of the lattice [28,31,32].

Raman spectroscopy as a complementary surface characterization of XRD was performed on the samples. The results

Table 1

Crystallite size, lattice parameter, and the main Raman line $\left(F_{2g}\right)$ of the samples.

Sample	Crystallite size	Lattice	Position of F_{2g}	FWHM of F2g	
	(nm)	parameter (Å)	(cm-1)	(cm-1)	
CeO ₂	10.8	5.4164	463	20.2	
$C_{6}A_{0.5}$	9.1	5.4095	461	35.1	
C_6M_4	7.9	5.4023	460	38.3	
$C_6M_4A_{0.25}$	7.1	5.3972	459	42.4	
$C_6M_4A_{0.5}$	6.6	5.3906	459	48.5	
$C_6M_4A_1$	6.2	5.3871	459	59.4	
$C_6M_4A_2$	5.7	5.3849	459	72.2	

are displayed in Fig. 2(b). CeO2 exhibited a strong band at 463 cm⁻¹ attributed to the F_{2g} vibration mode of cubic fluorite structure [14,33]. The M₄A_{0.5} sample showed a main band at 655 cm⁻¹ assigned to the A_{1g} vibration mode of hausmannite Mn₃O₄ [34,35]. However, both the Raman vibration modes of CeO₂ and Mn₃O₄ were detected at the corresponding positions for the C₆M₄, C₆M₄A_{0.25}, C₆M₄A_{0.5}, C₆M₄A₁, and C₆M₄A₂ samples. Interestingly, the Raman bands of these ceria-based mixed oxides were shifted to the low wavenumber direction slightly compared with CeO2 and Mn₃O₄ (Table 1), which further confirmed that a fraction of the Mnⁿ⁺ and Al³⁺ were successfully incorporated into the lattice of CeO₂, and the rest were highly dispersed on the surface of the samples [22,27]. Moreover, we can find that when Mnⁿ⁺ and Al³⁺ were added into CeO₂, the full width at half maximum height (FWHM) value of the ceria F_{2g} band was broadened remarkably (Table 1), which was related to the increase of defect concentration and the decrease of crystallite size [21,36]. Especially, the FWHM value (F2g) of Al-containing C₆M₄A_{0.25}, C₆M₄A_{0.5}, C₆M₄A₁, and C₆M₄A₂ mixed oxides were obviously larger than that of the C₆M₄ sample. Furthermore, it can be seen from Fig. 2(b) that the introduction of Al³⁺ into C₆M₄ sample led to the Raman intensity of ceria F_{2g} and hausmannite A_{1g} weakening remarkably, while the shift of position of F_{2g} was very slight, which indicated that the excess Al³⁺ was highly dispersed on the surface of these samples. All the observations were consistent with the XRD results. Based



Fig. 2. (a) XRD patterns and (b) Raman spectra of the samples.

on the XRD and Raman results, we concluded that the introduction of Al^{3+} into the C_6M_4 sample further decreased the crystallite size. In addition, a fraction of the Al^{3+} was incorporated into the lattice of CeO_2 , and the rest were highly dispersed on the surface of these samples.

3.3. Textural characterization (N₂ physisorption)

According to the results of the catalytic performance, the introduction of a small amount of Al3+ into C6M4 mixed oxide enhanced the catalytic performance. Especially, the C₆M₄A_{0.5} mixed oxide presented the best NO conversion and N2 selectivity. Therefore, in order to explore the influence of textural property on the catalytic performance of these samples, C₆M₄ and C₆M₄A_{0.5} mixed oxides were chosen as representative samples for N₂ physisorption measurement. The results are presented in Fig. 3. N2 adsorption-desorption isotherms and the BJH pore distribution curves of CeO₂ and C₆A_{0.5} are also exhibited in this figure for comparison. All the samples exhibited the classical type IV a isotherm with a well defined H2 type hysteresis loop, which is the characteristic of a wormhole-like and interstitial mesoporous structure formed by nanoparticle assembly [37,38]. Moreover, Fig. 3(b) shows that the pore size distribution curves of these samples obtained by the BJH method exhibited one single peak centered at 4 nm (in the mesoporous range of 2-50 nm), which further indicated that these samples possessed a mesoporous structure. The textural data of these samples are also displayed in Fig. 3. Interestingly, compared with CeO₂, when the doped ions were incorporated into the lattice of CeO2 (i.e., C₆A_{0.5}, C₆M₄, and C₆M₄A_{0.5} mixed oxides), the BET specific surface area increased from 39.8 to 89.5, 99.1, and 106.4 m²/g, accompanied with the increase of the pore volume from 0.1667 to 0.2600, 0.3102, and 0.4144 cm³/g. This would be related to the decrease of the crystallite size of these samples to some extent. Especially, the C₆M₄A_{0.5} mixed oxide exhibited the largest BET specific surface area and pore volume, which is beneficial for sufficient contact between catalyst and reactants, and further promotes the enhancement



Fig. 4. H₂-TPR profiles of representative samples.

of catalytic performance.

3.4. Reduction property (H₂-TPR)

The reduction property of the catalyst is a key factor in redox reactions. Hence, a H2-TPR test was performed on the representative samples of the C₆M₄ and C₆M₄A_{0.5} mixed oxides for obtaining the reduction property information, as shown in Fig. 4. In order to get a better understanding of the reduction behavior of manganese oxide, the H₂-TPR profile of the M₄A_{0.5} sample is also displayed. Furthermore, the H₂-TPR profiles of CeO₂ and C₆A_{0.5} mixed oxide are exhibited for comparison. It can be seen that CeO2 showed two reduction peaks at 511 and 806 °C, which were assigned to the reduction of surface CeO₂ and bulk CeO₂, respectively [21,39,40]. Similarly, the C₆A_{0.5} mixed oxide also exhibited the two reduction peaks. However, the relative area of the low-temperature reduction peak for the $C_6A_{0.5}$ mixed oxide was obviously larger than that of CeO_2 , which was because of the decrease of crystallite size, increase of BET specific surface area, and the interaction between Ce4+ and Al3+ [41]. A ceria-based mixed oxide with a smaller crystallite size has more exposed surface oxygen, which can readily



Fig. 3. (a) N2 adsorption isotherms, and (b) BJH pore distribution curves of representative samples.

interact with hydrogen in the reduction process.

It can be seen from Fig. 4 that the M₄A_{0.5} sample exhibited two reduction peaks at 350 and 490 °C, which were labeled as α and β . The low-temperature reduction peak (α) can be attributed to the reduction of MnO₂/Mn₂O₃ to Mn₃O₄, and the high-temperature reduction peak (β) can be assigned to the reduction of Mn₃O₄ to MnO [31,32]. Although only crystalline Mn₃O₄ was observed in the XRD pattern of the M₄A_{0.5} sample, MnO₂/Mn₂O₃ may be highly dispersed on the surface of crystalline Mn₃O₄. This needs to be further confirmed by XPS characterization. The C₆M₄ and C₆M₄A_{0.5} mixed oxides also presented two reduction peaks (α and β). Combined with the H₂-TPR profile of CeO₂, these reduction peaks were not only attributed to the reduction of manganese oxide, but also contained the reduction of surface CeO₂ [31]. Interestingly, the reduction peaks of the C₆M₄ and C₆M₄A_{0.5} mixed oxides were obviously shift to the low temperature direction compared with those of the M₄A_{0.5} sample, which indicated that some interaction may exist between Ce⁴⁺ and Mnⁿ⁺ to promote the reduction of manganese oxide. Especially, the C₆M₄A_{0.5} mixed oxide exhibited the lowest temperature of the reduction peaks among these samples, which may be related to its smallest crystallite size. Quantitative data from H₂-TPR for these samples are listed in Table 2. The reduction peak area ratio (S_{α}/S_{β}) of these samples was ranked by $M_4A_{0.5} < C_6M_4 < C_6M_4A_{0.5}$, which indicated that the

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Quantitative analysis of H ₂ -TPR for representative sampl	es

Sample	Peak temperature (°C)		H ₂ consumption (μmol/g)			Peak area ratio	
	α	β	α	β	α+β	$- (S_{\alpha}/S_{\beta})$	
C_6M_4	246	340	860	977	1837	0.88	
$C_6M_4A_{0.5}$	226	329	855	789	1644	1.08	
$M_4A_{0.5}$	350	490	1675	2912	4587	0.58	

 $C_6M_4A_{0.5}$ mixed oxide contained the largest amount of high valence manganese (such as Mn^{4+} and Mn^{3+}).

3.5. Surface chemical state analysis (XPS)

In order to further investigate the valence state, surface composition, and electron interaction of these samples, XPS was carried out on the representative samples of the C_6M_4 and $C_6M_4A_{0.5}$ mixed oxides. The results are displayed in Fig. 5. To facilitate comparison, the spectra of the $C_6A_{0.5}$ and $M_4A_{0.5}$ samples are also exhibited in this figure. The complex Ce 3d spectrum of these samples was fitted by eight photoelectron peaks corresponding to the four pairs of spin-orbit split doublets with the assignment shown in Fig. 5(a). It can be seen that all the $C_6A_{0.5}$, C_6M_4 , and $C_6M_4A_{0.5}$ mixed oxides exhibited six strong photoelectron peaks labeled u''' and v''', u and v,



Fig. 5. XPS profiles of representative samples. (a) Ce 3d; (b) Mn 2p; (c) Al 2p; (d) 0 1s.

 Table 3

 Surface composition of representative samples by XPS analysis.

Sample –		Atomic concentration (at%)					Atomic ratio (%)		
	С	Ce	Mn	Al	0	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$	$Mn^{4+}/(Mn^{2+}+Mn^{3+}+Mn^{4+})$	0″/0′	
$C_{6}A_{0.5}$	41.06	11.22	_	2.05	45.67	11.14	_	46.89	
C_6M_4	40.09	10.61	3.88		45.42	12.63	29.34	39.58	
$C_6M_4A_{0.5}$	38.84	10.42	3.24	1.28	46.22	13.89	32.55	63.09	
$M_{4}A_{0.5}$	26.65	—	11.12	9.63	52.60	—	24.75	78.03	

which were ascribed to Ce⁴⁺ [42–44]. Furthermore, two weak photoelectron peaks (u' and v') corresponding to Ce³⁺ were also observed on the three samples, which indicated that the chemical valence of Ce was mainly a +4 oxidation state, and a little of Ce³⁺ coexisted [43–45]. The relative content of Ce³⁺ in these samples can be calculated by the following equation based on the peak area [22,46]:

$$Ce^{3+} = \frac{S_{u'} + S_{v'}}{\sum (S_u + S_v)} \times 100\%$$

The surface atomic concentration and atomic ratio of the samples are summarized in Table 3. The Ce3+ content of the C₆M₄ and C₆M₄A_{0.5} mixed oxides was obviously larger than that of the C₆A_{0.5} sample, which may be related to electron interaction, doped amount, and crystallite size. Especially, the C₆M₄A_{0.5} mixed oxide exhibited the largest Ce3+ content. There were three possible reasons, the first is that electron interaction may be existed between Ce⁴⁺ and Mnⁿ⁺ (such as Ce⁴⁺ + Mn³⁺ \leftrightarrow Ce³⁺ + Mn⁴⁺, Ce⁴⁺ + Mn²⁺ \leftrightarrow Ce³⁺ + Mn³⁺, and 2Ce⁴⁺ + Mn²⁺ \leftrightarrow 2Ce³⁺ + Mn⁴⁺) [47]; the second is that the substitution of Ce^{4+} (r = 0.92Å) by Mn⁴⁺ (r = 0.54 Å), Mn³⁺ (r = 0.66 Å), Mn²⁺ (r = 0.80 Å), and Al³⁺ (r = 0.50 Å) leads to the contraction of the lattice of CeO₂ while the spontaneous transformation of Ce^{4+} (r = 0.92 Å) into larger Ce³⁺ (r = 1.03 Å) can compensate for this lattice contraction [19,22]; and the third is that the relative content of Ce^{3+} in the particles was inversely proportional to the crystallite size [48,49], which was supported by the XRD results.

The Mn 2p spectrum of the M₄A_{0.5}, C₆M₄, and C₆M₄A_{0.5} samples was numerically fitted with six photoelectron peaks (as shown in Fig. 5(b)), which indicated that the Mn species existed in the form of a mixed valence manganese system on the surface of these samples. It can be seen from Fig. 5(b) that Mn $2p_{3/2}$ contained three characteristic peaks, which were attributed to three Mn species, Mn²⁺ (640.0 eV), Mn³⁺ (641.3 eV), and Mn⁴⁺ (643.3 eV) [47,50]. The Mn 2p_{1/2} also showed three Mn species in the binding energy range of 650–658 eV. Table 3 shows that the relative content of Mn4+ in these samples was ranked by $M_4A_{0.5} < C_6M_4 < C_6M_4A_{0.5}$, which was consistent with the results of H₂-TPR. Especially, the C₆M₄A_{0.5} mixed oxide exhibited the largest Mn⁴⁺ content, which indicated that the incorporation of Al³⁺ into the C₆M₄ mixed oxide led to the redox cycles (Ce⁴⁺ + Mn³⁺ \leftrightarrow Ce³⁺ + Mn⁴⁺ and 2Ce⁴⁺ + Mn²⁺ \leftrightarrow 2Ce³⁺ + Mn⁴⁺) to shift to the right through decreasing the crystallite size. Moreover, it is widely reported that the Mn4+ species possessed the optimal redox property of the manganese-based catalysts, which is beneficial to the enhancement of catalytic performance for many redox reactions [47,51]. Hence, the largest Mn4+ content of C6M4A0.5 favored the best catalytic performance for NO elimination.

The Al 2p spectrum of the M₄A_{0.5}, C₆A_{0.5}, and C₆M₄A_{0.5} samples is displayed in Fig. 5(c). A single strong photoelectron peak centered at 73.5 eV was observed over the M₄A_{0.5} sample. The C₆A_{0.5} and C₆M₄A_{0.5} samples exhibited this peak at a lower binding energy of 73.3 eV, which indicated that some interaction existed between Ce4+ and Al3+. This observation suggested that the introduction of reductant Al³⁺ into the C₆M₄ sample weakened the interaction of Ce⁴⁺ and Mnⁿ⁺, which was harmful to the enhancement of catalytic performance. The high resolution spectrum of the 0 1s ionization feature of these representative samples was numerically fitted with two components, which are exhibited in Fig. 5(d). All these samples show a main peak (0') and a shoulder (0'') with a higher binding energy, which was attributed to the characteristic lattice oxygen bonded to metal cations, and surface adsorbed oxygen, respectively [22,47]. Compared with the $M_4A_{0.5}$ sample, the O' and O'' peaks of the C₆A_{0.5}, C₆M₄, and C₆M₄A_{0.5} mixed oxides were shifted to the low binding energy direction, which further suggested some interaction between cerium and the doped ions. Furthermore, it can be seen from Table 3 that the ratio of O''/O' for the C₆M₄A_{0.5} mixed oxide (63.09%) was obviously larger than that for the C_6M_4 mixed oxide (39.58%). This was related to the increase of defect concentration and the decrease of crystallite size caused by the incorporation of Al3+ (supported by the XRD and Raman results), which is beneficial for the adsorption of oxygen.

3.6. CO or/and NO interaction with the catalysts (in situ DRIFTS)

In situ DRIFTS of CO adsorption as a function of temperature was performed on the representative samples of the C₆M₄ and C₆M₄A_{0.5} mixed oxides to understand their reduction and adsorption properties. The results are presented in Fig. 6. When the C₆M₄ mixed oxide was exposed to CO at room temperature (25 °C), it exhibited two vibration bands at 1304 and 1570 cm-1, which were attributed to monodentate carbonate and carboxylate, respectively [17,22,52,53]. The intensity of these two bands weakened with the increase of temperature, and completely disappeared at 400 and 300 °C. Furthermore, when the temperature was increased to 150 °C, two new bands appeared at 1383 and 1473 cm⁻¹, which were assigned to the different vibration modes of bidentate carbonate [52,53]. Increasing the temperature to 250 °C led to a new band at 1548 cm⁻¹ corresponding to the vibration mode of formate, which was related to the surface hydroxyl group of the sample [53]. Interestingly, the intensity of these three new bands was enhanced with the increase of temperature due to the reduction



Fig. 6. In situ DRIFTS of CO interaction with (a) C₆M₄ and (b) C₆M₄A_{0.5} mixed oxides.

of Ce⁴⁺ by CO to generate more Ce³⁺ during the heating, and Ce³⁺ is beneficial to the adsorption of CO species [22,54,55]. With regard to the C₆M₄A_{0.5} mixed oxide, when it was exposed to CO at room temperature and during the heating, all of the vibration bands of monodentate carbonate, carboxylate, bidentate carbonate, and formate were detected, which is very similar to the C₆M₄ mixed oxide. However, on comparing Fig. 6(b) with Fig. 6(a), we can find that the intensity change of vibration bands for the C₆M₄A_{0.5} mixed oxide with the increase of temperature was more obvious than that for the C₆M₄ mixed oxide. This indicated that the incorporation of Al³⁺ into the

 C_6M_4 mixed oxide promoted the adsorption of CO, which resulted from the improvement of the reduction property, and benefited to generate more Ce^{3+} during the heating to adsorb CO species.

It is well known that the adsorption and desorption property of a denitration catalyst for NO is a key factor in the catalytic reduction of NO by CO. Therefore, *in situ* DRIFTS of NO adsorption was carried out on the representative samples of the C₆M₄ and C₆M₄A_{0.5} mixed oxides at various temperatures, as shown in Fig. 7. For the C₆M₄ mixed oxide, when it was exposed to NO at room temperature, several IR bands appear in the range of



Fig. 7. In situ DRIFTS of NO interaction with (a) C₆M₄ and (b) C₆M₄A_{0.5} mixed oxides.

1000-1700 cm⁻¹. The bridging bidentate nitrate exhibited a NO₂ symmetric vibration mode at 1011 cm⁻¹ and a N=O stretching mode at 1603 cm⁻¹. The chelating bidentate nitrate displayed two bands of symmetric and asymmetric vibration at 1237 and 1574 cm⁻¹, respectively. The linear nitrite presented a vibration band at 1285 cm⁻¹ [22,56,57]. Some interesting phenomena were observed in the heating process. First, when the temperature increased to 300 °C, the N=O stretching mode of the bridging bidentate nitrate (1603 cm⁻¹) and the linear nitrite (1285 cm⁻¹) disappeared completely. Second, a new band of free NO₃- ions appeared at 1356 cm⁻¹ when the temperature was up to 400 °C [57]. Finally, the NO₂ symmetric vibration band of the bridging bidentate nitrate (1011 cm⁻¹), as well as the symmetric and asymmetric vibration bands of the chelating bidentate nitrate (1237 and 1574 cm⁻¹) weakened with the temperature, but did not completely disappear even at 450 °C. These observations indicated that the adsorbed NO species on the surface of the C₆M₄ mixed oxide can be desorbed or converted or dissociated during the heating. Similarly, with regard to the C₆M₄A_{0.5} mixed oxide, all the vibration bands of the bridging bidentate nitrate, chelating bidentate nitrate, and linear nitrite were detected at room temperature. Comparing Fig. 7(b) with Fig. 7(a), some interesting phenomena can be observed with the elevation of temperature. First, the N=O stretching mode of the bridging bidentate nitrate (1605 cm⁻¹) and the linear nitrite (1284 cm⁻¹) disappeared at a lower temperature of 200 °C. Second, when the temperature was up to 350 °C, the symmetric and asymmetric vibration bands of the chelating bidentate nitrate (1237 and 1574 cm⁻¹) had disappeared completely. Third, free NO3- ions (1355 cm-1) appeared at a lower temperature of 200 °C. Finally, two new bands of anionic nitrosyl (NO-) and nitro (NO2-) appeared at 1211 and 1539 cm⁻¹ at 200 °C, and weakened with the further elevation of temperature, but did not completely disappear even at 450

°C [56,57]. These observations suggested that adsorbed NO species on the surface of the $C_6M_4A_{0.5}$ mixed oxide were more easily desorbed or converted or dissociated with the increase of temperature than those on the surface of the C_6M_4 mixed oxide. The reason may be that the incorporation of Al^{3+} into the C_6M_4 mixed oxide promoted the increase of Mn^{4+} content (supported by the H₂-TPR and XPS results), and Mn^{4+} is conducive to the desorption or conversion or dissociation of the adsorbed NO species by electron transfer [47].

In order to get more information about the reaction of NO reduction by CO, in situ DRIFTS of NO+CO co-adsorption were recorded on the representative samples of the C₆M₄ and C₆M₄A_{0.5} mixed oxides under simulated reaction conditions. The results are presented in Fig. 8. Exposing the C₆M₄ mixed oxide to NO and CO mixed gases at room temperature led to several vibration bands for nitrate and nitrite that appeared in the range of 1000-1700 cm-1, while the vibration signals of carbonate and carboxylate were absent, which indicated that NO molecules preferentially adsorbed on the surface of the C₆M₄ mixed oxide due to their unpaired electrons, and inhibited the adsorption of CO [17,30]. When the temperature increased to 400 °C, all the vibration bands for nitrate and nitrite had disappeared completely due to the desorption or conversion or dissociation of the adsorbed NO species. Therefore, some active sites were exposed to adsorb CO. Simultaneously, two new bands of hydrogencarbonate and bidentate carbonate appeared at 1347 and 1472 cm⁻¹, respectively [22,52]. Combining with the results of the catalytic activity and selectivity, we can say that the reaction between adsorbed CO species and gaseous NO molecules (above 400 °C) is more beneficial to the reduction of NO to N₂ than the reaction between adsorbed NO species and gaseous CO molecules (below 400 °C). Fig. 8(b) shows the NO+CO co-adsorption in situ DRIFTS of the C₆M₄A_{0.5} mixed oxide. Only NO species were adsorbed on the surface of the



Fig. 8. In situ DRIFTS of CO and NO co-interaction with (a) C₆M₄ and (b) C₆M₄A_{0.5} mixed oxides.

C₆M₄A_{0.5} mixed oxide at room temperature, which was very similar with the situation of the C_6M_4 mixed oxide (Fig. 8(a)). Interestingly, comparing with Fig. 8(a), we can find that the vibration signals of the adsorbed NO species disappeared at a lower temperature of 350 °C, which was because the incorporation of Al3+ into the C6M4 mixed oxide was conducive to the increase of Mn⁴⁺ content, and further promoted the desorption or conversion or dissociation of the adsorbed NO species [47]. When the temperature was up to 350 °C, CO species were adsorbed on the surface of the C₆M₄A_{0.5} mixed oxide to generate formate (1547 cm⁻¹), bidentate carbonate (1382 and 1472 cm⁻¹), hydrogencarbonate (1347 cm⁻¹), and CO_x coordinated to the reduced ceria (1060 cm⁻¹) [22,52,53]. Especially, these vibration singals of adsorbed CO species on the surface of the C₆M₄A_{0.5} mixed oxide were obviously stronger than those of the C₆M₄ mixed oxide. This was because that improved reduction property of the C₆M₄A_{0.5} mixed oxide was beneficial to the reduction of Ce⁴⁺ by CO to generate more Ce³⁺ at high temperature, and further promoted the adsorption of CO [22,54,55]. Therefore, the catalytic performance of the C₆M₄A_{0.5} mixed oxide for NO reduction by CO was better than that of the C₆M₄ mixed oxide.

3.7. Reaction mechanism of NO reduction by CO over the CeO₂-MnO_x-Al₂O₃ catalyst

Based on the characterization, a reaction mechanism of NO reduction by CO over the CeO₂-MnO_x-Al₂O₃ catalyst is proposed to further understand the excellent catalytic performance for this model reaction, as shown in Fig. 9. NO molecules are preferentially adsorbed on Mnⁿ⁺ sites owing to their unpaired electrons to form nitrate and nitrite species when the CeO₂-MnO_x-Al₂O₃ catalyst was exposed to NO and CO at room temperature (25 °C) [58]. Therefore, the adsorption of CO was inhibited, which was supported by the results of NO+CO co-adsorption by *in situ* DRIFTS. In this situation, gaseous CO molecules can react with adsorbed NO species to generate a small amount of N₂, and large amounts of N₂O and CO₂ at low temperature (LT, below 350 °C), which is consistent with the



Fig. 9. Reaction mechanism of NO reduction by CO over the CeO_2 -MnO_x-Al₂O₃ catalyst.

results of the catalytic performance. However, the interaction between CO and the CeO₂-MnO_x-Al₂O₃ catalyst at high temperature (HT, above 350 °C) results in the reduction of the catalyst to form more Ce³⁺ and oxygen vacancies. It is widely reported that Ce³⁺ is beneficial to the adsorption of CO, and the oxygen vacancy weakened the N–O bond to promote the dissociation of NO [22,54,55,58]. Therefore, gaseous NO can be dissociated into N and O radicals by the oxygen vacancy to react with adsorbed CO to form large amounts of N₂ and CO₂, as well as a small amount of N₂O at high temperature (HT, above 350 °C). Finally, the byproduct N₂O can be further reduced to the final product N₂ at the higher temperature.

4. Conclusions

A series of CeO₂-MnO_x-Al₂O₃ catalysts were prepared by a simple one-step inverse co-precipitation method for investigating the influence of the incorporation of Al^{3+} into CeO_2 -MnO_x mixed oxide on their physicochemical property and catalytic performance for the NO+CO model reaction. The conclusions drawn are as follows. (1) The incorporation of Mn^{n+} and Al^{3+} into the lattice of CeO₂ inhibited its grain growth, which led to the decrease of crystallite size. Especially, the crystallite size of Al-containing CeO₂-MnO_x-Al₂O₃ catalysts was obviously smaller than that of the CeO_2 -MnO_x mixed oxide, which indicated that the introduction of Al³⁺ can further decrease the crystallite size of the CeO_2 -MnO_x sample. (2) N₂ physisorption results showed that the incorporation of Al^{3+} into the CeO₂-MnO_x mixed oxide increased its BET specific surface area and pore volume remarkably, which was because of the decrease of crystallite size. The increase of BET specific surface area and pore volume is beneficial to the contact between catalyst and reactants, which enhanced catalytic performance. (3) The relative content of Ce3+ increased obviously when Al3+ was doped into the CeO_2 -MnO_x mixed oxide, which was related to the decrease of crystallite size. Simultaneously, the Mn4+ content also increased remarkably, which was caused by the shift of the redox cycles $(Ce^{4+} + Mn^{3+} \leftrightarrow Ce^{3+} + Mn^{4+} and 2Ce^{4+} + Mn^{2+} \leftrightarrow 2Ce^{3+} + Mn^{4+})$ to the right. Moreover, Ce³⁺ is beneficial to the adsorption of CO, while Mn4+ promoted the desorption or conversion or dissociation of NO. Therefore, the increase of Ce³⁺ and Mn⁴⁺ remarkably enhanced the catalytic performance for NO reduction by CO. (4) The CeO₂-MnO_x-Al₂O₃ catalyst with the optimal amount of Al³⁺ (Ce:Mn:Al mole ratio = 6:4:0.5) exhibited the best catalytic performance for the NO+CO model reaction, which was related to its smaller crystallite size, larger BET specific surface area and pore volume, excellent reduction property, as well as the higher contents of Ce3+ and Mn4+.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 1369–1380 doi: 10.1016/S1872-2067(15)61098-1

Preparation, characterization, and catalytic performance of high efficient CeO₂-MnO_x-Al₂O₃ catalysts for NO elimination

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The incorporation of a small amount of Al^{3+} into CeO_2-MnO_x mixed oxide improved its physicochemical property and enhanced the corresponding catalytic performance for NO reduction by CO efficiently.

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