

Analysis of Mn valence in the Mn based catalyst for NH₃-SCR process

Weizhe Lu, Xianji Zhou, and Zhekai Zhang*

*Institute of Catalytic Reaction Engineering, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China
Corresponding author email: zzk@zjut.edu.cn*

Keywords: NO_x removal, Mn based catalyst, Valence, low temperature activity, N₂ selectivity.

Abstract: A series of MnWO_x/TiO₂ catalysts were prepared by liquid phase deposition. The MnWO_x/TiO₂ catalyst was characterized by N₂ physical adsorption, X-ray diffraction, H₂ programmed temperature reduction, transmission electron microscopy and X-ray electron spectroscopy, and their NH₃-SCR performance were tested. The effect of Mn valence on the NH₃-SCR performance of MnWO_x/TiO₂ catalyst was analyzed and discussed. The results show that the active components are uniformly dispersed on the surface, and the average valence of manganese are different. The average valence state of manganese in Mn₃WO_x/TiO₂ catalyst is the highest and the activity at low temperature is the best. On the contrary, the average valence of manganese in MnWO_x/TiO₂ catalyst is the lowest while the N₂ selectivity is the best, which means that high valence of manganese is beneficial to its low temperature activity while low valence is favorable for its N₂ selectivity.

Original article, Published date: 2018-06-06

DOI: 10.23977/metf.2018.21001

ISSN 2515-1282

<https://www.clausiuspress.com/journal/METF.html>

1. Introduction

Nitrogen oxides (NO_x) are one type of the major pollutants that affect air quality and can cause many environmental problems such as acid rain, smog, and photochemical pollution. NO_x can also bring harm to the human body. High concentrations of NO_x can influence the human respiratory system. In the past decades, nitrogen removal has been a hot topic in the field of environmental catalysis, and it still receives considerable attention today^[1-3].

NO_x is mainly derived from the emission of exhaust gas from stationary sources or mobile sources such as power plants and automobiles. Many different denitration methods have been developed to deal with different situations. Representative denitrification technologies include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), adsorption, electron beam, pulse corona cryogenic plasma, and direct catalytic decomposition. While using NH₃ as the reducing agent, NO_x can be efficiently converted to environmentally harmless N₂ through selective catalytic reduction reaction (NH₃-SCR), which has thereby become one of the major technologies for NO_x removal^[4-6].

For the NH₃-SCR technology, the catalyst is the basic unit part. Till now, the representative NH₃-SCR catalyst is vanadium-based catalyst V₂O₅-WO₃(MoO₃)/TiO₂, which has been widely used in the industry^[7-8]. One of the disadvantages of the V₂O₅-WO₃(MoO₃)/TiO₂ catalyst is that the operating temperature window is mainly in the range of 300-400 °C, which means that it cannot effectively remove the nitrogen oxides in the low temperature environment and raise the energy consumption. Therefore, Researchers are working hard to develop new catalysts that have high NH₃-SCR activity at lower temperatures. Among these potential catalyst systems, manganese oxide exhibits the best deNO_x activity in the low temperature range due to its variable valence and good redox performance^[9]. However, due to the variable valence of manganese, the active components of manganese-based catalysts are very complex and has become one of the main factors affecting the catalytic activity of manganese-based catalysts^[10-15]. In this paper, a series of MnWO_x/TiO₂ catalysts with different average valence states were prepared using manganese nitrate and tungstate as raw materials. The influence of valence state of manganese on the NH₃-SCR was discussed.

2. Experimental

2.1. Preparation of MnWO_x/TiO₂ Catalyst

The MnWO_x/TiO₂ catalyst was prepared by liquid deposition. According to the target Mn: W molar ratios, suitable amount of manganese nitrate solution and ammonium tungstate were measured. Equal mass of oxalic acid was used to help dissolving ammonium tungstate. The total amount of metal salt precursor is 0.01 mol. The metal precursor was dissolved by adding an appropriate amount of deionized water, and then the TiO₂ support was added to the solution with stirring. 0.5 mol/L ammonia was used as a precipitant, and it was added dropwisely to the solution at a rate of 3 ml/min. The pH was adjusted to 10. The obtained product was filtered, washed, and calcined in a muffle furnace at 300 °C for 2 h. The target catalyst was obtained and was labelled as Mn₃WO_x/TiO₂, Mn₂WO_x/TiO₂ and MnWO_x/TiO₂ according to the molar ratio of manganese to tungsten.

2.2. NO_x removal test

Catalyst performance was tested with simulated flue gas. The composition of the reaction gas was as follows: the volume fraction of NO and NH₃ was 0.05%, the volume fraction of O₂ was 5%, and N₂ was used as the equilibrium gas. The total flow rate of the mixture was 500 ml/min and the calculated space velocity was 60,000 ml/g⁻¹h⁻¹.

The MnWO_x/TiO₂ catalyst was tableted, broken, and sieved to give 20-60 mesh solid particles. 0.5g catalyst was placed in a tube furnace, and the NO_x concentration before and after NH₃-SCR reaction was measured by a TH200 nitrogen oxide analyzer and a Thermo 1500 chromatography. The NO_x conversion and N₂ selectivity are calculated as follows:

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

$$S_{N_2}(\%) = \frac{([NO]_{in} + [NH_3]_{in}) - [NO_2]_{out} - 2[N_2O]_{out}}{([NO]_{in} + [NH_3]_{in})} \quad (2)$$

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. BET

Table 1 lists the texture properties of the MnWO_x/TiO₂ catalysts. The specific surface area, pore volume and pore size of TiO₂ are 197.9 m²/g, 0.305 cm³/g, and 6.2 nm, respectively. the loading of the active component MnWO_x reduces of the specific surface area and pore volume of the catalyst, but the specific surface area and pore volume of MnWO_x/TiO₂ catalysts are close to each other, indicates that there texture properties are similar.

Table 1 The texture properties of the MnWO_x/TiO₂ catalysts.

Samples	BET surface area(m ² /g)	Average pore diameter(nm)	Pore volume (cm ³ /g)
TiO ₂	197.9	6.2	0.305
Mn ₃ WO _x /TiO ₂	156.0	5.0	0.193
Mn ₂ WO _x /TiO ₂	142.3	6.1	0.221
MnWO _x /TiO ₂	168.2	5.4	0.226

3.1.2. XRD

Fig. 1 shows the XRD pattern of MnWO_x/TiO₂ catalyst. Only anatase TiO₂ characteristic diffraction peaks at 2θ = 25.3° , 37.7° , 48.1° , 55.1° , 62.7° , 70.4° , 75.1° are observed in the patterns. No characteristic peaks of the active species MnWO_x are found, indicating that the active species are evenly distributed on the support and there maybe no crystalline phase generated.

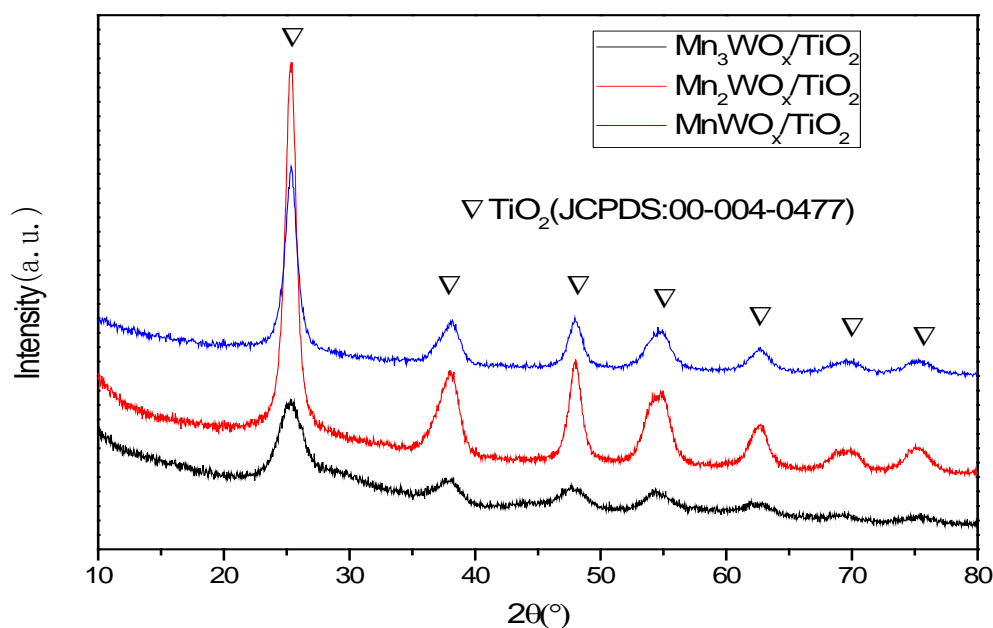


Fig.1 XRD patterns of MnWO_x/TiO₂ catalysts.

3.1.3. TEM

Fig. 2 displays TEM images of $\text{MnWO}_x/\text{TiO}_2$ catalysts, which disclose the microstructure of the $\text{MnWO}_x/\text{TiO}_2$ catalysts. It can be seen that each catalyst are made up of homogeneous nanoparticles. Fig. 2b points out the (101) and (102) face lattice fringes of anatase TiO_2 . Interestingly, lattice fringes of MnWO_4 can be observed in Fig. 2c & 2d, where the 0.483 nm interplanar spacing is attributed to the (100) face and the 0.245-nm interplanar spacing is attributed to the (200) face of MnWO_4 , indicating that manganese and tungsten may interact with each other. The formation MnWO_4 phase^[16] also proved that the active component has been successfully loaded on the support surface.

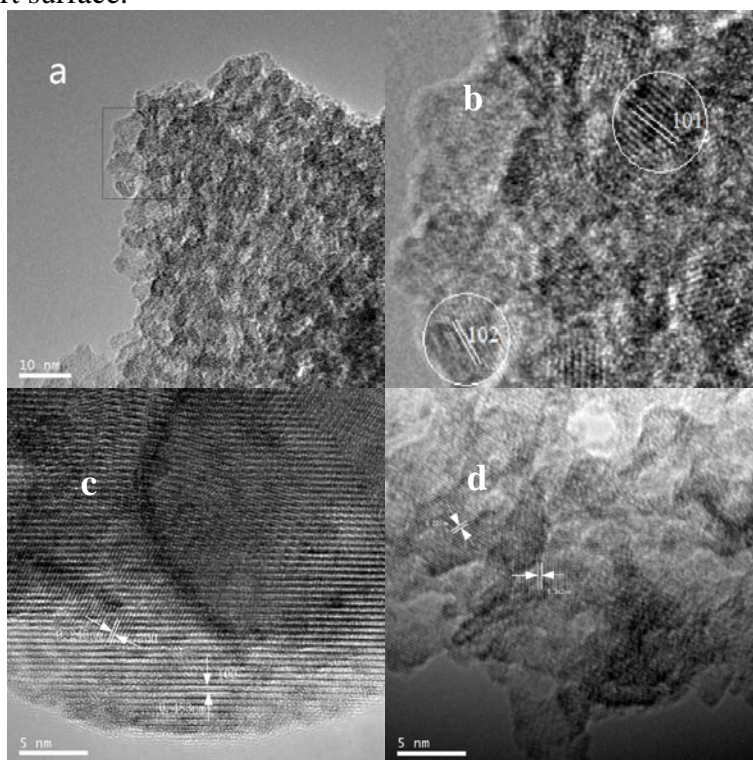


Fig. 2 The TEM images of the $\text{Mn}_a\text{WO}_x/\text{TiO}_2$ catalysts. a, b) $\text{Mn}_3\text{WO}_x/\text{TiO}_2$; c) $\text{Mn}_2\text{WO}_x/\text{TiO}_2$; d) $\text{MnWO}_x/\text{TiO}_2$.

3.1.4. XPS

XPS is one of the most powerful characterizations for determining the valence states of the surface elements. Fig.3 shows the $\text{Mn}2p_{3/2}$ spectra of the $\text{MnWO}_x/\text{TiO}_2$ catalyst. The $\text{Mn}2p_{3/2}$ of the $\text{MnWO}_x/\text{TiO}_2$ catalyst can be divided into three sub-peaks by peak deconvolution: 642.0-642.6eV can be attributed to Mn^{4+} , 640.6-641.4eV can be attributed to Mn^{3+} , and Mn^{2+} is at 643.4-644.5eV^[16-17]. combining Fig. 3 and Table 2, the valence of Mn species in the $\text{Mn}_3\text{WO}_x/\text{TiO}_2$ catalyst is mainly Mn^{4+} , while in the $\text{Mn}_2\text{WO}_x/\text{TiO}_2$ catalyst and the $\text{MnWO}_x/\text{TiO}_2$ catalyst, the Mn species are mainly at Mn^{3+} and Mn^{2+} , respectively. This proves that the valence state of manganese in the catalyst can be adjusted by changing the Mn/W ratio of the catalyst, and the average valence state of manganese decreases with the tungsten content increasing.

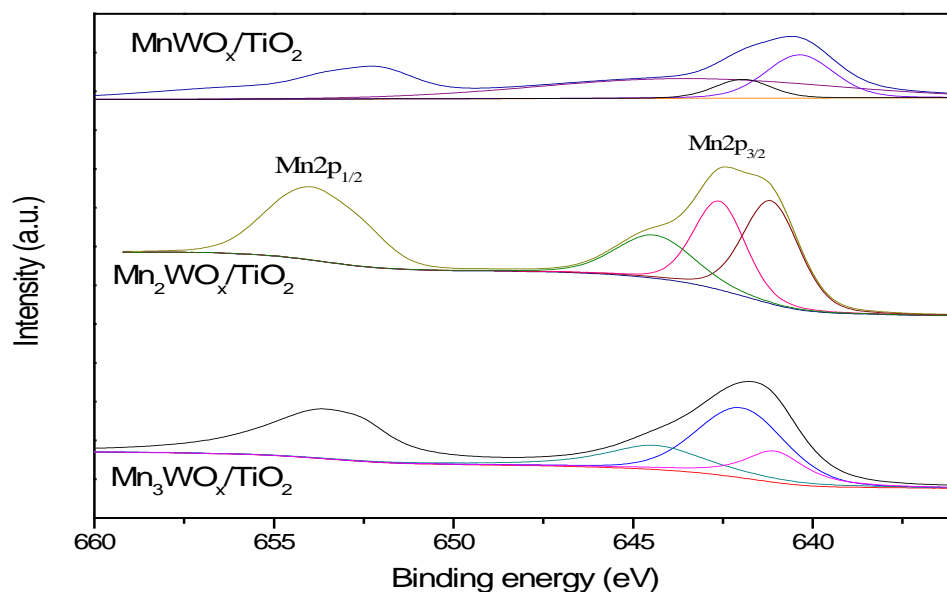


Fig. 3 Mn 2p XPS spectra of the $\text{MnWO}_x/\text{TiO}_2$ catalyst.

Table 2 Quantitative results of Mn2p XPS spectra of $\text{MnWO}_x/\text{TiO}_2$.

Samples	Mn^{4+}		Mn^{3+}		Mn^{2+}		Average valence
	BE(ev)	Per. %	BE(ev)	Per.%	BE(ev)	Per.%	
$\text{Mn}_3\text{WO}_x/\text{TiO}_2$	642.3	65.27	640.9	22.11	643.9	12.63	3.5
$\text{Mn}_2\text{WO}_x/\text{TiO}_2$	642.6	33.26	641.1	42.37	644.4	24.37	3.1
$\text{MnWO}_x/\text{TiO}_2$	642.0	11.36	640.8	31.72	643.4	56.92	2.5

3.1.5. H_2 -TPR

Fig. 4 displays H_2 -TPR profiles of the $\text{MnWO}_x/\text{TiO}_2$ catalysts. The $\text{MnWO}_x/\text{TiO}_2$ catalysts show 4 reduction peaks at 4 different temperatures of 220 °C, 300 °C, 400 °C and 460 °C. The latter three reduction peaks can be assigned as $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$, $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ and $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}^{[18]}$. In the $\text{Mn}_3\text{WO}_x/\text{TiO}_2$ catalyst, the reduction peak is mainly $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$, and the valence state of Mn in MnO_2 is +4. The reduction peak of Mn in $\text{Mn}_2\text{WO}_x/\text{TiO}_2$ and $\text{MnWO}_x/\text{TiO}_2$ catalysts shifted to high temperature, indicating the decrease of Mn valence in the catalyst. The results are consistent with the results of XPS characterization.

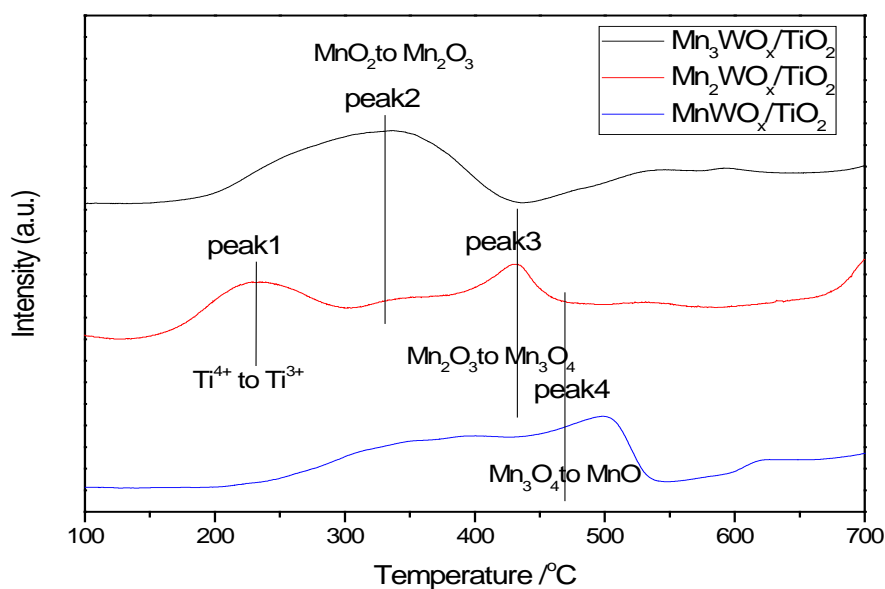


Fig 4. The H₂-TPR profiles of the MnWO_x/TiO₂ catalysts.

3.2. NH₃-SCR Performance of MnWO_x/TiO₂ Catalysts

3.2.1. NH₃-SCR Performance

Fig. 5 shows the NH₃-SCR performance of the MnWO_x/TiO₂ catalysts. Taking 90% NO_x conversion as criteria, in Fig. 5a, the Mn₃WO_x/TiO₂ catalyst activity temperature window is between 100 °C -250 °C; while Mn₂WO_x/TiO₂ and MnWO_x/TiO₂ catalysts have an activity temperature window of 120 °C -280 °C and 130 °C -340 °C, respectively. It can be clearly observed that when the valence state of Mn species is higher, its low temperature activity NH₃-SCR is better; when the valence state of Mn species is decreased, the activity window moves to high temperature attitude.

Fig. 5b shows the N₂ selectivities variation of the MnWO_x/TiO₂ catalysts, which exhibits a different trend with the activity profiles. The Mn₃WO_x/TiO₂ catalyst possesses the worst N₂ selectivity in the high temperature range. while with the decrease of Mn valence, the N₂ selectivity of the MnWO_x/TiO₂ catalyst increases gradually. Although it can not exclude the effect of tungsten, it is known that high valence Mn has a strong redox ability, which is easy to promote the non-selective oxidation of NH₃ in the high-temperature range and cause the formation of N₂O. Therefore, high valence may be not favourable for the N₂ selectivity. The decrease of the Mn valence reduces the redox properties and decreases the NH₃-SCR activity of the MnWO_x/TiO₂ catalysts in the low temperature region, but it may also help to avoid the occurrence of non-selective oxidation, thereby improving the N₂ selectivity.

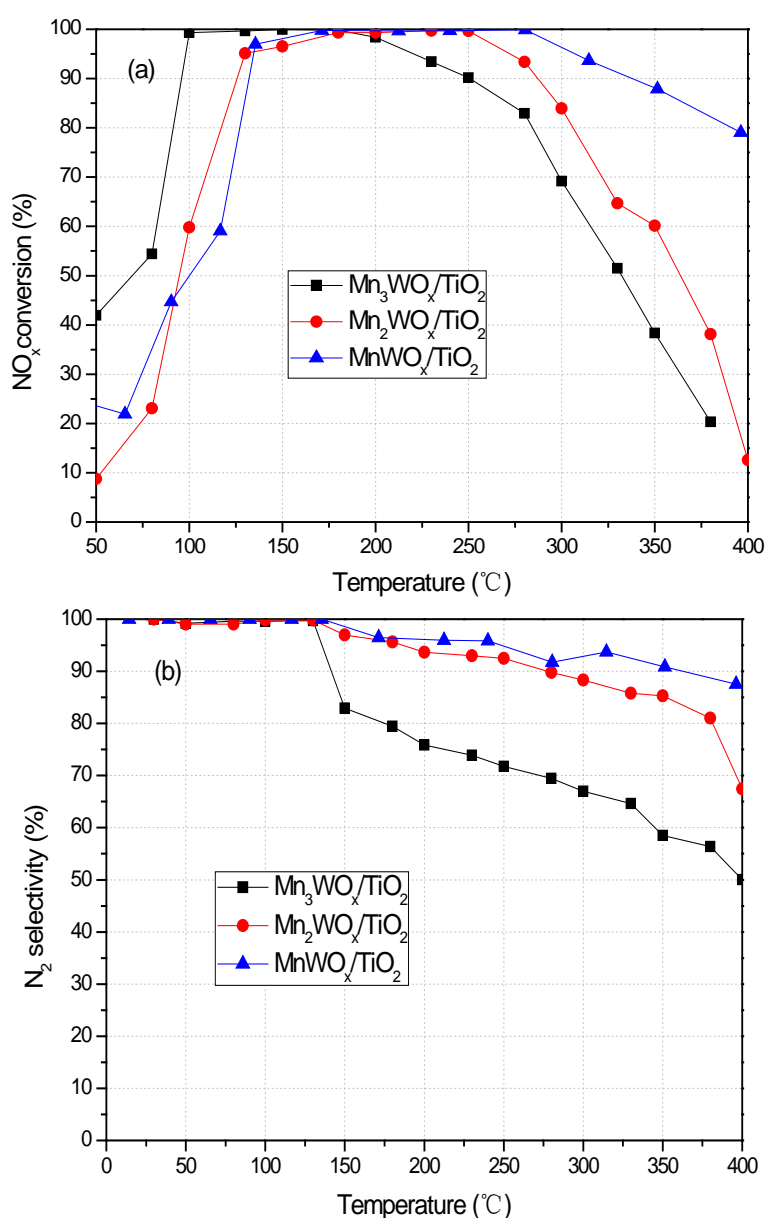


Fig. 5 The NH₃-SCR activity of the MnWO_x/TiO₂. A. activity B. N₂ selectivity.

3.2.2. SO₂ resistance

Fig. 6 shows the SO₂ resistance of the MnWO_x/TiO₂ catalyst. When SO₂ is introduced, the NO_x conversion of Mn₃WO_x/TiO₂ and Mn₂WO_x/TiO₂ catalysts immediately decreases and begins to stabilize at a certain degree, while the decrement degree on Mn₂WO_x/TiO₂ catalyst is lower than that of Mn₃WO_x/TiO₂. For MnWO_x/TiO₂ catalyst, the introduction of SO₂ does not immediately lead to a decrease in the conversion, i.e., its SO₂ resistance is improved. Similarly, this cannot exclude the effect of tungsten, but it also means that the reduction in the valence of manganese contributes to the improvement of its sulfur resistance. One reason may be that high valence Mn has strong oxidative ability to SO₂, which will quickly oxidize SO₂ to SO₃, generating sulfate and blocking the pores of the catalyst, thus decreasing the NO_x removal ability of the catalyst. The oxidizing ability of low valence Mn to SO₂ is decreased, which also slows down the formation of sulfate on the catalyst.

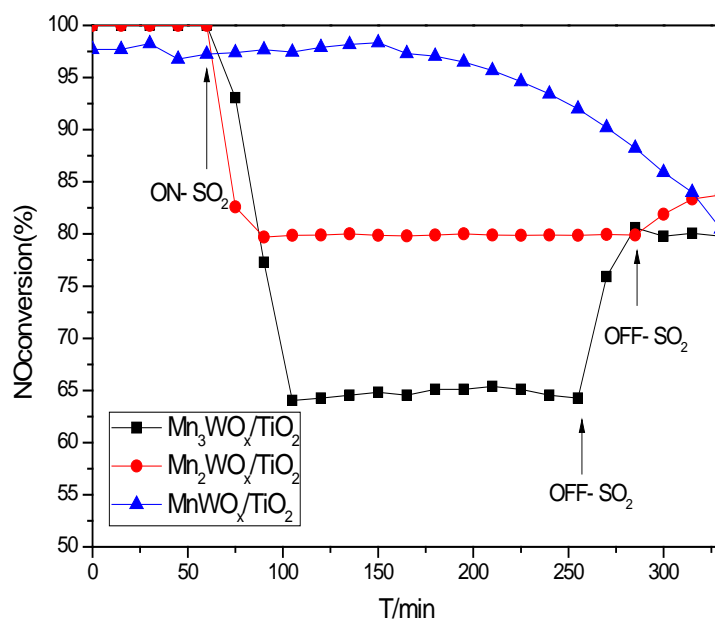


Fig. 6 The activity of MnWO_x/TiO₂ at 260 °C in the presence of 100ppm SO₂.

4. Conclusions

In this paper, a series of MnWO_x/TiO₂ catalysts with different Mn/W molar ratios were prepared by liquid deposition method. The MnWO_x/TiO₂ catalysts were characterized and their NH₃-SCR performances were investigated. Through the characterization, it was found that the as-prepared MnWO_x/TiO₂ catalyst had good dispersion of active components, and the valence of Mn decreased with the decrease of Mn/W molar ratio. Among MnWO_x/TiO₂ catalysts with different Mn valences, Mn₃WO_x/TiO₂ catalyst exhibits the highest low-temperature NH₃-SCR activity, while MnWO_x/TiO₂ catalyst exhibits the best N₂ selectivity, which indicates that the high valence is favourable for the NH₃-SCR activity and low valence is for N₂ selectivity.

References

- [1] Ronald, M.H., (1999) *Catalytic abatement of nitrogen oxides-stationary applications*, *Catalysis Today*, 53(4): 519-523.
- [2] Seinfeld, J.H., (1989) *Urban air pollution: state of the science*, *Science*, 243(4892): 745-752.
- [3] Tion, H.Z., Liu, K.Y., Hao, J.M., (2013) *Nitrogen Oxides Emissions from Thermal Power Plants in China: Current Status and Future Predictions*. *Environmental Science & Technology*, 47, 11350-11357.
- [4] Tadao, N., Akira, M., (1991) *Removal technology for nitrogen oxides and sulfur oxides from exhaust gases*, *Catalysis Today*, 10(1): 21-31.
- [5] Chen, L., Si, Z.H., Wu, X.D., et al. (2014) *Rare earth containing catalysts for selective catalytic reduction of NO_x with ammonia: A Review*. *Journal of Rare Earths*, 32(10):907-917.
- [6] Liu, C., Shi, J.W., Gao, C., et al. (2016) *Manganese oxide-based catalysts for low-temperature selective catalytic reduction of NO_x with NH₃: A review*. *Applied Catalysis A: General*, 522: 54-69.
- [7] Chae, H.J., Nam, I.S., Ham, S.W., et al. (2004) *Characteristics of vanadia on the surface of V₂O₅/Ti-PILC catalyst for the reduction of NO by NH₃*. *Applied Catalysis B: Environmental*, 53(2): 117-126.
- [8] Djerad, S., Tifouti, L., Crocoll, M., Weisweiler, W., (2004) *Effect of vanadia and tungsten loadings on the physical and chemical characteristics of V₂O₅-WO₃/TiO₂ catalysts*, *Journal of Molecular Catalysis A: Chemical*, 208(1-2): 257-265.
- [9] Evgenii, V.K., Javier, P.R., (2005) *Transient studies on the effect of oxygen on the high-temperature NO reduction by NH₃ over Pt-Rh gauze*, *Applied Catalysis A: General*, 289(1): 97-103.
- [10] Zhang, Q.L., Qiu, C.T., Xu, H.D., et al. (2011) *Novel promoting effects of tungsten on the selective catalytic reduction of NO by NH₃ over MnO_x-CeO₂ monolith catalyst*. *Catalysis Communications*, 16(1):20-24.

- [11] Yang, S.J., Wang, C.Z., Li, J.H., et al. (2011) Low temperature selective catalytic reduction of NO with NH₃ over Mn-Fe spinel: Performance, mechanism and kinetic study. *Applied Catalysis B: Environmental*, 110(41):71-80.
- [12] Huang, H.Y., Yang, R.T., (2001) Removal of NO by Reversible Adsorption on Fe-Mn Based Transition Metal Oxides. *Langmuir*, 17(16):4997-5003.
- [13] Kapteijn, F., Singoredjo, L., Andrrini A. (1994) Activity and selectivity of pure manganese oxides in the selective catalytic reduction of nitric oxide with ammonia. *Applied Catalysis B: Environmental*, 3(2-3): 173-189.
- [14] Tatsuji, Y., Albert, V., (1996) NO Decomposition over Mn₂O₃ and Mn₃O₄. *Journal of Catalysis*, 163(1):158-168.
- [15] Tang, X.F., Li, J.H., Sun, L., et al. (2010) Origination of N₂O from NO reduction by NH₃ over β-MnO₂ and α-Mn₂O₃. *Applied Catalysis B: Environmental*, 99(1-2): 156-162.
- [16] Liu, F.D., Shan, W.P., Lian, Z.H., et al. (2013) Novel MnWO_x catalyst with remarkable performance for low temperature NH₃-SCR of NO_x. *Catalysis Science & Technology*, 3(10): 2699-2707.
- [17] Li, X., Lunkenbein, T., Pfeifer, V., et al. (2016) Selective Alkane Oxidation by Manganese Oxide: Site Isolation of MnO_x Chains at the Surface of MnWO₄ Nanorods. *Angewandte Chemie*, 55(12):4092-4096.
- [18] Padmanabha, R.E., Neeraja, E., Sergey, M., et al. (2007) Surface characterization studies of TiO₂ supported manganese oxide catalysts for low temperature SCR of NO with NH₃. *Applied Catalysis B: Environmental*, 76(1-2): 123-134.