

Poisoning Effect of Lead Doping on MnWO_x Catalysts for Selective Catalytic Reduction of NO by NH₃

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Lead has been proved to have deactivation effect on selective catalytic reduction (SCR) catalyst. The poisoning effect of lead doping on MnWO_x catalyst for selective catalytic reduction of NO by NH₃ was investigated in this paper. It was found that the MnWO_x catalyst was observed to be seriously poisoned by the doping of lead. As can be seen from the characterization results of BET, H₂-TPR, NH₃-TPD and XPS, the deactivation of MnWO_x catalyst by lead doping should be resulted from the decreased surface area and defects, redox ability, surface acidity and surface chemisorbed oxygen.

Keywords: Selective catalyst reduction, MnWO_x Catalyst, Lead, Deactivation.

INTRODUCTION

Selective catalytic reduction (SCR) process has been put into commercial application for controlling NO_x emitted from stationary sources such as coal-power plants¹. As the most widely used selective catalytic reduction catalyst, V₂O₅-WO₃/TiO₂ catalyst shows high activity in a narrow temperature window of 300-400 °C². But the deactivation of V₂O₅-WO₃/TiO₂ catalyst by SO₂ and dust in the flue gas make it necessary to develop new kind selective catalytic reduction catalyst with high activity at low temperature.

During the past several years, Mn-based catalyst has drawn much attention because of its high activity for low temperature selective catalytic reduction of NO with NH₃^{3,4}. Several transitional metals such as Ce and W have been found to have a promotion effect on Mn-based selective catalytic reduction catalyst^{5,6}. It is recognized that the doping of W on MnO_x catalyst can increase its surface acidity and facilitate the NO/NH₃ reaction, as a result, MnWO_x shows good performance in the temperature range of 60 to 250 °C⁶.

It is well known that alkali metals (Na, K), alkaline earth metals (Ca, Mg) and heavy metal (Pb, As) can cause the deactivation of selective catalytic reduction catalysts⁷. Till now, much work is focused on the deactivation effect of alkaline metal or heavy metal on the performance of V-based catalyst^{8,9} and there are very few literatures on the effect of heavy metal on low temperature selective catalytic reduction catalyst could

be found. Therefore, MnWO_x catalyst was prepared by using coprecipitation method and the deactivation effect of lead doping on it was also studied and discussed based on the characterization results.

EXPERIMENTAL

Catalyst preparation: MnWO_x catalyst was prepared by using citric acid method. Mn(NO₃)₂, (NH₄)₆H₂W₁₂O₄₀·5H₂O and citric acid were mixed adequately and the mole ratio among Mn, W and citric acid was kept at 3:1:4. After stirred at room temperature for 1 h, the solution was dried at 100 °C for 12 h, and finally a porous, foam-like solid was obtained. Then the foam-like precursor was calcined in air at 500 °C for 5 h to obtain the catalyst.

The Pb-doped catalyst (denoted as PbMnWO_x) was prepared by impregnating the as-prepared MnWO_x catalyst the aqueous solutions Pb(NO₃)₂ (the molar ratio between Pb and Mn was set as 2:15), which was then dried at 100 °C for 12 h and calcined in air at 500 °C for 5 h.

Catalyst characterization: The specific surface areas of the catalysts were measured by N₂ adsorption at 77 K by the BET method using a Quantachrome Autosorb-1 instrument. X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 advance system with CuK_α radiation. The temperature programmed reduction with hydrogen (H₂-TPR) and the temperature programmed desorption with

ammonia (NH₃-TPD) were carried out on an Autosorb-iQ-C chemisorption analyzer (Quantachrome Instruments, USA), the signal of H₂ or NH₃ was recorded with a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) was used to analyze the surface atomic state of catalyst with Al K_α X-rays (Axis Ultra, Kratos Analytical Ltd.)

Selective catalytic reduction activity measurements:

The selective catalytic reduction activities of the catalysts were measured in a fixed bed reactor (i.d. 8 mm) within the temperature range of 100–400 °C. The simulated flue gas contained 600 ppm NO, 600 ppm NH₃, 5 % O₂ and balance Ar, the total flow rate was 1 L/min, corresponding to a gas hourly space velocity of 108000 h⁻¹. The concentrations of NO_x before and after reaction were monitored with a non-dispersive infrared (NDIR)-based gas analyzer (Model 60i, Thermo Scientific Inc.)

RESULTS AND DISCUSSION

Catalytic activity: The selective catalytic reduction activities of MnWO_x and PbMnWO_x as a function of the reaction temperature are shown in Fig. 1. It is clear that the doping of Pb has a distinct deactivation effect on MnWO_x catalyst. The deactivation effect is more and more serious with the increase of reaction temperature. When the reaction temperature is 100 °C, the deactivation effect could be neglected, while when the reaction temperature is 400 °C, the drop of NO conversion is more than 70 %. In addition, when the reaction temperature is over 250 °C, it can be observed that both the activities of MnWO_x and PbWO_x begin to decrease, which may be caused by the oxidation of NH₃ by O₂¹⁰.

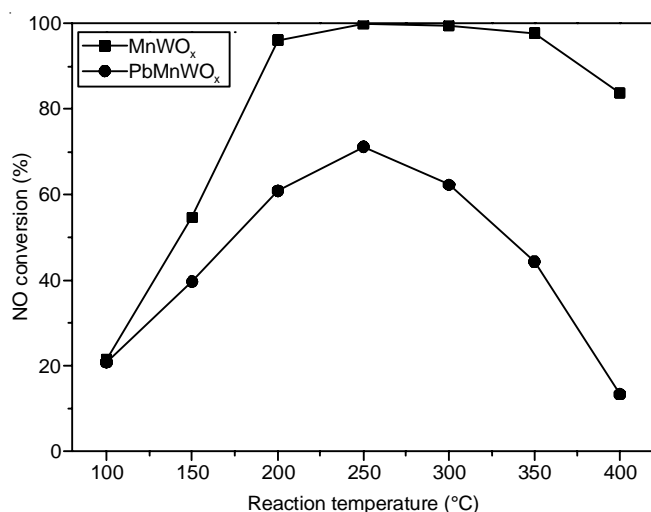


Fig. 1. NO conversion as a function of reaction temperature reaction conditions: [NO] = [NH₃] = 600 ppm, [O₂] = 5 %, balance Ar, GHSV = 108,000 h⁻¹

BET and XRD measurements: The textural properties of the two samples are listed in Table-1. As shown in Table-1,

the values of BET surface area, total volume and average diameter decrease after Pb doping, which may be caused by the block of micropore during Pb doping process.

X-Ray diffraction was used to study the crystal structures of MnWO_x and PbMnWO_x catalysts. The XRD patterns of the two samples are shown in Fig. 2. As can be seen from Fig. 2, the diffraction peaks of Mn₃O₄, MnO and W₁₈O₄₉ could be found on both of the two samples. No diffraction peak corresponding to a crystalline phase containing Pb could be observed, which reveals the strong interaction among Mn, W and Pb in PbMnWO_x. In addition, the intensities of the diffraction peaks in PbMnWO_x is lower than that in MnWO_x, therefore, the doping of Pb has a strong inhibition effect on the crystallization of the MnOx phase.

As reported by other researchers, Mn₃O₄ is the key active sites for NH₃-SCR reaction on MnWO_x catalyst⁶. The mean crystallite size of Mn₃O₄ is also listed in Table-1. It is obvious that the doping of Pb causes an increase of Mn₃O₄ grain size. And larger crystallite size means less lattice defects¹¹. Thus the doping of Pb could increase the stability of Mn₃O₄ grain, which is unfavourable to selective catalytic reduction reaction.

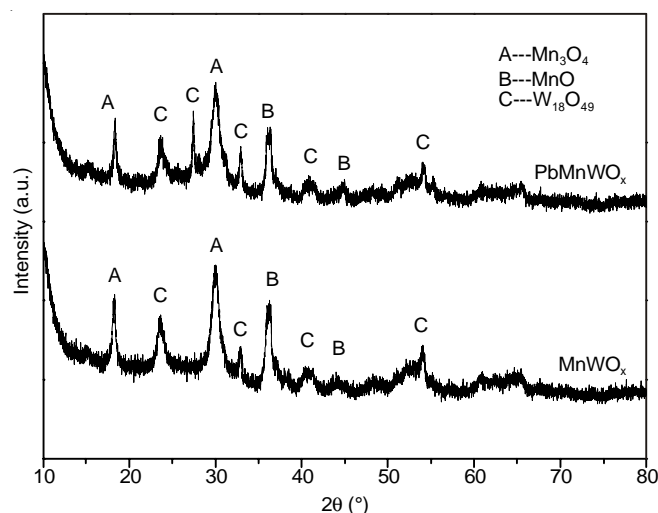
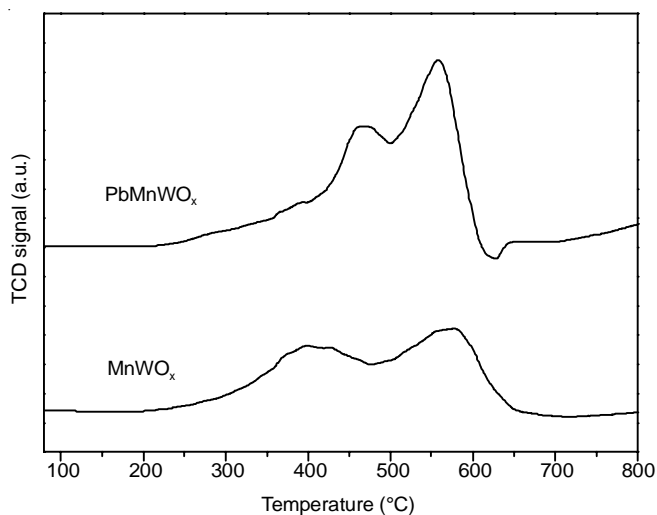


Fig. 2. XRD patterns of the two catalysts

H₂-TPR analysis: The redox properties of MnWO_x and PbMnWO_x catalysts were analyzed by H₂-TPR. The results are illustrated in Fig. 3. As shown in Fig. 3, there are two main reduction peaks could be observed in the profile of each catalyst. The first peak in the TPR curve centered about 400 °C can be assigned to the reduction of MnO₂ to Mn₂O₃ and the second one at about 575 °C could be related to the reduction of Mn₃O₄ to MnO¹². As for PbMnWO_x, the two peaks could be attributed to the reduction of Mn₂O₃ to Mn₃O₄ and the reduction of Mn₃O₄ to MnO, respectively¹². In addition, the first reduction peak in the profile of PbMnWO_x shifts to a higher reduction temperature compared with that in the profile

TABLE-1
TEXTURAL PROPERTIES AND Mn₃O₄ CRYSTALLITE SIZE OF THE TWO CATALYSTS

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Mean crystallite size of Mn ₃ O ₄ (nm)
MnWO _x	29.69	0.4508	34.00	14.74
PbMnWO _x	18.24	0.3559	30.81	15.17

Fig. 3. H₂-TPR profiles of the two catalysts

of MnWO_x, which indicates that the doping of Pb could increase the stability of Mn species and make them less reducible. As a result, MnWO_x shows higher activity than PbMnO_x in the temperature range of 100-400 °C.

NH₃-TPD analysis: To investigate the surface acidities of the two catalysts, NH₃-TPD analysis was performed and the results are presented in Fig. 4. It is obvious that there are acid sites of different strength. MnWO_x contains two major desorption peaks. The first one ranges from 120-400 °C, indicating the distribution of weak acid sites of Brønsted nature; and the second one centered about 625 °C could be assigned to Lewis acid sites¹². The two desorption peaks in the profile of PbMnWO_x are of the similar nature. Besides that, the total acidity of MnWO_x is higher than that of PbMnWO_x, as listed in Table-2. Therefore, the decrease of surface acidity after Pb doping should be another reason for the low activity of PbMnWO_x.

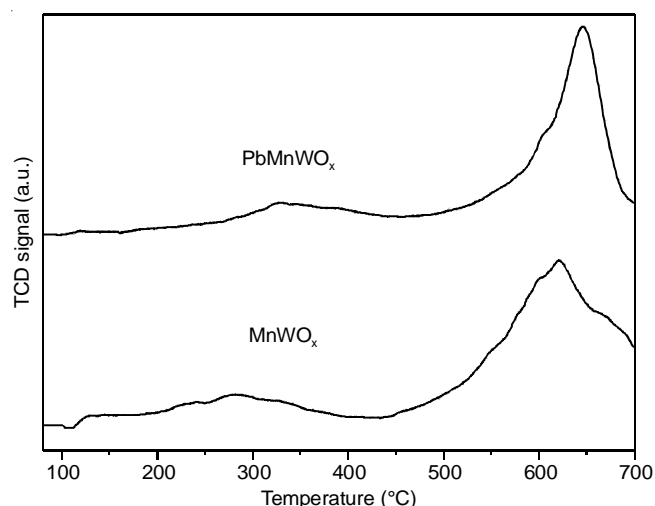
Fig. 4. NH₃-TPD profiles of the two catalysts

TABLE-2
SURFACE ACIDITY OF THE TWO CATALYSTS

Samples	Surface acidity (mmol/g)
MnWO _x	4.02
PbMnWO _x	3.45

XPS analysis: XPS analysis was used to investigate the chemical state of oxygen on the surfaces of the two samples and the results are shown in Fig. 5. There are two types of surface oxygen *i.e.*, lattice oxygen (O_I) (529-530 eV) and chemisorbed oxygen (O_{II}) (531.3-531.9 eV)¹⁴. It is well recognized that chemisorbed oxygen is the active oxygen species in selective catalytic reduction reaction, which could easily exchange with the oxygen in the gas or in the molecules absorbed on the catalysts¹⁵. As shown in Fig. 5, the chemisorbed oxygen disappears from catalyst surface after Pb doping. Thus the great decrease of chemisorbed oxygen may also contribute to the low selective catalytic reduction activity of PbMnWO_x.

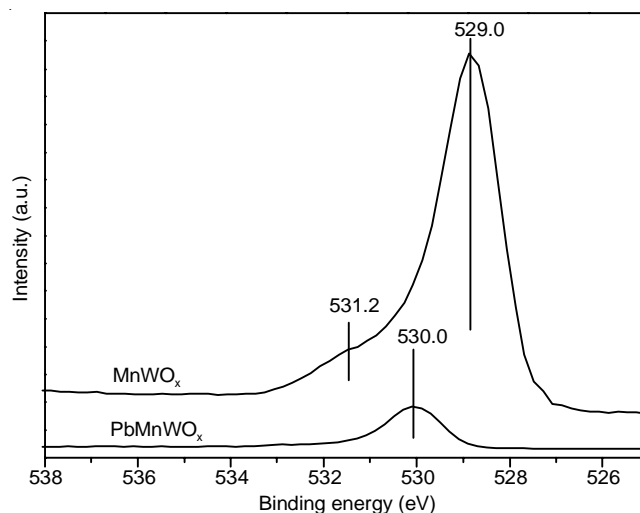


Fig. 5. O1s XPS spectra of the two catalysts

Conclusion

The deactivation effect of Pb doping on MnWO_x catalyst was investigated in this study. The experimental results showed that Pb has a serious deactivation effect on MnWO_x catalyst. Small surface area, enlargement of Mn₃O₄ grain, low redox ability and surface acidity and the disappearance of chemisorbed oxygen might be the main reasons for the bad performance of PbMnWO_x catalyst.

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