

Effect of Discharge Atmosphere on Structure and Performance of Composite Metal Oxides Catalysts

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Abstract: The manganese-cerium composite oxides catalysts were prepared with the pretreatment of plasma. The effects of the discharge atmosphere of the plasma, including N₂, Ar, and air, on the structure and performance of manganese-cerium oxides were investigated. The physical and chemical properties of the samples were characterized by means of the BET surface area, X-ray diffraction, X-ray photoelectron spectra and H₂-temperature programmed reduction analysis. Plasma pretreatment can improve the catalytic oxidation performance of the catalyst. The catalyst pretreated by air plasma displays the highest catalytic activity, whose NO oxidation efficiency is about 75% at 275 °C, which is 20% higher than the catalyst prepared by the traditional method. Plasma pretreatment can improve oxygen mobility and oxidation-reduction ability at low temperatures. According to the characterization of the catalysts, the improvement of the redox ability and catalytic activity is attributed to the enhancement of the formation of solid solution structure between MnO_x and CeO₂ with plasma pretreatment, leading to an increase of specific surface area, the ratio of Ce³⁺ at catalyst surface and the amount of surface active oxygen, which result in the improvement of the redox ability and catalytic activity.

Key words: plasma; manganese oxide; cerium oxide; NO; catalytic oxidation

CLC number: 0643.36

Document code: A

Nitrogen oxides (NO_x) emission from fossil fuel combustion is one of the most important environmental problems because it contributes to the formation of acid rain, photochemical smog and ozone depletion. Oxidizing NO into NO₂ by O₂ is an essential pre-requisite step for NO_x removal as NO₂ promotes the selective catalytic reduction and enhances the absorption of NO in wet flue gas desulfurization system^[1]. One of the effective methods to increase the proportion of NO₂ in exhaust gas is passing gas over a strong oxidation catalyst.

Transition metal oxides, supported noble metal catalyst, active carbon and zeolite are the primary catalysts for NO catalytic oxidation reaction^[1-4]. Among these catalysts, transition metal oxides have been studied widely due to its excellent redox ability and the moderate cost. Many studies reported that cerium oxide

has strong ability for oxygen storage and shows a good performance in oxidation reactions^[5]. Manganese oxides present high low-temperature catalytic activity and shows strong ability to interact with cerium oxide which leads to the formation of solid-solution structure, the promotion of the activity of lattice oxygen, and the enhancement of catalytic activity^[6]. Therefore, the manganese-cerium composite catalysts have been studied extensively in treatment of liquid and gaseous pollutants due to their superior catalytic performance^[5,7-9].

However, compared with the commercially noble metal supported catalyst, the catalytic activity for NO catalytic oxidation of the manganese-cerium composite oxides catalyst under current preparation method is still lower, which limits it to be the substitute of commer-

Received date: 2017-11-17; **Revised date:** 2017-12-30.

Foundation: This work has been supported by the National Key Research and Development Plan (2017YFB0603200) and the Postdoctoral Research Funding Plan of Jiangsu Province (1701029A).

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cial catalyst. Therefore, it is of great significance to carry on research on how to enhance the catalytic oxidation ability of this transition metal oxide catalyst. In recent years, non-thermal plasma has been applied in the preparation of catalysts as plasma-assisted preparation can change catalyst properties and improve catalytic activity. Non-thermal plasma contains a large number of active species, including excited particles, electrons and ions, with a macroscopic temperature of 25~200 °C. These active species can help decompose nitrates and organics in precursor of the catalyst and lead to the formation of surface defects and active sites^[10-13]. Thus pretreatment of the catalyst using plasma shows a promising method to improve the redox ability and catalytic performance of the manganese-cerium mixed-oxides catalyst^[12,14-16]. In this work, MnCeO_x catalysts were prepared using the plasma-assisted sol-gel method and tested in the oxidation of NO. The effects of plasma in different discharge atmosphere including Ar, N₂ and air were compared. The physical and chemical properties of the catalysts were characterized.

1 Experimental

1.1 Catalyst preparation

MnCeO_x precursor with a Mn : Ce atom ratio of 3 : 1 was prepared by the sol-gel method^[15]. The sol was heated at 80 °C till gel was formed. The sample was dried at 110 °C overnight. This sample was denoted as MnCeO_x w/o P or C. Then the sample divided into two portions. One portion calcined in air at 300 °C. The obtained sample was denoted as MnCeO_x-C. The other portion of the sample was put into the discharging tube and treated by plasma for 90 min, followed by the calcination in air at 300 °C. The plasma was generated by high-frequency dielectric barrier discharge with discharge power of 180 W. This sample was nominated as MnCeO_x-M (M was noted as discharge atmosphere, Ar, N₂ or Air).

1.2 Catalytic activity tests

Experiments of NO catalytic oxidation were carried out at atmospheric pressure in the temperature range of 100~350 °C in a cylindrical fixed-bed quartz reactor

(diameter = 8 mm) containing 0.2 g catalyst of 60~80 mesh. The reactor was connected to Testo 350XL gas analyser for NO and NO₂ measurement. The gas flow and gas hourly space velocity (GHSV) in all experiments were 1 200 mL/min and 360 000 mL⁻¹g⁻¹h⁻¹; The simulated gas mixtures used contained 400 ppm NO, 5% O₂ and balance N₂. The NO oxidation efficiency (X) and the rate constant (k) were calculated as follows:

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

$$k = -\frac{F}{W} \ln(1 - X) \quad (2)$$

Where $[NO]_{in}$ and $[NO]_{out}$ represented the inlet and outlet concentrations of gaseous NO, respectively; F was the total flow rate and W was the weight of the catalyst.

1.3 Catalyst characterization

Thermogravimetric analysis (TGA) was performed by using a TA Q500 TGA instrument. The samples (3~4 mg) were heated from 50 to 800 °C in nitrogen at a heating rate of 10 °C/min.

Fourier-transform infrared spectroscopy (FTIR) was carried out to investigate the functional groups species using a Nicolet 5700 spectrometer. The spectrum was generated and collected 32 times and the background line obtained was automatically subtracted. The spectra were recorded from 4 000~400 cm⁻¹.

The BET surface area and pore size distribution were obtained by measuring N₂ adsorption and desorption at liquid nitrogen temperature (77 K) with Micromeritics ASAP 2020 system. Prior to N₂ adsorption, the samples were degassed at 250 °C for 3 h.

The powder X-ray diffraction (XRD) was carried out on a Rigaku D/max-rA system using monochromated Cu K α radiation (40 kV, 200 mA) at a scan rate of 4°/min with a 0.0167° step size in the 2 θ range between 10° and 90°.

Temperature programmed reduction (TPR) of hydrogen was performed on a custom-made TCD setup using 100 mg catalysts to measure the redox properties. Prior to each measurement, the samples were pretreated under flowing pure Ar at 200 °C for 30 min, and this

was followed by cooling to 50 °C in atmosphere of Ar containing 10% H₂ at a flow rate of 30 mL/min. TPR runs were carried out from 50 ~ 700 °C with linear heating rate (10 °C/min) in the same atmosphere.

The X-ray photoelectron spectra (XPS) measurement of O 1s, Mn 2p, and Ce 3d regions was performed a Thermo ESCALAB 250 electron spectrometer equipped with an Al K α X-rays ($h\nu=1\,486.6$ eV) and

a hemispherical electron analyzer being operated at a constant pass energy (20 eV). Sample charging effects were eliminated by correcting the observed spectra with a C 1s binding energy (BE) value of 284.6 eV.

2 Results and Discussion

2.1 Catalytic activities

Fig.1(a) shows the NO oxidation efficiency of the

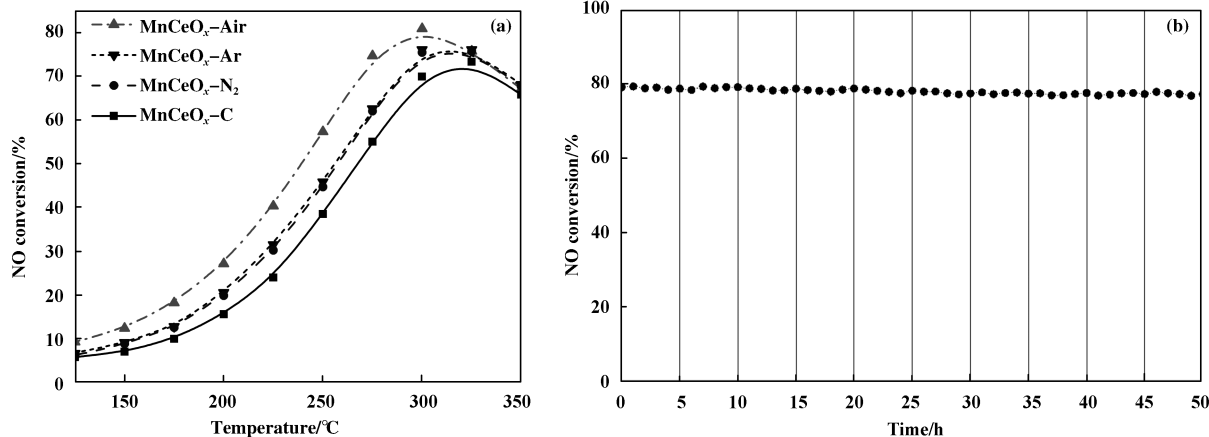


Fig.1 (a) Catalytic activity of the catalysts along with temperatures; (b) Catalytic performance of the MnCeO_x-Air catalyst within 50 h

manganese-cerium oxides catalysts prepared by plasma pretreatment and traditional method. The oxidation efficiency increases as the temperature increases until reaches the equilibrium of the reaction. The order of oxidation efficiency is as follows: MnCeO_x-Air > MnCeO_x-Ar \approx MnCeO_x-N₂ > MnCeO_x-C. Compared with the catalyst prepared by traditional method, the catalytic activities are improved by the pretreatment of plasma, especially at 250 ~ 275 °C. The NO conversion of MnCeO_x-Air is 75% at 275 °C, which is 20% higher than that of MnCeO_x-C. In Fig.1(b), it can be seen that the MnCeO_x-Air catalyst has a favorable stability within 50 h.

2.2 Analysis of the samples treated by plasma

FTIR

To study the characters and components at the surface of the precursor treated by plasma in different discharge atmosphere, FTIR was utilized to analyze these samples. The results are displayed in Fig.2. The surface of the precursor without treatment has numerous groups including —COOH, —NO₃⁻, —OH, C—O—

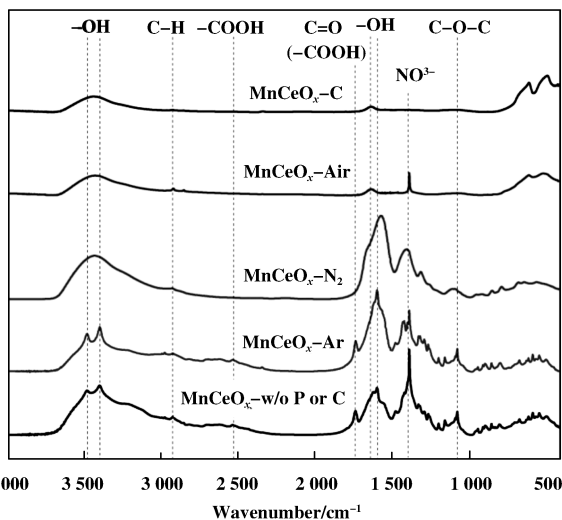


Fig.2 The FTIR spectra of the catalyst precursors before calcination

C and C = O. The peak at 1388 cm⁻¹ is corresponding to the nitrates. The peak is weakened by Ar plasma treatment, which demonstrates that Ar plasma could decompose partial nitrates. The peak at 1734 cm⁻¹ is contributed to the C = O in —COOH, and the peak at

$1\,073\text{ cm}^{-1}$ is contributed to C—O—C in polyethylene glycol (PEG). No obvious change for these two peaks is observed after Ar plasma treatment, which demonstrates that Ar plasma cannot decompose organics. This is because the active species in Ar plasma is only metastable Ar atoms^[17], which have weak reaction with the precursor.

After N_2 plasma treatment, the —COOH peak vanishes and both the C—O—C and — NO_3^- peaks weaken notably. It demonstrates that N_2 plasma treatment can decompose all carboxyl group and partial polyethylene glycol and nitrates, which results from the reactions between the precursor and excited or metastable N and N_2 in N_2 plasma, which is more active than metastable Ar.

The infrared spectroscopy of the sample treated by air plasmas is almost the same with that of the sample after calcination, except trace amount of residue nitrates. As our experimental experience, if catalyst were placed in the plasma discharge zone, NO and NO_2 could be oxidized by O_2 in air, and then adsorbed by the catalyst. Therefore the residue nitrates maybe caused by the decomposition-adsorption equilibrium. It indicates that air plasmas could decompose nitrates and organic matters almost completely and gain pure oxides with trace nitrates. That is because the oxidative active components including O, O_3 formed in air plasma can decompose nitrates and organics in the precursor of catalyst efficiently.

TGA

The results of TGA for the samples treated by plasma but without calcinations are displayed in Fig.3. Compare with the result of FTIR, it is found that the weight loss before the temperature of $230\text{ }^\circ\text{C}$ is attributed to the desorption of absorbed water, and the decomposition of carboxyl group and nitrates to intermediates, such as $\text{Mn}(\text{OH})_2$. The precursor without any treatment shows an obvious weight loss about 11% at $200\text{ }^\circ\text{C}$. Its weight loss at $250\sim 270\text{ }^\circ\text{C}$ could be contributed to the decomposition of the intermediates and the organics to Mn_2O_3 . Then the weight does not change as the temperature continues rising. The whole weight loss is about 66% eventually.

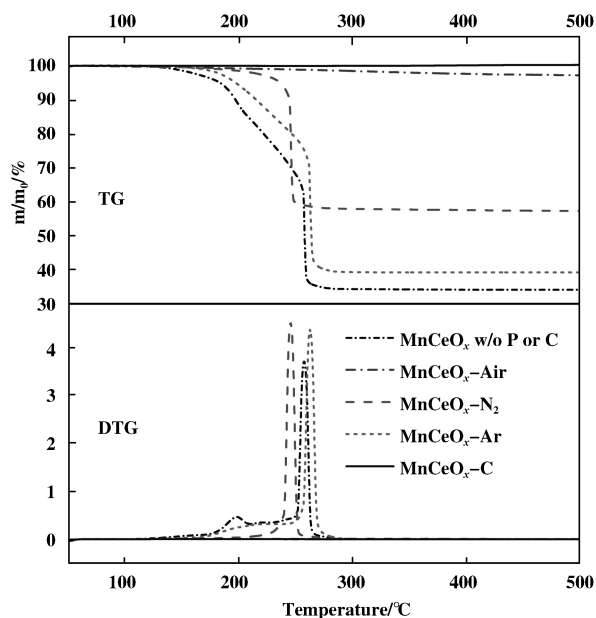


Fig.3 TG and DTG curves of the catalyst precursors before calcination

The sample prepared by Ar plasma shows a whole weight loss of 61.6%, which was just 4.4% lower than the precursor without plasma treatment. This is assistance with the result of FTIR, that Ar plasma could only decompose partial nitrates. The sample treated by N_2 plasma shows a weight loss of about 42.5%. The peak at $200\text{ }^\circ\text{C}$ disappears, and the weight loss for organics oxidation moves to a lower temperature of $230\text{ to }252\text{ }^\circ\text{C}$. Because the N_2 plasma decomposes the organics to some matters which are easy to be oxidized, the weight loss of the sample treated by N_2 plasma shifts to a lower temperature. The sample treated by air plasma shows weight loss about 4.5% and no noticeable weight loss peak is observed. It indicates that the nitrates and organics have been decomposed almost completely in the treatment process by air plasma. Therefore the pretreatment of air plasma help avoid sintering and agglomeration occurring at high temperature in calcination.

2.3 Characteristics of the catalysts

BET

Table 1 gives the specific surface area, pore volume and pore size of the catalysts prepared by plasma pretreatment and traditional calcination method. The catalysts pretreated by N_2 and Ar plasma shows little difference in specific surface area, pore volume and

Table 1 The physical characteristics of the catalysts

Samples	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	Pore volume/ $(\text{cm}^3 \cdot \text{g}^{-1})$	Pore size/nm
MnCeO _x -C	68.9	0.131	6.78
MnCeO _x -N ₂	63.8	0.112	7.15
MnCeO _x -Ar	65.9	0.126	7.87
MnCeO _x -Air	165	0.461	9.18

pore size with the sample prepared by traditional method, while the sample treated by air plasma shows much larger values of all the parameters. The specific surface area of MnCeO_x-Air is 165 m²g⁻¹, which is 2.4 times larger than that of MnCeO_x-C.

XRD

The XRD patterns of the samples prepared by plasma pretreatment and traditional method are displayed in Fig.4. As shown in Fig.4, in the pattern of

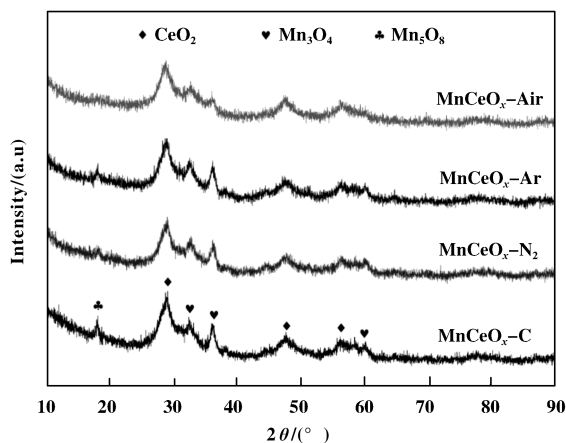


Fig.4 XRD patterns of the catalysts

MnCeO_x-C, the peaks of CeO₂, Mn₃O₄ and Mn₅O₈ can be found. The CeO₂ peaks of the samples treated by plasmas are weaker than that of MnCeO_x-C, which suggests that plasma treatment promotes the dispersion of CeO₂ component. The Mn₅O₈ peaks of MnCeO_x-N₂ and MnCeO_x-Ar are much weaker than that of MnCeO_x-C, while the Mn₅O₈ peak of MnCeO_x-Air vanishes. It demonstrates that plasma pretreatment enhance the interaction of MnO_x and CeO₂, and more solid solution structure is formed. The peak of CeO₂, Mn₃O₄ and Mn₅O₈ in MnCeO_x-Air is weaker than that of other samples, which demonstrates the solid solution structure of MnCeO_x is well formed in MnCeO_x-Air. As re-

ported in the research of MnO_x-CeO₂ mixed oxides, the solid solution has higher oxidation efficiency than MnO_x and CeO₂^[18-19], which is in the good agreement with the results of this study.

XPS

The formation of solid solution structure can change the valence of Mn and Ce in mixed-oxides and increase the amount of active oxygen. In order to analyze the valence states of the metal element and the type of oxygen on the surface of the studied samples, XPS spectra of O 1s and Ce 2p were measured, and the results are shown in Fig.5 and Table 2. Table 2 shows the percentage of oxygen on catalyst surface. It is found that the catalysts surface gets relatively rich in O value with the pretreatment of plasma. The spectra in Fig.5 are deconvolved for the convenience of observation. The oxygen species on catalyst surface plays a significant role in catalytic oxidation. The peak at 529 eV is contributed to lattice oxygen (noted as O_β) in oxides, while the peak at 531 eV is attributed to the surface adsorbed oxygen (noted as O_α), such as the chemical absorbed oxygen and the hydroxyl-like group at catalyst surface^[20]. The O_α which is more active than O_β is the major species for oxidation reaction and has significant effect on catalytic activity^[21]. As shown in Fig.5 and Table 2, the samples pretreated by plasma present higher O_α/(O_α+O_β) values than the sample prepared by traditional method. Quantitatively, it was found that the O_α/(O_α+O_β) value of MnCeO_x-Air, MnCeO_x-Ar and MnCeO_x-N₂ is 14.0%, 2.2% and 3.6% higher than that of MnCeO_x-C (26.2%), respectively, which suggests that plasma pretreatment can notably increase the oxygen vacancies and surface active oxygen, which is beneficial for catalytic oxidation.

In the Ce 3d spectra, the U, U'', U''', V, V''

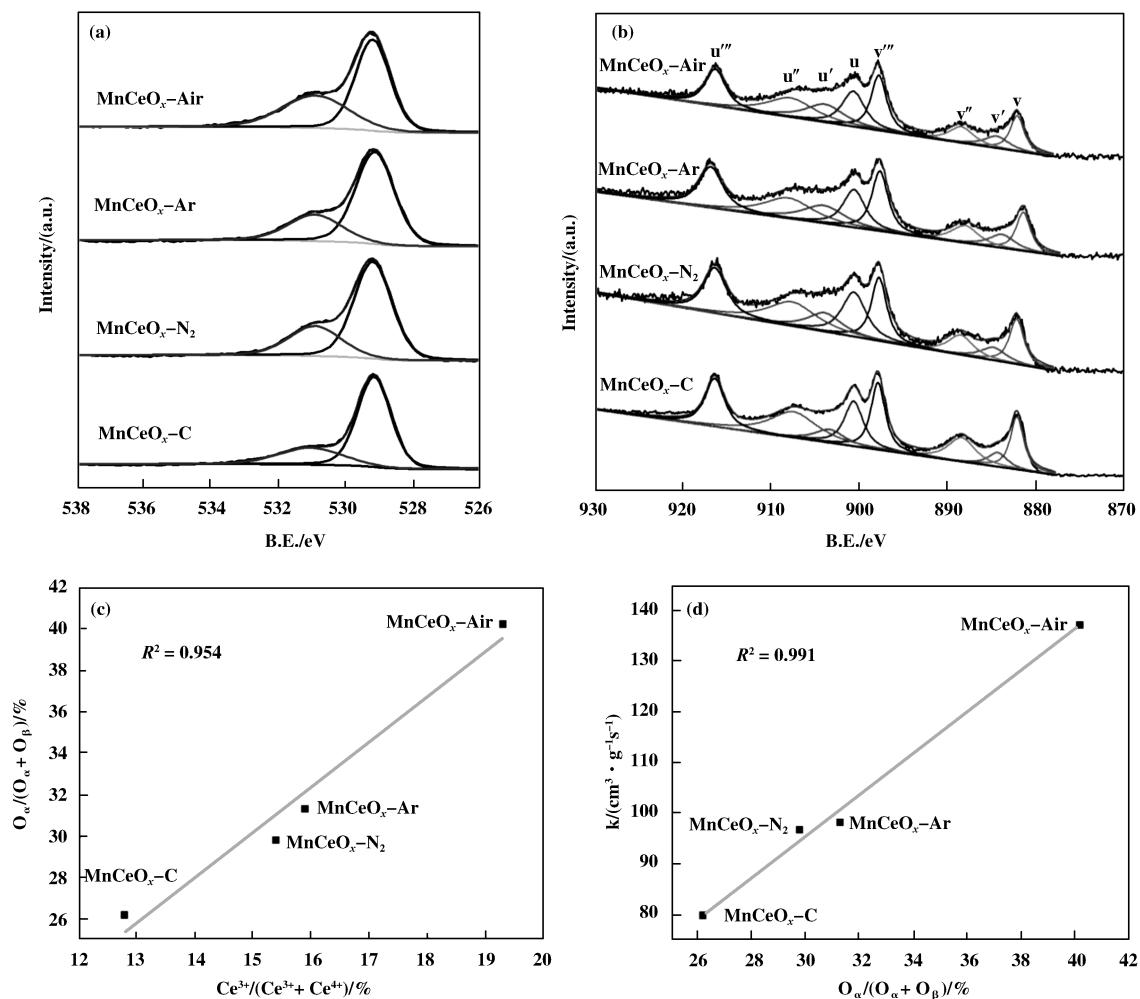


Fig.5 XPS spectra for (a) O 1s and (b) Ce 3d. (c) Correlations between the relative concentrations of surface-adsorbed oxygen $O_{\alpha}/(O_{\alpha}+O_{\beta})$ and the relative concentrations of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$. (d) Correlations between the relative concentrations of surface-adsorbed oxygen $O_{\alpha}/(O_{\alpha}+O_{\beta})$ and the rate constant (k) at 275 °C

Table 2 XPS results of the catalysts

Samples	O/%	$Ce^{3+}/(Ce^{3+}+Ce^{4+})/\%$	$O_{\alpha}/(O_{\alpha}+O_{\beta})/\%$
MnCeO _x -Air	69.14	19.3	40.2
MnCeO _x -Ar	67.01	15.9	28.4
MnCeO _x -N ₂	67.67	15.4	29.8
MnCeO _x -C	65.85	12.8	26.2

and V''' peaks are contributed to Ce⁴⁺, while the U' and V' peaks are attributed to Ce³⁺. Table 2 summarizes the calculated values of quantitative analysis. MnCeO_x-Air has the highest proportion of Ce³⁺, which is 6.5% higher than that of MnCeO_x-C. And the proportion of Ce³⁺ in MnCeO_x-Ar and MnCeO_x-N₂ is 3.1% and 2.6% higher than that of MnCeO_x-C, respectively.

The existence of Ce³⁺ is important to the formation of the surface active oxygen on catalyst surface, because Ce³⁺ can lead to charge imbalance, oxygen vacancies and unsaturated chemical bonds^[22]. Due to more solid solution is formed by plasma pretreatment, as discussed in XRD, the portion of the relative amount of Ce³⁺/(Ce³⁺+Ce⁴⁺) is increased. As a result, oxygen

vacancies and surface active oxygen in plasma-assisted prepared catalysts increase, which is confirmed by the results of relative concentration ratios of $O_\alpha/(O_\alpha+O_\beta)$. As presented in Fig.5(c), good correlation can be observed between the relative concentration ratios of $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ and relative concentration ratios of $O_\alpha/(O_\alpha+O_\beta)$, indicating that the relative concentration ratios of surface adsorbed oxygen are directly related to the concentration of Ce^{3+} on catalyst surface. Therefore, the well-formed solid solution results in the increase of relative amount of Ce^{3+} and the increase of oxygen vacancies and surface active oxygen, which has higher mobility than lattice oxygen and contributes to the enhanced catalytic performance. As shown in Fig.5(d), the rate constant (k) has a linear correlation with relative concentration ratios of $O_\alpha/(O_\alpha+O_\beta)$, indicating the catalytic performance is sufficiently related to the relative concentration ratios of surface adsorbed oxygen.

H_2 -TPR

Fig.6 shows the H_2 -TPR profiles of the studied catalysts. Profile of the catalysts showed two reduction

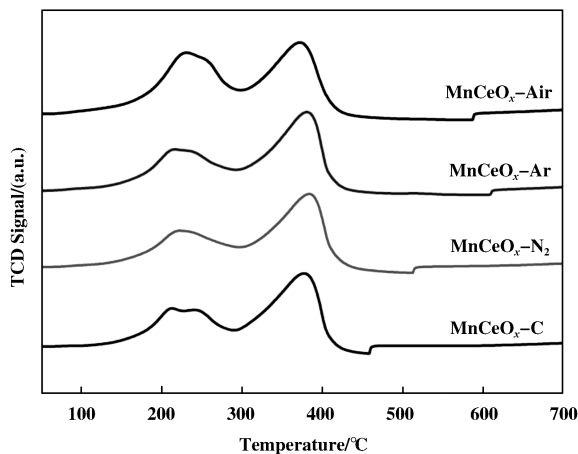


Fig.6 H_2 -TPR profiles of the catalysts

peaks. One locates in low temperature between 200 to 250 °C, which is attributed to the reduction of Mn^{4+} to Mn^{3+} , and the other in high temperature between 350 to 400 °C, is attributed to the reduction of Mn^{3+} to Mn^{2+} . The catalysts pretreated by plasmas displays stronger peaks in low temperature and weaker peaks in high temperature compared with the catalyst prepared

by traditional method, which indicates that plasma pretreatment can improve oxygen mobility and oxidation-reduction ability at low temperature^[23]. As discussed above in XPS results, there is more oxygen species and higher portion of surface adsorbed oxygen on plasma pretreated catalysts, which is easier to be reduced by H_2 and has an important influence on catalytic oxidation^[24].

In conclusion, plasma treatment can form more Mn-Ce solid solution structures and enhance the specific surface area of the catalysts and the Ce^{3+} component at catalyst surface, all of which can notably increase the oxygen vacancies and surface active oxygen. The increase of surface oxygen species enhances the redox performance of catalyst leading to the improvement of catalytic activity. Besides, the air plasma pretreatment shows the largest influence on the physical and chemical properties of the catalyst. The influence of the N_2 or Ar plasma treatment on catalyst is similar, and both of them are weaker than that of air plasma. That is because the oxidative active components including O, O_3 formed in air plasma can decompose nitrates and organics in the precursor of catalyst efficiently and lead to the formation of oxides before calcination. However, there are only some metastable Ar atoms in Ar plasma and some excited or metastable N and N_2 active components in N_2 plasma. These active components have weak reaction with the precursor of the catalyst, so have a weak influence on the catalytic performance.

3 Conclusion

Plasma pretreatment can notably enhance the catalytic oxidation activity of $MnCeO_x$ catalyst. The NO conversion efficiency of $MnCeO_x$ -Air is 20% higher than that of $MnCeO_x$ -C. Air plasma treatment has the largest influence on the physical and chemical properties, while the influences of N_2 and Ar plasmas treatments are similar and both of them were weaker than air plasma. Plasma pretreatment, especially in air discharge atmosphere, enhances the formation of solid solution between MnO_x and CeO_2 , which results in higher portion of Ce^{3+} , more surface active oxygen and the improvement of redox ability of the catalysts. All of

them are the major reasons for the improvement of catalytic performance.

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放电气氛对复合金属氧化物催化剂结构和活性的影响

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摘要: 采用等离子体辅助溶胶凝胶法制备了复合金属氧化物 MnCeO_x 催化剂, 研究了 N₂、Ar、空气等气氛产生的等离子体预处理对催化剂结构和活性的影响, 通过低温氮吸附-脱附、X 射线衍射 (XRD)、X 射线光电子能谱 (XPS) 和程序升温还原 (H₂-TPR) 等手段对催化剂表面的物理化学特性进行了表征分析. 结果表明不同气氛的等离子体可以不同程度地分解催化剂前驱体中的硝酸盐和有机物, 并有效提高催化剂的氧化活性. 经空气等离子体预处理制备的催化剂在 275 ℃ 时的对 NO 氧化效率为 75%, 比直接煅烧方法制备的催化剂的氧化效率高 20%. 等离子体预处理制备催化剂能够使 MnO_x 和 CeO₂ 之间的相互作用增强, 从而提高催化剂的比表面积, 提高催化剂表面 Ce³⁺ 的比例, 显著增加催化剂表面的化学吸附氧和弱结合的氧物种. 等离子体预处理对催化剂表面的物理化学性质的优化, 提高了催化剂的氧化还原性能和催化氧化性能.

关键词: 等离子体; 锰氧化物; 二氧化铈; NO; 催化氧化