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ARTICLE

Effect of Preparation Methods on Structure and Properties of Mn-La Catalyst for Low Temperature NH_3-SCR

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Abstract: Mn-La catalysts were prepared by solid-state reaction (SSR) and co-precipitation methods (CPM). The effects of preparation methods on denitration and SO_2/H_2O resistance of the catalysts were investigated. The structure and physicochemical properties of the catalysts were characterized by XRD, BET, H_2-TPR, NH_3-TPD and XPS. The results show that La doping decreases the crystallinity of MnO_x and increases the specific surface area and pore volume of MnO_x. The bond cooperation of Mn-O-La promotes the dispersion of Mn on the catalyst surface, while the highly dispersed Mn are easier to be reduced. The reduction temperature of the catalyst moves to lower temperature, and the redox ability is improved. After La doping, the amount of Brønsted acid and total acid increase on the catalyst surface, and the concentration of Mn^{4+} and the surface chemisorption oxygen also increase. Therefore, La doping is beneficial to the denitration activity of the catalyst. The results of reaction evaluation show that MnLa-CPM catalyst exhibits the best denitration efficiency, which is close to 100% at 80 °C. In the presence of H_2O and SO_2, the denitration efficiency of MnLa-CPM catalyst can still reach 80%, showing good SO_2/H_2O resistance performance.

Key words: catalyst; Mn-La; preparation method; denitration efficiency

Nitrogen oxides are one of the main atmospheric pollutants, which not only cause environmental problems such as acid rain and photochemical smog, but also cause serious harm to human health. Selective catalytic reduction of NO_x by NH_3-selective catalytic reduction (NH_3-SCR) is currently the most widely used technology for removing NO_x from flue gas. The V_2O_5-WO_3(MoO_3)/TiO_2 series catalyst with an active temperature window between 300 and 400 °C is a commonly used commercial SCR catalyst. It is usually placed before the desulfurization and dust removal device. During the operation, V_2O_5-WO_3(MoO_3)/TiO_2 catalyst is subjected chronically to the scouring of flue gas containing high concentration of dust and SO_2, so it is easy to cause catalyst attrition and poisoning and shorten the service life of the catalyst. The low temperature SCR technology disposed after the desulfurization and dust removal device can effectively avoid the above problems. However, the flue gas temperature is greatly reduced (<200 °C) under this condition, and the denitration effect of the vanadium-based catalyst is not satisfactory. Therefore, the development of a new low-temperature and high-efficiency SCR catalyst has become the focus.

The transition metal element Mn shows excellent activity of denitration at low temperatures. This is mainly due to the special valence layer electron configuration of Mn element (3d54s2), which makes the valence state of Mn change widely. The valence states of manganese include +2, +3, +4, +5 and some non-integer valence. Different valence states of Mn can realize mutual conversion to produce redox, which can promote the reduction of NO, thus promoting SCR reaction[1-5]. The study of Wu[6] showed that the MnO_x/TiO_2 catalyst prepared by sol-gel method exhibits good low temperature denitration activity. Kapteijn[7] studied the effects of preparation methods and precursors on the denitration activity of MnO_x catalyst, and found that MnO_2 has the highest activity per unit area. Jiang[8] prepared MnO_x/TiO_2 catalyst through three different methods. Among them, MnO_x/TiO_2 catalyst prepared by sol-gel method has strong interaction among components, and a large amount of manganites exist in

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amorphous form, showing the best NH_3-SCR catalytic performance.

Single Mn based SCR catalyst is easy to be poisoned and inactivated in flue gas containing SO_2. The addition of one or more rare earth elements can effectively improve the surface area, redox performance and surface acid strength of the catalyst, and then significantly improve the denitration activity and sulfur resistance of the catalyst. Rare earth metal lanthanum (La) has stable performance, which can promote the dispersion and reduction of active components of the catalyst and improve the migration ability of lattice oxygen, which is conducive to the catalytic reaction. Hu[9] studied Mn/Al_2O_3 catalyst for methane catalytic combustion. The dispersion of Mn active component was improved by doping La and the low temperature activity of Mn/Al_2O_3 catalytic combustion was significantly improved. Shen[10] doped La into Mn/Ti-PILC by impregnation method. It was found that La can significantly increase the activity of SCR denitration at low temperatures.

Because of the advantages of high selectivity, high yield and simple process, solid state reaction has become one of the main methods to prepare new solid materials. However, the traditional solid-state reaction is usually carried out at high temperatures, which has the disadvantages of high energy consumption, serious equipment corrosion, large particle size and uneven distribution. Co-precipitation method can directly obtain homogeneous nano powder materials through various chemical reactions in solution, which can realize uniform doping at the molecular level. Compared with the solid-state reaction, its chemical reaction is easier to carry out, and it only requires a lower synthesis temperature, so it is easy to prepare nano powder materials with small particle size and uniform distribution. Therefore, Mn-La composite oxide catalysts were prepared by solid state reaction and co-precipitation in this study. The structure and physicochemical properties of the catalyst were characterized by XRD, BET, H_2-TPR, NH_3-TPD and XPS. The low-temperature denitration activity and SO_2/H_2O resistance of the catalyst were also investigated.

1 Experiment

1.1 Preparation of catalyst

1.1.1 Pure MnO_x

A certain amount of manganese acetate was ground in a dry mortar for 0.5 h. Then it was placed in an oven at 80 °C for 24 h. The obtained samples were put into a muffle furnace and calcined at 500 °C for 4 h. Finally, black Mn oxide powder was obtained, which was labeled as MnO_x (Fig.1).

1.1.2 Solid state reaction

Manganese acetate of 24.51 g and lanthanum acetate of 5.27 g (Mn/La molar ratio is 6:1) were weighed and ground in a dry mortar for 0.5 h. Then it was placed in an oven at 80 °C for 24 h. The samples were put into a muffle furnace and calcined at 500 °C for 4 h. Finally, the black Mn-La powder was obtained, which was labeled as MnLa-SSR (Fig.2).

1.1.3 Co-precipitation method

Manganese acetate of 24.51 g and lanthanum acetate of 5.27 g (Mn/La molar ratio is 6: 1) were weighed, and the volume was adjusted to 150 mL with deionized water. The pH value of the mixed solution was adjusted to 11 with ammonia water, and stirred for 0.5 h The precipitate was washed with deionized water until pH was neutral, and then dried in an oven at 110 °C until the water evaporated completely to obtain solid powder. The obtained solid powder was put into a muffle furnace and calcined at 500 °C for 4 h. Finally, black Mn-La powder was obtained, which was labeled as MnLa-CPM (Fig.3).

1.2 Characterization of the catalyst

A D8 advance X-ray diffractometer produced by German Bruker was used to characterize the catalyst. The test conditions were: current in the tube of 40 mA, voltage in the tube of 40 kV, Kα as the radiation source, Cu as the target, scanning range 2θ=10°~80°, step=0.02°.

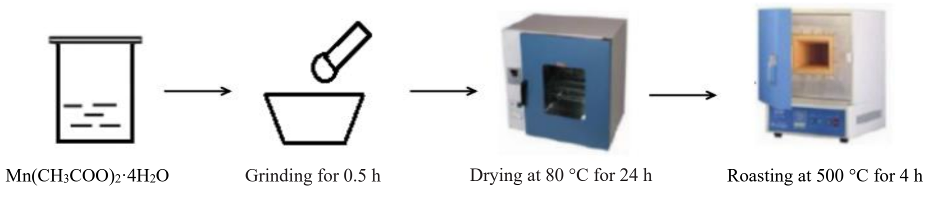


Fig.1 Synthesis procedure of MnO_x

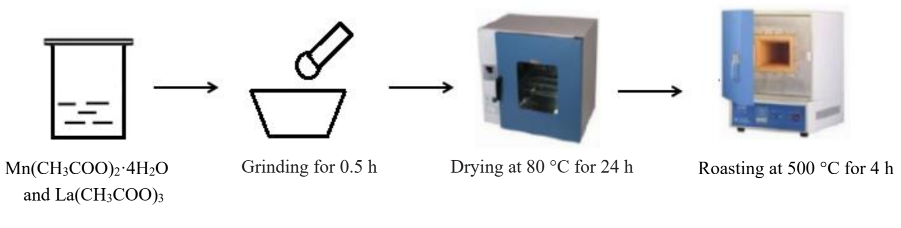


Fig.2 Synthesis procedure of MnLa-SSR

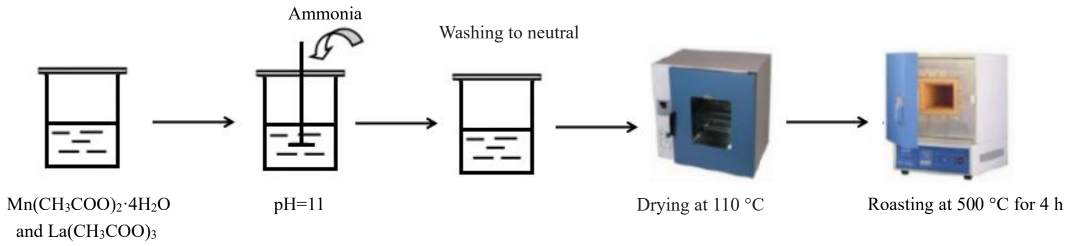


Fig.3 Synthesis procedure of MnLa-CPM

The N_2 physical adsorption test of the catalyst was carried out by the Autosorb-iQ physical adsorption instrument of Quantachrome Company of the United States to determine the specific surface area and pore structure characteristics of the catalyst. First, a certain mass of sample (0.25~0.3 g) was heated and evacuated at 240 °C for 2 h, and then tested under liquid nitrogen (−196 °C). The specific surface area was calculated using the multi-point BET equation, and the pore size and pore volume were measured using the BJH method.

The H_2-TPR characterization of the catalyst was carried out by the Auto Chem II 2920 type chemical adsorption instrument of Mike Corporation. The sample (50 mg, particle size of 0.3~0.45 mm) was pretreated at 300 °C for 0.5 h in pure Ar atmosphere, and then cooled to 50 °C. Under the condition of 10vol% H_2/Ar (20 mL/min), the temperature was programmed to 900 °C at a rate of 10 °C/min. The H_2 consumption during this process was also detected by the TCD thermal conductivity detector.

The NH_3-TPD characterization of the catalyst was carried out by the Auto Chem II 2920 type chemical adsorption instrument of Mike Corporation. The sample (100 mg, particle size of 0.3~0.45 mm) was pretreated at 400 °C for 0.5 h in a pure He (20 mL/min) atmosphere, and then cooled to 50 °C. Next, the sample was fed with 5vol% NH_3/N_2 (20 mL/min) for 0.5 h for NH_3 adsorption, then purged with pure He atmosphere for 1 h, and finally programmed to 550 °C at a rate of 10 °C/min. The attached NH_3 was detected by the TCD thermal conductivity detector.

The Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer of American Thermoelectric Group was used for XPS characterization of the catalyst. The vacuum degree of the analysis chamber was 8×10^{-10} Pa, the excitation source adopted Al Kα ray (h_v=1253.6 eV), the working voltage was 12.5 kV, the filament current was 16 mA, and the signal accumulation of 10 cycles was performed.

1.3 Activity evaluation of the catalyst

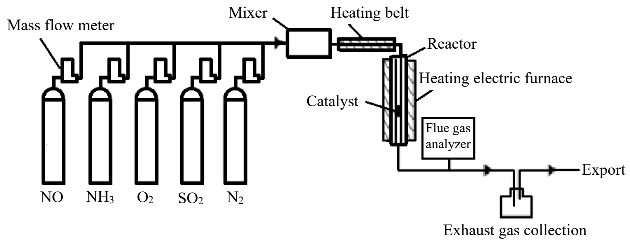


Fig.4 Schematic diagram of catalyst activity evaluation device

The activity evaluation of the catalyst was carried out in a stainless steel SCR fixed reactor. The temperature was controlled by the external heating of the tube furnace. The inside of the tube furnace was a stainless steel tube where the catalyst was placed. The stainless steel mesh prevents the catalyst from leaking. The schematic diagram of the specific experimental device is shown in Fig. 4. The standard steel cylinder gas was used to simulate flue gas, and the mass flow meter was used to control the flow. The composition of the simulated flue gas is as follows: 0.05vol%NO, 0.05vol%NH_3, 6vol% O_2, and N_2 as the equilibrium carrier gas. The catalyst was in the form of granules, 40~60 mesh, and the accumulation volume was 3 mL, which was measured with a measuring cylinder. The total gas flow rate was 1000 mL/min, and the space velocity was 20000 h^{-1}. The activity was evaluated at 80~360 °C, the German Testo 350 flue gas analyzer was used to detect the NO concentration before and after the reaction, and the NO removal rate was calculated according to Eq.(1).

$$\eta = \frac{[NO_{in}] - [NO_{out}]}{[NO_{in}]} \times 100\% \qquad (1)$$

2 Results and Discussion

2.1 XRD analysis of the catalyst

Fig. 5 shows the XRD pattrerns of catalysts prepared by different methods. It can be seen that the intensity and width of diffraction peaks of samples prepared by different methods are quite different. The typical diffraction peaks of Mn_2O_3

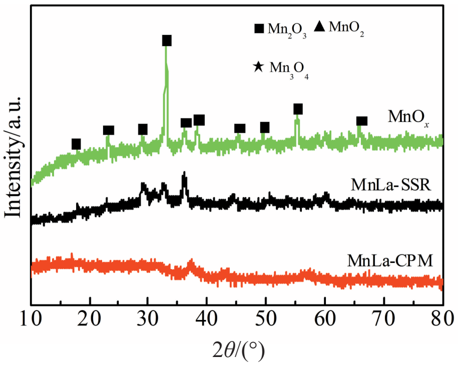


Fig.5 XRD patterns of the catalysts

(JCPDS No. 24-0508) appear at 18.8°, 23.1°, 28.4°, 32.9°, 35.6°, 38.2°, 45.1°, 49.3°, 55.1° and 65.7° in pure MnO_x catalyst. The crystal growth of single MnO_x is faster, and Mn_2O_3 has high crystallinity and large particle size. Therefore, the diffraction peaks show high intensity, the half peak width is smaller and the peak type is sharper. However, after adding La, the peak width of Mn_2O_3 increases, and the characteristic peak of MnLa-CPM catalyst prepared by co-precipitation method has the widest peak and the least intensity. The reason is that La^{3+} (0.119 nm) with larger radius enters the lattice of Mn_2O_3 (Mn^{3+} radius is 0.058 nm) and forms Mn-La solid solution, which leads to the increase of crystal disorder in MnO_x. The connected network formed by Mn-O-La bond restricts the transportation of Mn_2O_3, then the growth rate of Mn_2O_3 slows down, and the grain size becomes smaller, and finally the crystallinity decreases[11]. Due to the low adding content of La, no diffraction peak of LaO_x is found in the catalysts. When Mn^{3+} is replaced by La with larger radius, lattice distortion will occur in Mn_2O_3-La_2O_3 network, which are reflected in the shift of diffraction peaks in XRD. The lattice distortion is bound to form a lot of oxygen vacancies, which is beneficial to promote the transfer of oxygen species and improve the redox property of samples[12].

2.2 N_2 adsorption-desorption analysis of the catalyst

Fig.6 and Fig.7 show the N_2 adsorption-desorption isotherm and pore size distribution of the catalyst, respectively. It can be seen from Fig. 6 that MnO_x sample displays a type I isotherm, and the sharp rise at relatively low pressure (P/P_0< 0.01) is relevant to the presence of micropores[13,14]. The adsorption isotherms of MnLa-SSR and MnLa-CPM catalysts belong to type IV and H_3 type hysteresis loop, indicating that these catalysts have micropore and mesopore structures. There is no obvious saturated adsorption platform on the isotherm, which indicates that the pore structure of the catalyst is very incomplete, mainly including flat slit structure, crack and wedge structure[15]. According to the pore size distribution in Fig.7, the pore size distribution of pure MnO_x ranges from 0 to 5 nm. The pore size distribution of MnLa-SSR and MnLa-CPM catalysts is bimodal, the small aperture is 0~5 nm and the large aperture is 5~20 nm. Properly increasing the pore size of catalyst is conducive to the adsorption and desorption of reaction gas at the active sites on the catalyst surface, thus promoting the catalytic reaction[16].

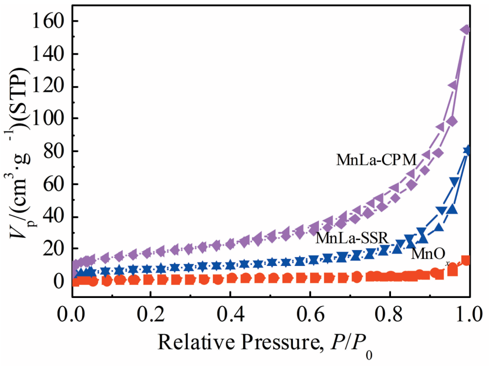


Fig.6 Adsorption and desorption curves of the catalyst

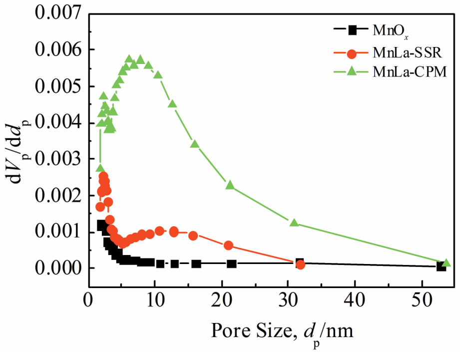


Fig.7 Pore size distribution curves of the catalyst

The specific surface area and pore volume are important factors affecting the catalytic reaction. The increase of specific surface area is beneficial to the dispersion of active species and the adsorption of reactants, and it also increases the number of surface active sites to a certain extent. The increase of pore volume is beneficial to the adsorption and diffusion of reaction medium, which increases the contact opportunity between the catalyst and the reaction medium, thus increasing the catalytic reaction rate. Table 1 shows the characterization results of specific surface area (S_{BET}) and pore structure of the catalyst. It can be seen that pure MnO_x has the smallest surface area (5.7 m^2/g) and pore volume (V) (0.021 cm^3/g). The specific surface area and pore volume of La doped MnLa-SSR catalyst increases significantly; the specific surface area increases from 5.7 m^2/g to 27.0 m^2/g, and the pore volume increases from 0.021 cm^3/g to 0.067 cm^3/g. Compared with pure MnO_x and MnLa-SSR catalysts, MnLa-CPM catalyst has the largest specific surface area and pore volume, which are 63.3 m^2/g and 0.239 cm^3/g, respectively. It is found that La-O bond is shorter than Mn-O bond, so La atom will replace part of Mn atoms, resulting in lattice deformation, then pore structure becomes more complex, and total pore volume and specific surface area increase.

2.3 H_2-TPR analysis of the catalyst

The redox ability of the catalyst is one of the important factors affecting the catalytic performance of the catalyst in the NH_3-SCR reaction. It directly affects the oxidation of NO to NO_2, and further promotes the reaction through "fast SCR"[17]. Fig. 8 shows the H_2-TPR spectra of the catalyst. It can be seen that a continuous and wide reduction peak appears

Table 1 Specific surface area and pore structure parameters of catalysts

Sample	S_{BET}/ m^2·g^{-1}	d/nm	V/ cm^3·g^{-1}	H_2 consumption/ μmol·g^{-1}
MnO_x	5.7	13.95	0.021	3856.53
MnLa-SSR	27.0	10.21	0.067	3106.41
MnLa-CPM	63.3	14.63	0.239	5291.53

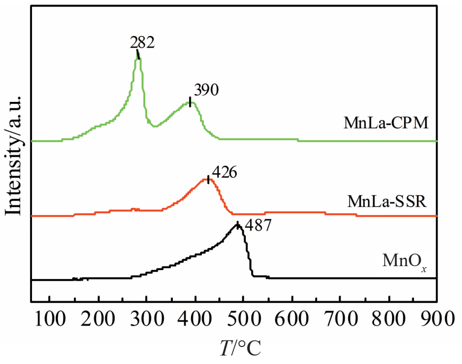


Fig.8 H_2-TPR spectrum of the catalyst

at 300~510 °C for pure MnO_x and MnLa-SSR catalysts, which is mainly attributed to the superposition reaction of $MnO_2 \rightarrow Mn_2O_3$ and $Mn_3O_4 \rightarrow MnO$. This may be due to the poor dispersibility of MnO_x in different valences, leading to agglomeration. Compared with the single reduction peak of pure MnO_x and MnLa-SSR catalysts, there are two obvious reduction peaks of MnLa-CPM catalyst, corresponding to 282 and 390 °C. The low-temperature reduction peak is attributed to the reduction of Mn^{4+} species to Mn^{3+}, and the high-temperature reduction peak is reduction of Mn^{3+} species to Mn^{2+} [18]. In the MnLa-CPM catalyst, the interaction between Mn and La is the strongest. The Mn-O-La bond promotes the dispersion of manganese species on the catalyst surface, while the highly dispersed manganese species are easier to be reduced. Therefore, the temperature of reduction peak of MnLa-CPM catalyst moves to low temperature and it shows the strongest oxidation-reduction ability at low temperatures. Combined with the hydrogen consumption in Table 1, the hydrogen consumption of MnLa-CPM catalyst is the highest (5291.53 μmol/g), followed by pure MnO_x catalyst (3856.53 μmol/g), and MnLa-SSR catalyst has the lowest hydrogen consumption (3106.41 μmol/g). The more hydrogen consumption, the more reducible species. The reducibility of the catalyst is determined by the grain arrangement and grain size. After La doping, Mn-O-La bond interacts with Mn-O bond and La-O bond, which makes the original crystal arrangement disordered and show strong reducibility, so MnO_x is easier to be reduced[19]. In addition, the position of the reduction peak is related to the ability of the catalyst to combine adsorbed oxygen and lattice oxygen. The reduction peak moves to lower temperature, which indicates that the chemically adsorbed oxygen and lattice oxygen on the surface of the catalyst or oxygen vacancy are easier to move, and the reduction performance of the catalyst is enhanced[20].

2.4 NH_3-TPD analysis of the catalyst

In NH_3-SCR reaction, NH_3 is an alkaline reaction gas, which is firstly adsorbed on the acid site of the catalyst for activation, and then participates in SCR reaction. Therefore, the type and strength of acid sites on the surface of the catalyst determine the denitration activity of the catalyst to a certain extent[17]. According to research, the adsorption of NH_3 on the catalyst surface mainly occurs in two states: one is adsorbed on Brønsted acid site in the form of NH_4^+, and the other is adsorbed on Lewis acid site in the form of coordination state NH_3[21]. Among them, the thermal stability of ammonia species adsorbed on Brønsted acid site is lower than that on Lewis acid site. It can be seen from Fig. 9 that there is a NH_3 desorption peak between 450 and 525 °C in pure MnO_x catalyst, which belongs to the desorption of ammonia species on Lewis acid site with strong acidity. The temperature of the desorption peak in the high temperature range of the MnLa-SSR and MnLa-CPM catalysts shifts to the low temperature direction. At the same time, the two catalysts form a new desorption peak in the low temperature range, which is mainly attributed to the desorption of ammonia species adsorbed on the weakly acidic site (Brønsted acid). It is speculated that after doping La, in order to ensure electronegativity, electrons move to La atom, resulting in the increase of electronegativity of La atom. The formation of Mn-O-La bond and the -OH group on LaO_x species lead to the increase of Brønsted acid on the catalyst surface. These acids are weaker than those on MnO_x species, and the adsorbed NH_3 is easier to desorb. Therefore, it is helpful to improve the low-temperature denitration activity of the catalyst[22].

2.5 XPS analysis of the catalyst

The Mn 2p orbital electron spectra of the catalyst are shown in Fig. 10a. It can be seen that there are two main peaks at about 642 and 653 eV for each catalyst, corresponding to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively. From the peak fitting, it can be seen that the two main peaks are composed of Mn^{2+}, Mn^{3+} and Mn^{4+}, which indicate that MnO_x exists in the form of mixed valence of Mn^{2+}, Mn^{3+} and Mn^{4+}. The activity of MnO_x obeys the following rules: $MnO_2 > Mn_5O_8 > Mn_2O_3 > Mn_3O_4 > MnO$. Therefore, the higher the ratio of $Mn^{4+}/(Mn^{2+}+Mn^{3+}+Mn^{4+})$, the stronger the denitration ability of the catalyst[23]. The relative content of Mn^{n+} was obtained by calculating the characteristic peak area. It can be seen from Table 2 that the Mn^{4+} ion concentration of MnLa-CPM catalyst is the highest (32.16%), followed by MnLa-SSR catalyst (30.81%), and the Mn^{4+} ion concentration of pure MnO_x catalyst is the lowest (28.18%). The results show that La doping increases the content of Mn^{4+}.

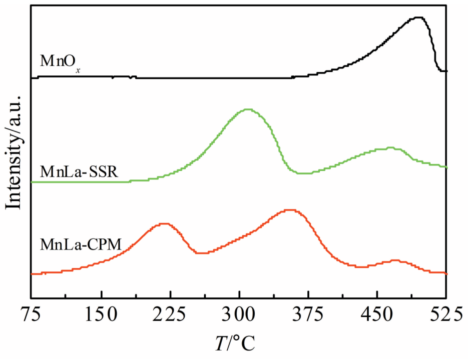


Fig.9 NH_3-TPD spectra of the catalyst

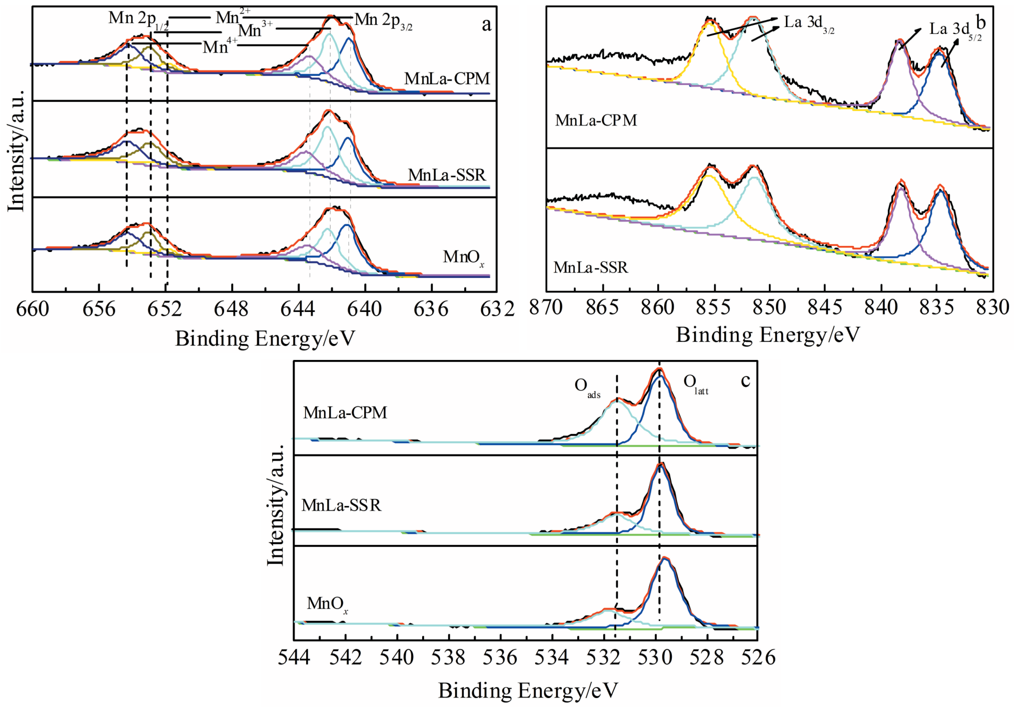


Fig.10 XPS spectra of different catalysts: (a) Mn 2p, (b) La 3d, and (c) O 1s

Table 2 Atomic concentration on the catalyst surface (at%)

Sample	Mn^{2+}	Mn^{3+}	Mn^{4+}	La^{3+}	O_{latt}	O_{ads}
MnO_x	35.94	35.88	28.18	-	69.58	30.42
MnLa-SSR	26.15	43.04	30.81	50.49	64.34	35.66
MnLa-CPM	30.02	37.82	32.16	53.41	48.07	51.93

The La 3d orbital electron spectra of the catalyst are shown in Fig. 10b. The binding energies of La $3d_{5/2}$ and La $3d_{3/2}$ are 834.6~834.8 and 851.2~851.4 eV, respectively[24,25]. Compared with pure La_2O_3, the binding energy of La in MnLa-SSR and MnLa-CPM catalysts has a certain extent of drift, indicating that in addition to La_2O_3, some La interacts with Mn and O to form Mn-O-La bonds. Besides the main peak of La 3d, there are strong shake-up peaks at the binding energies of 838.2~838.3 and 855.1~855.5 eV. The ratio of the intensity of the main peak to that of the accompanying peak is related to the ability of the ligand to give the central ion La[26]. It can be seen from Table 2 that the La^{3+}/(La^{3+}+accompanying peak) ratio of MnLa-CPM catalyst is large, which is 53.41%, indicating that La element has high activity in SCR reaction. However, the La^{3+}/(La^{3+}+accompanying peak) ratio of MnLa-SSR catalyst is low, which is 50.49%, It is indicated that the activity of La is low, which is also the reason for its poor low temperature activity.

The O1s orbital electron spectra of the catalyst are shown in Fig. 10c. It can be seen that there are two characteristic peaks at 530 and 531.5 eV, which are attributed to lattice oxygen (O^{2-}, denoted as O_{latt}) and surface chemically adsorbed oxygen (O^-, O_2^{2-}, O_2^-, denoted as O_{ads}), respectively[27,28]. It can be seen that compared with pure MnO_x, the amount of chemically adsorbed oxygen (O_{ads}) on the catalyst surface increases after adding La. This is mainly due to the fact that the adsorption capacity of oxygen is related to oxygen vacancy. When La enters the Mn lattice, the electron imbalance on the surface of the catalyst is caused, the increased oxygen vacancies and unsaturated chemical bonds provide a new adsorption site for adsorbed oxygen, and the concentration of chemically adsorbed oxygen on the surface increases[29,30]. The surface chemisorption oxygen concentration of MnLa-CPM catalyst is the highest, which is 51.93%. Surface chemically adsorbed oxygen (O_{ads}) is active oxygen species in the redox reaction. Its mobility is stronger than that of lattice oxygen (O_{latt}). It is easy to react with adsorbed NO, and plays a good role in promoting SCR reaction at low temperatures.

2.6 Denitration performance test of the catalyst

Fig. 11 shows the denitration activity curves of catalysts

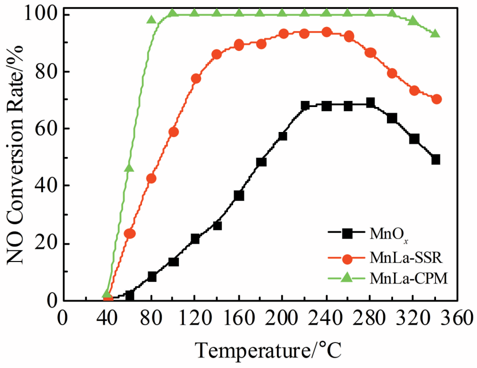


Fig.11 Denitration activity curves of the catalysts

prepared by different methods. It can be seen that with the increase of temperature, the NO conversion rate of each catalyst also increases, but when the temperature rises to a certain extent, the NO conversion rate gradually decreases. This is mainly due to the fact that NH_3, as a reducing agent, is oxidized to NO at high temperatures. The amount of reducing agent decreases, the content of NO increases and the denitration efficiency decreases. Pure MnO_x catalyst has the worst denitration activity and the highest denitration efficiency is about 70%. The denitration efficiency of the catalyst with La element is significantly improved, and the highest denitration efficiency is more than 90%. The order of denitration activity of catalysts prepared by different methods is as follows: MnLa-CPM>MnLa-SSR>MnO_x. The main reason for the poor denitration performance of the single metal catalyst is that sintering occurs easily in the preparation process of the single metal catalyst, which leads to the decrease of the dispersion and specific surface area of the catalysts. On the one hand, element doping can inhibit the sintering of the catalyst in the preparation process, so that the active components of the catalyst can obtain a good dispersion and a large specific surface area; on the other hand, the mixture of metal oxides forms after doping metal elements, which has a new crystal structure and can improve the low-temperature denitration activity of catalysts[31,32].

2.7 SO_2/H_2O resistance of the catalyst

Although the low-temperature NH_3-SCR device is arranged after desulfurization and dust removal, there are still a certain amount of SO_2 and H_2O in the flue gas. Therefore, the influence of SO_2 and H_2O on the performance of the catalyst is one of the important factors to evaluate the advantages and disadvantages of the catalyst. 10vol% H_2O and 0.03vol% SO_2 are introduced into the simulated flue gas at 180 °C to study the SO_2/H_2O poisoning resistance performance of the catalyst. Fig. 12 shows that when 10vol% H_2O and 0.03vol% SO_2 are added, the denitration efficiency of pure MnO_x catalyst decreases significantly, from 70% to 40%, with a decrease of 30%. However, the NO conversion rate of MnLa-SSR and MnLa-CPM catalysts is decreased by 20% (MnLa-SSR catalyst decreases from 90% to 70%, and MnLa-CPM catalyst decreases from 100% to 80%). The results show that H_2O and SO_2 have serious toxicity to the catalyst, and MnLa-CPM catalyst has better resistance to SO_2/H_2O poisoning in the presence of H_2O and SO_2. This is due to the fact that the active components are evenly dispersed in the preparation process of co-precipitation, forming low crystallinity or amorphous structure, and the interaction between Mn and La is strong, and then more active sites are formed[33]. When H_2O and SO_2 are stopped, the activity of the catalyst increases, but it cannot return to the initial level, which indicates that the toxicity of H_2O and SO_2 to the catalyst is irreversible. This is mainly due to the formation of sulfate species on the surface of the catalyst in the presence of H_2O and SO_2. The sulfate species on the catalyst surface reduce the active sites on the catalyst surface and block some pore channels of the catalyst, resulting in catalyst deactivation[34]. The decomposition temperature of sulfate is generally 280 °C, and the activation treatment at 300 °C can make the activity of the catalyst recover to the initial level.

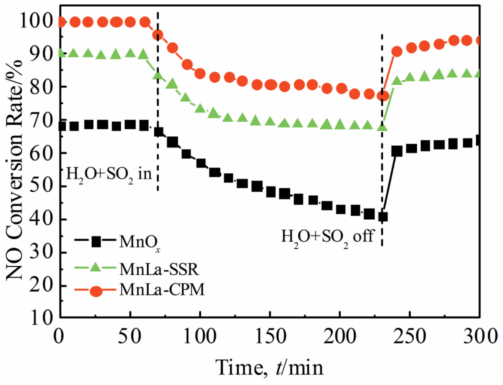


Fig.12 Effect of SO_2 and H_2O on denitration activity of the catalysts

2.8 Denitration mechanism

MnO_x species are the main active components of the catalyst, and the performance of MnO_x species is closely related to SCR activity. The characterization and analysis of the catalysts before and after lanthanum doping show that La is doped in the synthesis process of MnO_x catalyst by co-precipitation method. LaO_x enters the complex network structure to form La-O-Mn bond, which restricts the transportation of MnO_x, and then controls the size of MnO_x particles in MnO_x/LaO_x composite oxide. Because Mn atom is replaced by La atom, the lattice is deformed, the specific surface area of the catalyst is greatly increased, the pore size is refined, and the dispersion of Mn and La active components is improved. According to the acid characterization results, the addition of La increases the content of Brønsted acid on the surface of the catalyst. These acids are weaker than those on MnO_x species, and the adsorbed NH_3 is easier to desorb. Therefore, it is helpful to improve the activity of the catalyst for low temperature denitration. In addition, La entering the lattice of manganese oxide, causes the electron imbalance on the surface of the catalyst, and thus the number of oxygen vacancies and unsaturated chemical bonds is increased, which provides a new adsorption site for adsorbed oxygen, and increases the concentration of chemically adsorbed oxygen on the surface. Through the redox cycle on the surface of the catalyst, the adsorbed oxygen will be continuously converted into active oxygen, which can improve the catalytic oxidation performance of NO to NO_2 at low temperatures, and then increase the concentration of NO_2 on the catalyst surface, and finally enhance the "rapid SCR reaction" of the catalyst. At the same time, the addition of rare earth element La can also improve the low-temperature oxidation-reduction ability of the catalyst. In conclusion, the addition of rare earth element La can improve the low-temperature SCR denitration performance of manganese oxide catalyst.

Many scholars have done a lot of research on the denitration mechanism of single manganese oxide catalyst, and most of them think that the catalytic process of Mn is more in line with Eley-Rideal mechanism. They believe that gaseous NH_3 is adsorbed on Lewis acid sites on the catalyst surface to form coordinated NH_3, and the coordinated NH_3 forms NH_2 groups under the action of hole oxygen on the catalyst surface. These surface hole oxygen is formed by the valence state conversion and electron transfer between MnO_2 and Mn_2O_3. After that, NH_2 group will react with NO in gas phase to form the key intermediate product NH_2NO, which will be decomposed into N_2 and H_2O. The detailed steps of these reactions are as follows:

$$NH_3(g) \xrightarrow{MnO_x} NH_3(a) \tag{2}$$

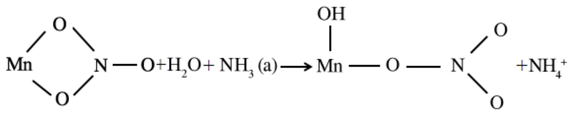
$$NH_3(a) + O(a) \rightarrow NH_2(a) + OH(a) \tag{3}$$

$$NH_3(a) + NO(g) \rightarrow NH_2NO(a) \tag{4}$$

$$NH_2NO(a) \rightarrow H_2O(a) + N_2(g) \tag{5}$$

At the same time, it is considered that the addition of La increases the content of Brønsted acid on the catalyst surface because of the formation of La-O-Mn bond and -OH group after doping La into MnO_x. NH_3 is adsorbed on the newly added Brønsted acid site, which is oxidized to form bidentate nitrate. The reaction of bidentate nitrate with coordinated NH_3 forms a new acid site, which leads to the decrease of the concentration of bidentate coordination nitrate and the removal of NO by another way. The specific reaction steps are as follows:

$$NH_3(g) \xrightarrow{LaO_x/MnO_x} NH_3(a) \tag{6}$$



(7)

$$NO_2(a) + 2NH_4^+ \rightarrow NO_2\left[NH_4^+\right]_2 \tag{8}$$

$$NO_2\left[NH_4^+\right]_2 + NO \rightarrow \cdots \rightarrow 2N_2 + 3H_2O + 2H^+ \tag{9}$$

3 Conclusions

1) Compared with pure MnO_x, the addition of La significantly increases the denitration activity of the catalyst.

2) Among the Mn-La catalysts prepared by different methods, the Mn-La prepared by co-precipitation method shows the best denitration activity. The denitration efficiency is close to 100% at 80 °C and maintains above 90% in the temperature range of 80~340 °C. In the presence of H_2O and SO_2, MnLa-CPM catalyst also shows good resistance to SO_2/H_2O poisoning. This is mainly because the components in MnLa-CPM catalyst are uniformly dispersed and exist in the form of low crystallinity or amorphous structure, with a large specific surface area and pore volume, strong redox ability and high surface acid content.

3) The higher concentration of Mn^{4+} and the chemically adsorbed oxygen are beneficial to the oxidation of NO to NO_2, which promotes the “fast SCR” reaction, thus significantly improving the low-temperature SCR activity of the catalyst.

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制备方法对低温NH_3-SCR催化剂Mn-La结构与性能的影响

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摘　要：采用固相反应法、共沉淀法制备了Mn-La复合氧化物催化剂，考察了制备方法对催化剂脱硝性能及抗SO_2/H_2O性能的影响。并通过XRD、BET、H_2-TPR、NH_3-TPD、XPS等手段对催化剂的结构和物理化学特性进行了表征。结果表明，La掺杂降低了MnO_x的结晶度，增大了催化剂的比表面积和孔体积。Mn-O-La键合作用促进了锰在催化剂表面的分散，而高分散的锰更容易被还原，催化剂的还原温度向低温方向迁移，氧化还原能力得到提高。掺杂La之后，催化剂表面Brønsted酸和总酸量增加，同时Mn^{4+}和表面化学吸附氧的浓度也得到提高。因此，La掺杂有利于促进催化剂的脱硝活性。反应评价结果表明，共沉淀法制备的MnLa-CPM催化剂表现出最佳的脱硝效率，在80 ℃时脱硝效率接近100%。在H_2O和SO_2存在的条件下，MnLa-CPM催化剂的脱硝效率仍能达到80%，表现出了较好的抗硫水性能。

关键词：催化剂；Mn-La；制备方法；脱硝

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