

Original Research

Preparing Mn-CoO-Supported Pyrolysis Coke Catalyst with Plasma and its Application in the SCO Denitration Process

Zhang Lei^{1*}, Chen Jihao¹, Lei Zhang², Sha Xiangling³, Li Yonghui², Fan Min¹

¹School of Geology and Environment, Xi'an University of Science and Technology, Xi'an, China

²China National Heavy Machinery Research Institute Co. Ltd, Xi'an, China

³Shandong Baichuan Tongchuang Energy Co. Ltd, Jinan, China

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Abstract

In order to reduce nitrogen oxides in the flue gas and improve the quality of the atmosphere, an Mn-CoO-supported pyrolysis coke catalyst was prepared using equivalent-volume impregnation, and then its denitration efficiency was studied in a simulated flue gas denitrification device in the paper. The composition of the flue gas was a mixture of N₂, O₂, NO, and SO₂. Good denitration catalysts were prepared by changing plasma modification time and modified power, MnO load and Mn-CoO load. The denitration mechanism of the catalyst was analyzed by XRD, BET and SEM. The results are: optimal modified power in the plasma system was 60W, and the best modified time in plasma system was 3min; after being modified by plasma, the denitration efficiency of catalysts were significantly higher than conventional calcination catalyst; among catalysts with different CoO loadings (5%, 8%, 10%), 8% CoO loading had the best denitration efficiency, the best denitration efficiency reached 98% and time of higher denitration efficiency had also been extended a lot; Mn-CoO-supported catalysts had a certain SO₂-resistance, and the denitration efficiency of Mn-CoO-supported catalyst > MnO-supported catalyst > un-supported catalyst.

Keywords: equivalent-volume impregnation, plasma modified, supported catalyst, denitration

Introduction

Coal combustion produces a lot of nitrogen oxides, and they are very harmful to human health and environmental pollution [1]. Nowadays, the technology of nitrogen oxide removal is mainly selective catalytic reduction (SCR) technology [2]. SCR is when NH₃ is

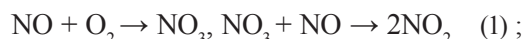
added to the flue gas system, and then nitrogen oxides are reduced to N₂ under the action of a catalyst. However, SCR technology requires very high temperature, and energy consumption is relatively large [3]. SCR is a relatively mature technology. But a large amount of NH₃ is needed, the cost is large, and the reduction products have no reusable value. NH₃ has played a role in the formation of PM2.5, and SCR has the problem of NH₃ escaping [4]. Therefore, in the process of treatment, we must strictly control NH₃ and avoid secondary pollution.

*e-mail: 136750178@qq.com

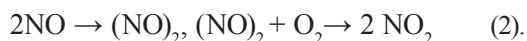
Selective catalytic oxidation (SCO) is when NO is oxidized to NO₂ by utilizing O₂ in flue gas and the reaction can be carried out at low temperature [5-7]; therefore, energy consumption is smaller. SCO can make up for the defects of SCR. Therefore, SCO can be well applied in flue gas denitration [8]. So it is a highly competitive technology of flue gas denitration.

At present, there are two mechanisms of oxidation. The mechanisms of SCO denitration are:

The first mechanism:



The second mechanism:



There is a competitive relationship between the two reactions. Since the reaction of NO polymerization of the second mechanism is exothermic, the second mechanism occupies an advantage at low temperature [9].

However, SCO needs an economical and efficient catalyst. Currently, molecular sieves [10], active carbon [11], metal oxides [12], and noble metals [13] are common catalyst materials. Molecular sieves as catalysts are mostly used in reduction and decomposition processes [14], but are not suitable for SCO. Active carbon has a large surface area and special hole structure, and the price of active carbon is cheap. But the shortcoming of active carbon is that it has low activity at high temperature, so it is not a good catalyst in the process of flue gas denitration. The noble metal catalyst has good activity and it can also meet the requirements under high temperature conditions. But the expensive price limits its wide range of application and promotion [15]. However, the supported metal catalyst is a good catalyst.

Pyrolysis coke is a solid residue produced after coal pyrolysis [16]. Pyrolysis coke is difficult to have a good follow-up value. However, it has a rich pore structure and it contains many oxygen-containing functional groups on the surface [17], therefore pyrolysis coke itself has a good effect. Pyrolysis coke can adsorb NO and other gaseous pollutants, which is a good carrier of adsorbent and catalyst. A catalyst prepared by pyrolysis coke realizes waste utilization and it also has less environmental pollution. Pyrolysis coke is impregnated with the solution, metal active component is loaded on the carrier, and the activity of the catalyst is greatly improved. Manganese oxide and cobalt oxide are good active components and can be loaded onto the carrier by impregnation. By roasting, an inexpensive, low energy and stable catalyst is prepared [18].

The preparation process of a traditional catalyst is calcined in a muffle furnace. This process consumes high energy, and the active components are easily agglomerated. Therefore, this process affects the activity of a catalyst. The preparation process of the catalyst prepared by plasma modification not only reduces energy consumption, but it also makes the

better dispersion of the active component, and obviously improves the activity [19-20]. Therefore, the catalyst prepared by plasma has a better effect.

The innovative points of this paper are as follows: pyrolysis coke is used as the carrier and is supported with a metal active component; the traditional catalyst is modified by plasma; the catalyst is applied in the SCO denitration process. Different MnO contents and different CoO contents are supported on pyrolysis coke carrier, the catalysts are modified with different powers and different time, and then the denitration efficiency is investigated in the SCO denitration process. The denitration mechanisms are obtained by the characterization analysis results of XRD, XPS, SEM and BET.

Experimental

Experimental Material and Experimental Medicines

Experimental material is lignite and the diameter of lignite is 1-2 mm. Pyrolysis coke is made of lignite.

Experimental medicines: manganese nitrate solution, Mn(NO₃)₂, (Tianjin Fuchen Chemical Reagent Factory, 50% purity); six cobalt nitrate hydrate, Co(NO₃)₂·6H₂O, (Guangdong Guanghua Sci-Tech Co., Ltd. analytical purity ≥ 99%)

Preparing the Catalysts

Preparing Pyrolysis Coke

A certain quality of lignite particles were taken and placed into a tubular furnace. The inner diameter of the tube is 22 mm and the outer diameter is 26 mm. Argon is a protective gas and the flow rate is 40ml/min. The temperature rises from 24°C to 750°C, the lignite is pyrolyzed for 4 hours, then the temperature of the pyrolysis furnace drops from 750°C to 24°C. The remainder is taken, which is 750°C pyrolysis coke.

Preparation of Conventional MnO-Supported Catalyst

Manganese nitrate solution is configured, and the MnO loading is 8%. 10g pyrolysis coke is impregnated with equal volume impregnation. It is statically placed for 12 hours, then placed in a drying box at 120°C and baked for 30 minutes. Then it is put into a muffle furnace at 450°C. It was roasted for 4 hours. The temperature is lowered to room temperature. It is taken out, which is a conventional 8% MnO-supported catalyst.

Preparing MnO-Supported Catalyst by Plasma Modification

Argon gas is used as a plasma-modified gas. The gas flow is 40ml/min.

- (1) The 10 g conventional 8%MnO-supported catalyst is taken and put into the plasma. The modification time is 10 minutes. The modification power is 30W, 60W and 90W, respectively. They are 8%MnO-supported catalysts of different power (C30W, C60W and C90W, respectively).
- (2) The 10 g conventional 8% MnO-supported catalyst is taken and put into the plasma. The modification power is 60W. The modification time is 3 minutes, 10 minutes and 15 minutes, respectively. They are 8%MnO-supported catalysts of different times (C3T, C10T and C15T, respectively).
- (3) Manganese nitrate solution is configured, and the MnO loading is 1%, 3%, 5% and 8%, respectively. The conventional 1%, 3%, 5% and 8% MnO-supported catalyst are prepared. The 10g conventional MnO-supported catalyst is taken and put into the plasma, respectively. The modification power is 60W, and the modification time is 3 minutes, respectively. They are 1%, 3%, 5% and 8% MnO-supported catalyst by plasma modification (C1, C3, C5 and C8, respectively).

Preparing the Mn-CoO-Supported Catalyst by Plasma Modification

Argon gas is used as a plasma-modified gas. The gas flow is 40ml/min.

Cobalt nitrate solution is configured, and the loading amount of CoO is 5%, 8% and 10%, respectively. The 10g conventional 8%MnO-supported catalyst is impregnated with equal volume impregnation. A conventional catalyst was prepared using the same method, they are conventional 5%, 8% and 10% Mn-CoO-supported catalyst, respectively.

The 10g conventional Mn-CoO-supported catalyst is taken and put into the plasma, respectively. The modification power is 60W. The modification time is 3 minutes. They are 5%, 8% and 10% Mn-CoO-supported catalysts (C8-5, C8-8 and C8-10, respectively).

Catalyst Characterization Method

Specific surface area (BET): The JW-BK122W type surface and pore size analyzer is used to measure the specific surface area of different types of catalysts.

X-ray analysis (XRD): XD-3 type ray diffractometer; test parameters: voltage is 36 KV, current is 20 mA, the target is Cu, $2\theta/\theta$ is 10° to 80° , and scanning speed is $10^\circ/\text{min}$.

Scanning electron microscope (SEM): JSM-6460LV, working voltage 20kV, magnification 5000 times.

X-ray electron spectroscopy (XPS): XPS is an important tool for analyzing the surface structure and composition of an element, and it can get the composition of the test object.

Experimental Device and Detection Method

The test device is shown in Fig. 1. The device can be divided into three parts: a gas distribution system, a reaction system and a detection system. The gas distribution system consists of four cylinders: N_2 , O_2 , NO, and SO_2 ; the reaction system is mainly composed of a mass flow meter, a mixing bottle, two reaction towers and an air pipeline, the detection system is a gas collection bottle at the end, and Testo340 is used to detect nitrogen oxides.

The temperature of reaction tower A and reaction tower B is raised to 150°C . The total gas flow is 1000ml/min; the NO content is 450ppm and the flow is 18ml/min; the O_2 content is 6% and the flow is 60 ml/min; the rest is filled with N_2 . SO_2 is increased during the sulphur resistance test. Its content is 0.2% and the flow is 50 ml/min.

In each experiment, the 10g catalyst is placed in reaction tower, and the changes of NO are detected by Testo340 (German production) and recorded. Reaction tower A and reaction tower B are in series.

The denitration efficiency of 750°C pyrolysis coke, conventional 8% MnO-supported catalyst,

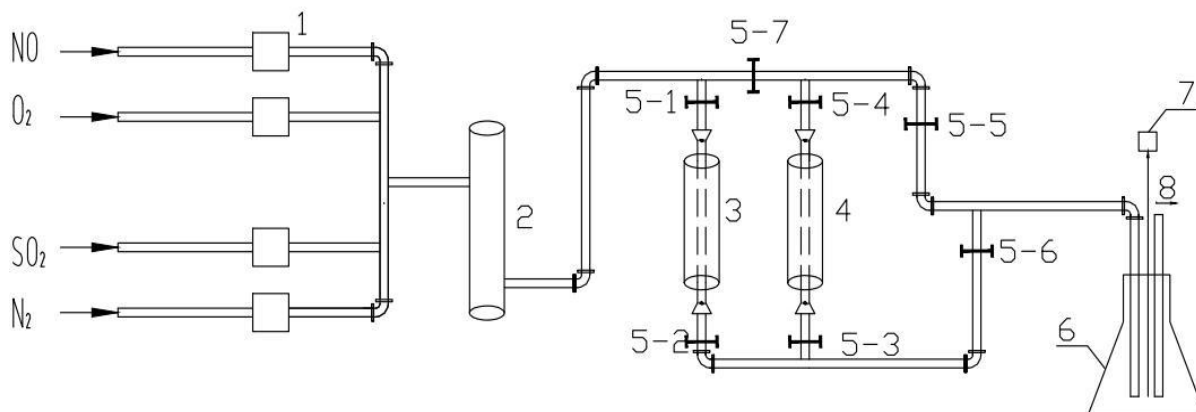


Fig. 1. Test device

1. flowmeter 2. mixed gas cylinders 3. reaction tower A 4. reaction tower B 5-1 to 5-7 valve control 6. test the cylinder 7. condensing unit 8. absorb the gas.

8%MnO-supported catalysts of different power, 8%MnO-supported catalysts of different time, MnO-supported catalyst by plasma modification and Mn-CoO-supported catalysts are respectively tested. The denitration efficiency of different types of catalysts are discussed.

750°C pyrolysis coke, MnO-supported catalyst by plasma modification and Mn-CoO-supported catalysts are placed in the reaction tower, and SO₂ is pumped into the reactor. The SO₂-resistance of the catalysts is detected.

Results and Discussion

Denitration Efficiency of MnO-Supported Catalyst

Denitration Efficiency of 8%MnO-Supported Catalysts of Different Power

Fig. 2 shows the effect of different powers on denitration efficiency. Most of the supported catalysts complete the catalytic process through the cooperation of metal and carriers. During the reaction process there are frequent material exchanges and energy transfers between the metal and the carrier, this process takes place through the interface between the metal and the carrier, therefore the interfacial properties greatly affect catalytic efficiency. In this experiment, argon plasma modification is adopted to change the interaction between metal and carrier. And it can be seen that the denitration efficiency of the catalyst increases and then decreases with the increase of the modified power. The power increases from 30W to 60W, and the denitration efficiency of the catalyst is improved. There are several reasons for this. The modification has no significant effect on the dispersibility of the nitrate material, the metal material migrates from the channel of pyrolysis coke to external surface of pyrolysis coke with the increase of the modified power, and then the metal particles are firmly fixed on the surface and are prevented from migrating and agglomerating during the subsequent roasting process. At the same time, the

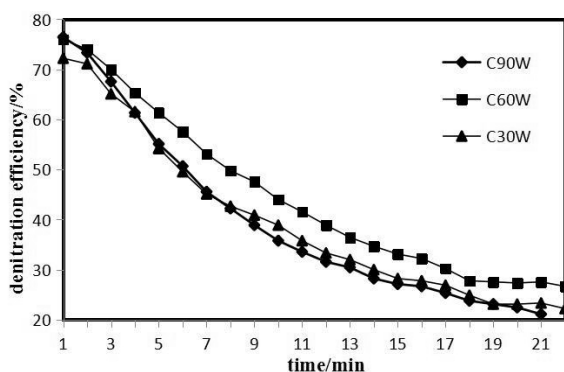


Fig. 2. Effect of different modified power of plasma on denitration efficiency.

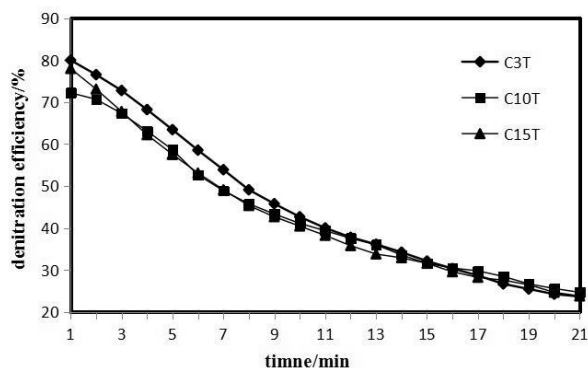


Fig. 3. Effect of different modified time of plasma on denitration efficiency.

metal particles are prevented from leaving the surface of the carrier during the subsequent roasting process, the interaction between the metal and the carrier is improved, and the denitration efficiency of the catalyst is increased. When the power is 90W, denitration efficiency decreases. The reasons are: the power is too large, the surface defects of the pyrolysis coke are repaired, and the dispersivity of active metal on the surface of pyrolysis coke is reduced. Therefore, the denitration efficiency of the catalyst decreases. So, the 60W modified catalyst is the best for denitration.

For each catalyst denitration efficiency is reduced. The reason is that the amount of gas is always very sufficient and the amount of the catalyst is very small, and the activity of the catalyst slowly decreases with the denitration reaction.

Denitration Efficiency of 8% MnO-Supported Catalysts of Different Time

Fig. 3 shows that denitration efficiency decreases with the increase of time of reaction. The denitration effect of C3T is the best in the first 10 minutes, and the denitration effect of C3T, C10T and C15T is basically the same after 10 minutes. So 3 minutes is the best modification. The reason are: the metal particles are thinned by plasma treatment and migrate from the pore of pyrolysis coke to the outer surface, and the dispersivity of the active metal is increased; however, with the growth of plasma modification time, the surface defects of pyrolysis coke are repaired, the pore structure of pyrolysis coke is destroyed, and the dispersivity of active metal on the surface of pyrolysis coke is reduced so that denitration efficiency decreases. Therefore, the catalyst modified for 3 minutes has the best effect on denitration efficiency.

Denitration Effect of MnO-Supported Catalyst of Different Content

Fig. 4 shows the effect of different MnO contents on denitration efficiency. With the increase of MnO

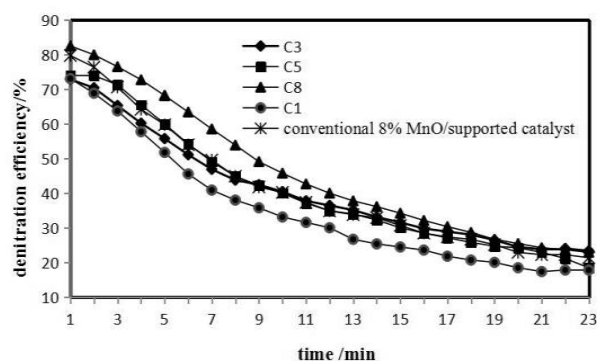


Fig. 4. Effect of different MnO content on denitration efficiency.

content, denitration efficiency is increasing. The denitration efficiency of C5 and the conventional 8% MnO-supported catalyst is similar, and that of the conventional 8% MnO-supported catalyst and C3 is similar. Therefore, it can be concluded that the activity of the catalyst is obviously increased after the plasma modification, and the efficiency of the plasma modification is equal to the increase of the metal content. The surface-free radical was formed on the surface by plasma modification, which enhanced the polarity. The dispersion of active components is increased, and the relationship between active components and carriers is enhanced so that denitration efficiency of plasma-modified catalyst is improved.

Denitration Efficiency of Mn-CoO-Supported Catalyst by Plasma Modification

The 10g catalyst is placed in a reaction tower. The temperature of reaction towers is raised to 150°C. The total gas flow is 1000ml/min; the NO content is 450ppm and the flow is 18ml/min; the O₂ content is 6% and the flow is 60 ml/min, the rest is filled with N₂. SO₂ is increased during the sulphur resistance test. Its content is 0.2% and the flow is 50 ml/min.

Fig. 5 shows the effect of different CoO content on denitration efficiency. And it can be seen that denitration efficiency increases and then decreases with the increase of CoO content. The reason is that CoO and MnO have a synergistic effect on the surface of the catalyst,

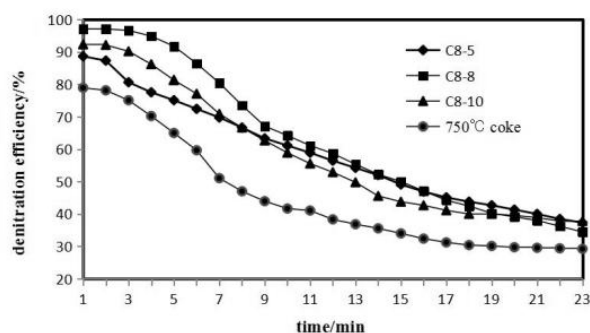


Fig. 5. Effect of different CoO content on denitration efficiency.

which reduces the energy of NO oxidized to NO₂, and improves the activity at low temperatures. However, when the content of CoO is too much, a large number of CoO crystals are dispersed in the pores of the pyrolysis coke, which leads to a decrease of the dispersion of CoO and the reduction of denitration efficiency.

When metal oxide is a non-stoichiometric compound, an N-type or P-type semiconductor is produced by introducing impurity ions or atoms. An N-type or P-type semiconductor is produced by introducing impurity ions or atoms. Impurities are distributed in metal oxide crystals in the form of atoms, ions, or groups, and exist on the surface of the crystal or at the junction of the lattice. These impurities can cause the appearance of the impurity energy level in the forbidden band of semiconductor. An N-type semiconductor is a kind of impurity semiconductor and its free electron concentration is much more than the hole concentration. Such impurities provide electronic carriers with a negative charge, which are called donor impurities or N-type impurities. In the N-type semiconductors, the free electrons are majority carriers, the holes are minority carriers, and the free electrons conduct electricity. Because the current charge of an N-type semiconductor is equal to the negative charge, N-type semiconductor is electrically neutral. Free electrons are supplied mainly by impurity atoms and the holes are created by heat. The more impurities added, the higher the concentration of free electrons and the stronger the electrical conductivity. P-type semiconductors, free electrons are minority carriers, the holes are majority carriers, and the holes conduct electricity. Because the current charge of a P-type semiconductor is equal to the negative charge, a P-type semiconductor is also electrically neutral. The holes are supplied mainly by impurity atoms and free electrons are created by heat. The more impurities added, the higher the concentration of the holes, the stronger the electrical conductivity and the higher the oxidation performance.

It can be seen from XRD that the main oxide of Mn is MnO₂ and that of Co is Co₃O₄. The denitration efficiency of a bimetal-supported catalyst has been improved. The reason is that MnO₂ is a P-type semiconductor that conducts electricity by the holes. When Co₃O₄ is loaded, the valence of cobalt is lower than that of manganese, acting as the main impurity.

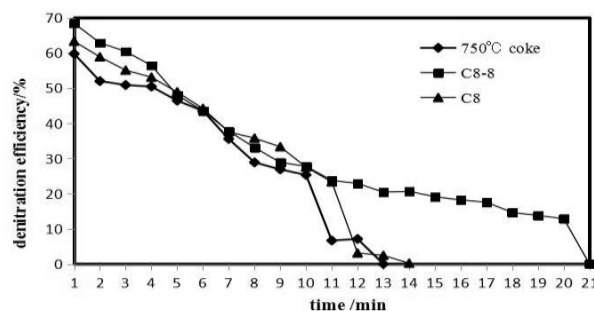


Fig. 6. SO₂-resistance of the catalyst.

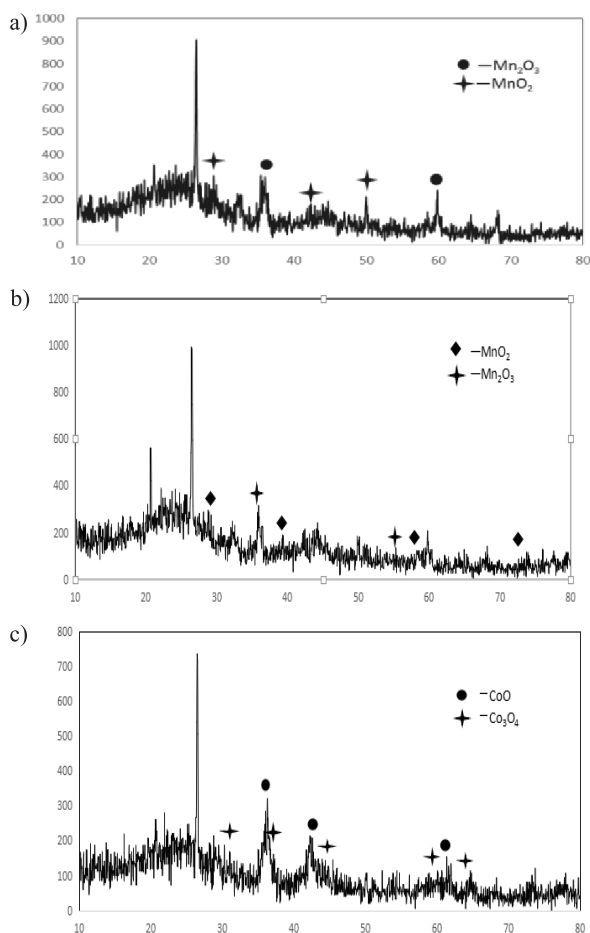


Fig. 7. XRD spectra of catalysts under different conditions: a) the conventional 8% MnO-supported catalyst, b) C8, c) C8-10.

The holes of MnO_2 have been increased and the conductivity of P-type semiconductor MnO_2 is increased. Therefore, the reactive power of the NO oxidation process is reduced and the denitration efficiency of the catalyst is improved.

Experiment on SO_2 Resistance of the Catalyst

In Fig. 6, when SO_2 is added, the denitration efficiency changes. Denitration efficiency was obviously reduced when SO_2 was entered. The time of stabilizing denitration efficiency of 750°C pyrolysis coke is 10 minutes and that of C8 is only 11 minutes, so the

performance of their SO_2 resistance is poor. However, when CoO is added, the Mn-CoO-supported catalyst can maintain a stable denitration efficiency for about 20 minutes, which shows that the addition of CoO has obviously optimized the disadvantage of the poor toxicity of MnO.

The reason is that in the reaction tower, SO_2 reacts with O_2 , and then SO_3 is generated. The SO_3 reacts with the metal oxide, and the sulfate is produced. SO_3 reacts with metal oxide, and the sulfate is produced. The sulfate slowly covers the surface of the catalyst and the void is blocked on the surface, thus the active sites of metal oxides are reduced, and then denitration efficiency is reduced.

At the same time, the Mn-CoO-supported catalyst has certain SO_2 -resistance. The relationship between SO_3 and SO_2 , NO is competitive adsorption, and SO_3 is more easily adsorbed. The adsorption site of SO_2 is mainly O^{2-} , the dentate sulfate is formed, and then it plays a protective role. Therefore, NO can only react with the catalyst in the form of molecular diffusion, and then the activity time is prolonged. It is inferred that the Mn-CoO-supported catalyst has good antitoxicity.

Characterization of the Catalysts

XRD Characterization

Fig. 7 shows that the main oxide of Mn is MnO_2 and the main oxide of Co is Co_3O_4 . It can be seen that the peak height of the manganese and cobalt spectral peak is smaller, the spectral peak is wide and flat, and then big crystals do not appear. The plasma increases well the dispersivity of active component on the surface of the carrier, the active component of the catalyst is evenly distributed and it also improves reactivity. With high denitration efficiency, the dispersion of active ingredients is good.

XPS Characterization

XPS of 8% MnO-Supported Catalyst by Plasma Modification

In order to further understand the energy of metal oxide on the surface of the catalyst, XPS characterization

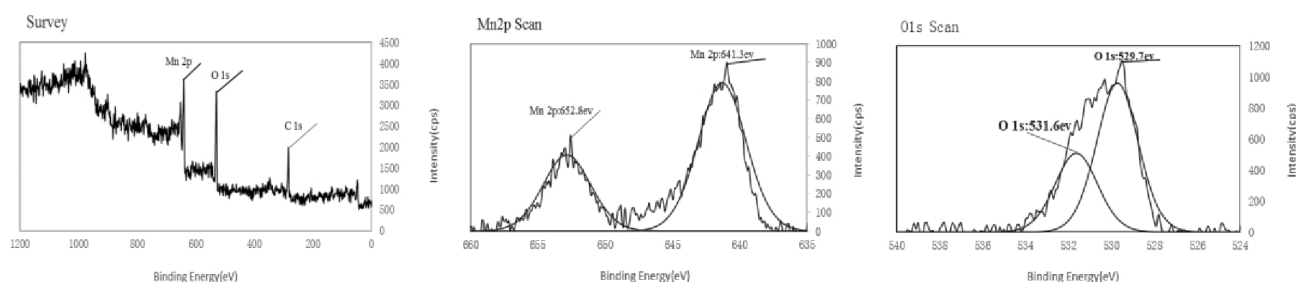


Fig. 8. XPS of 8% MnO-supported catalyst by plasma modification.

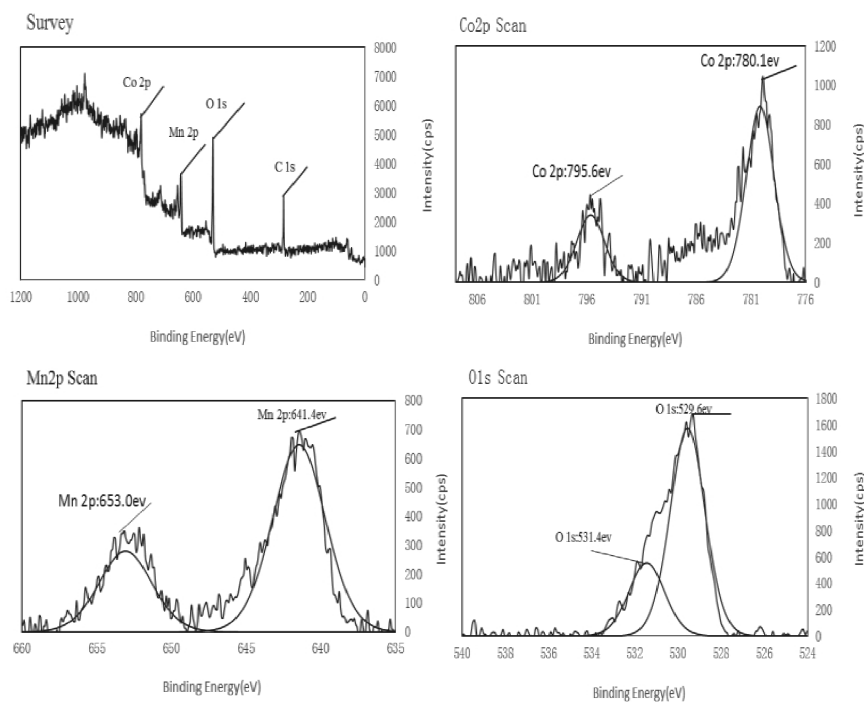


Fig. 9. XPS of Mn-CoO-supported catalyst by plasma modification.

is made. Fig. 8 is XPS spectra of C8. Fig. 8 shows that the peaks of manganese are two on the catalyst surface and there are two kinds of different valence states of oxide: 641.3 eV is Mn^{4+} and 652.8 eV is Mn^{3+} . A lot of Mn^{4+} and a bit of Mn^{2+} are included in the catalyst, combined with XRD. Active metal oxide is generated on the surface more easily in the process of the catalyst by plasma roasting, and efficiency is beneficial. From the peak split of oxygen, it can be seen that the form of two kinds of oxygen exists: 529.7 eV lattice oxygen and 531.6 eV chemical adsorption of oxygen, and the number of lattice oxygen is obviously more than chemical oxygen adsorption state. It improves reactivity.

XPS of Mn-CoO-Supported Catalyst by Plasma Modification

Fig. 9 shows that the peaks of cobalt are two on the catalyst surface and there are two kinds of different valence states of oxide: 780.1 eV is CoO and 795.6 eV

is Co_3O_4 . Cobalt metal joined does not significantly improve manganese oxide, but the oxygen spectra is a great change and the amount of lattice oxygen increases obviously. Combined with the Fig. 5, it can be seen that the addition of CoO obviously improves denitration efficiency, and namely the lattice oxygen plays a positive role in the catalytic process. The increase of the lattice oxygen content makes that the number of holes and micro oxidation reaction increases, the formation energy that NO is oxidized and NO_2 is reduced and the catalytic reaction happens more easily. When the reaction happens to a certain time, metal oxide loses the activity in the system, lattice oxygen loses the reaction of platform and denitration efficiency declines.

SEM Characterization

Fig. 10 is the result of SEM characterization of the catalysts. Fig. 10(b-d) and 10a) contrast and show that the grain of crystal appears obviously on the surface

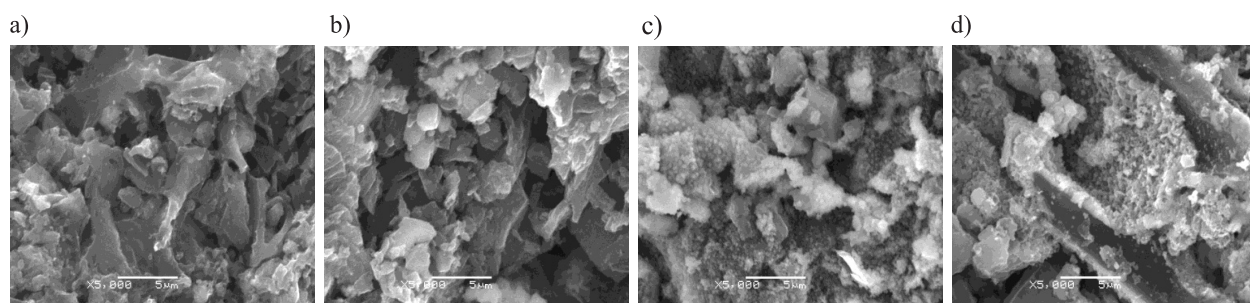


Fig. 10. SEM of catalysts: a) 750C pyrolysis coke, b) Conventional 8% MnO-supported catalyst, c) C8, d) C8-10.

Table 1. BET the results of specific surface area measurements.

The type of catalyst	Specific surface area (m ² / g)
The conventional 8% MnO/supported catalyst	151.08931
C8	145.39247

of the active component. And it can be seen that the catalysts of plasma modification compared with the pyrolysis coke, crystal particle of the former is more uniform and crystallinity of the former is poorer. The plasma modification combined muffle furnace roasting improves the uniformity and the dispersivity of active component, and it also improves reactivity. Comparing Fig. 10d) with Fig. 10c), we find obviously another kind of crystal in the Fig. 10d). Combined with the results of XRD and XPS, this kind of crystal particle is likely to be cobalt metal.

BET Characterization

Table 1 shows the specific surface area of the conventional 8% MnO-supported catalyst and C8. The specific surface area of the catalyst prepared by plasma modification is similar to that of a conventional 8% MnO-supported catalyst. However, combined with experimental data, it can be found that the denitration efficiency of C8 is significantly higher than that of the conventional 8% MnO-supported catalyst. We can conclude that there is no direct relationship between the change of the specific surface area of the catalyst and the activity of the catalyst.

Conclusions

The pyrolysis coke is the carrier, and the supported catalyst is prepared by using equal volume impregnation. By changing the powers and modification time of the plasma, the optimum power and the optimum modification time are explored. Then, under optimal plasma conditions, second kinds of metals are continued to be loaded. The effect of different metal loads on denitration efficiency is explored. The results showed:

- 1) The optimal modified power in a plasma system is 60W and the best modified time in plasma system is 3 min.
- 2) After being modified by plasma, the denitration efficiency of catalysts are significantly higher than conventional calcination catalyst.
- 3) Among catalysts with different Co loadings (5%, 8%, 10%), 8% Co loading had the best denitration efficiency.
- 4) Mn-CoO-supported catalysts had certain SO₂-resistance, and the denitration efficiency of Mn-CoO-supported catalyst > MnO-supported catalyst > unsupported catalyst.

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Conflict of Interest

The authors declare no conflict of interest.

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