

### **Influence of tungsten on the NH<sub>3</sub>-SCR activity of MnO<sub>2</sub> based catalysts**

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Table S1 The main peak's positions of characterization of Mn<sub>a</sub>WO<sub>x</sub>/TiO<sub>2</sub> systems by H<sub>2</sub>-TPR method

samples	P1	P2	P3	P4	P5	P6	P7	P8
MnO <sub>2</sub> /TiO <sub>2</sub> -SHS	230	300	390	460				
Mn <sub>5</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	220	260	330	430	-	-	730	
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	220	260	330	430	-	-	750	
MnWO <sub>x</sub> /TiO <sub>2</sub> -SHS	-	-	-	-	-	-	800	
WO <sub>3</sub> /TiO <sub>2</sub> -SHS	-	-	-	-	520	650	820	

Table S2 Quantitative analysis data of H<sub>2</sub>-TPR profiles

Catalysts	H <sub>2</sub> - consumption(mmol/g)							Sum
	Peak1	Peak2	Peak3	Peak4	Peak5	Peak6	Peak7	
WO <sub>3</sub> /TiO <sub>2</sub> -SHS	-	-	-	-	0.68	0.62	0.53	1.83
MnO <sub>x</sub> /TiO <sub>2</sub> -SHS	0.017	0.026	0.080	0.009	-	-	-	0.132
MnWO <sub>x</sub> /TiO <sub>2</sub> -SHS	-	-	-	-	-	-	0.88	0.88
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	0.22	0.13	0.12	0.19	-	-	0.58	1.24
Mn <sub>5</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	0.16	0.094	0.066	0.17	-	-	0.28	0.77

Table S3 elements distribution via EDX/TEM

Samples	Elements/(Atomic%)				Mn:W ratio
	O(K)	Mn(K)	W(L)	Ti(K)	
Mn <sub>2</sub> WO <sub>x</sub> -SHS	71.84	16.89	11.25	-	1.5
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	66.72	1.80	2.35	29.10	0.8
Mn <sub>2</sub> WO <sub>x</sub> -CP	75.45	9.48	15.06	-	0.6
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -IMP	73.79	7.42	6.95	11.81	1.1

Table S4 elements distribution via EDS/SEM

Samples	Elements/(Atomic%)				Mn:W
	O(K)	Mn(K)	W(L)	Ti(K)	ratio
MnWO <sub>x</sub> -SHS	59.93	20.08	19.99	-	1.00
Mn <sub>2</sub> WO <sub>x</sub> -SHS	57.72	27.93	14.36	-	1.94
Mn <sub>2</sub> WO <sub>x</sub> -CP	59.27	20.79	19.94	-	1.04
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	58.35	4.61	1.85	35.19	2.49

TableS5. Bulk Mn<sub>a</sub>WO<sub>x</sub> catalysts via self-propagating high-temperature synthesis(SHS)

samples	molar ratio of Mn to W	metal salt precursor	The amount of glycine (10times amount of metal-salts )
MnO <sub>2</sub> -SHS	-	0.01molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	0.1mol
WO <sub>3</sub> -SHS	-	0.001mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O	0.01mol
MnWO <sub>x</sub> -SHS	1:1	0.006molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O +0.0005mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O	0.065mol
Mn <sub>2</sub> WO <sub>x</sub> -SHS	2:1	0.012molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O +0.0005mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O	0.125mol
Mn <sub>5</sub> WO <sub>x</sub> -SHS	5:1	0.012molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O +0.0002mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O	0.122mol
Mn <sub>10</sub> WO <sub>x</sub> -SHS	10:1	0.012molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O +0.0001mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O	0.121mol

TableS6. The supported  $Mn_aWO_x/TiO_2$  catalysts via self-propagating high-temperature synthesis(SHS), The loading amount of active components is kept at 20wt%.

samples	molar ratio of Mn to W	The amount of metal salt precursor	The amount of glycine(three times of the total amount of metal-salts and $TiO_2$ )
$MnO_2/TiO_2$ -SHS	-	0.00431mol $Mn(NO_3)_2 \cdot 4H_2O + 1.5gTiO_2$	0.0692mol
$WO_3/TiO_2$ -SHS	-	0.000131mol $(NH_4)_{10}W_{12}O_{41} \cdot xH_2O + 1.5gTiO_2$	0.0567mol
$MnWO_x/TiO_2$ -SHS	1:1	0.00157mol $Mn(NO_3)_2 \cdot 4H_2O + 0.000131mol(NH_4)_{10}W_{12}O_{41} \cdot xH_2O + 1.5gTiO_2$	0.0613mol
$Mn_2WO_x/TiO_2$ -SHS	2:1	0.00256mol $Mn(NO_3)_2 \cdot 4H_2O + 0.000107mol(NH_4)_{10}W_{12}O_{41} \cdot xH_2O + 1.5gTiO_2$	0.0643mol
$Mn_5WO_x/TiO_2$ -SHS	5:1	0.00408mol $Mn(NO_3)_2 \cdot 4H_2O + 0.68 \cdot 10^{-5}mol(NH_4)_{10}W_{12}O_{41} \cdot xH_2O + 1.5gTiO_2$	0.0685mol
$Mn_{10}WO_x/TiO_2$ -SHS	10:1	0.00511mol $Mn(NO_3)_2 \cdot 4H_2O + 0.426 \cdot 10^{-5}mol(NH_4)_{10}W_{12}O_{41} \cdot xH_2O + 1.5gTiO_2$	0.0716mol

		O+1.5 gTiO <sub>2</sub>	
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TableS7. The supported MnWO<sub>x</sub>/TiO<sub>2</sub> catalysts via impregnation method (the loading amount of active components is kept at 20wt%)

samples	molar ratio of Mn to W	metal salt precursor
MnWO <sub>x</sub> /TiO <sub>2</sub> -IMP	1:1	0.00209molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O+0.000174mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O+2gTiO <sub>2</sub>
Mn <sub>2</sub> WO <sub>3</sub> /TiO <sub>2</sub> -IMP	2:1	0.0034molMn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O+0.000142mol(NH <sub>4</sub> ) <sub>10</sub> W <sub>12</sub> O <sub>41</sub> ·xH <sub>2</sub> O+2gTiO <sub>2</sub>

TableS8. The MnWO<sub>x</sub> catalysts via Co-precipitation synthesis

method

samples	molar ratio of Mn to W	metal salt precursor
MnWO <sub>x</sub> -CP	1:1	0.01molMnCl <sub>2</sub> ·4H <sub>2</sub> O+0.01molNa <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O
Mn <sub>2</sub> WO <sub>x</sub> -CP	2:1	0.02molMnCl <sub>2</sub> ·4H <sub>2</sub> O+0.01molNa <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O

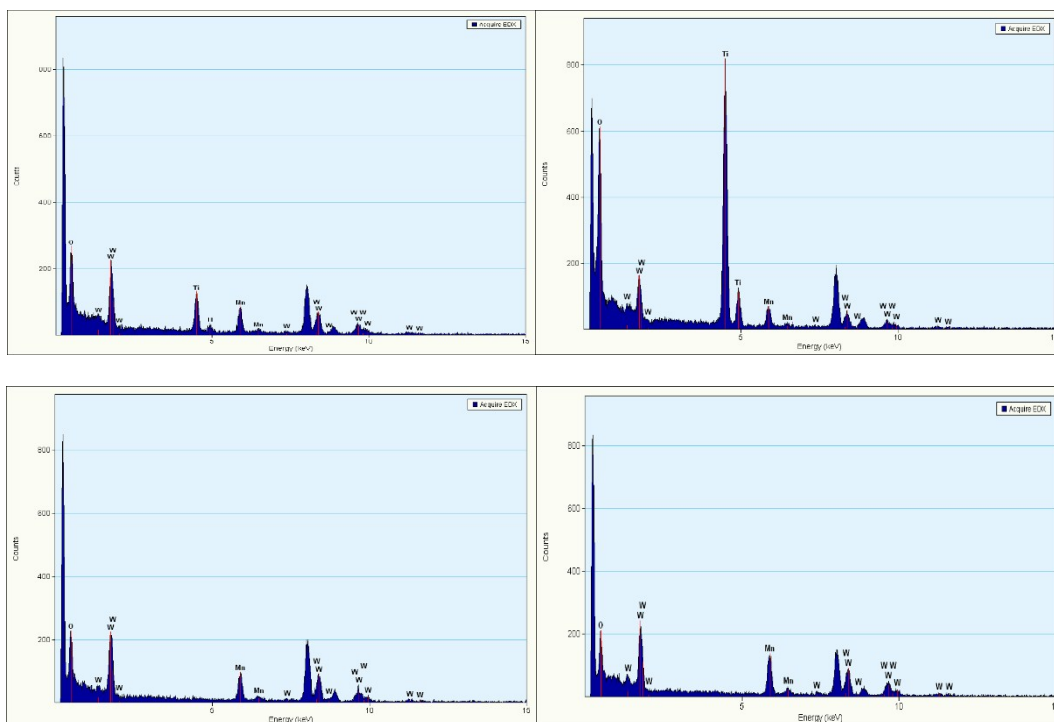


Fig.S1 EDX patterns of the bulk and supported  $Mn_aWO_x$  catalysts with different preparation methods

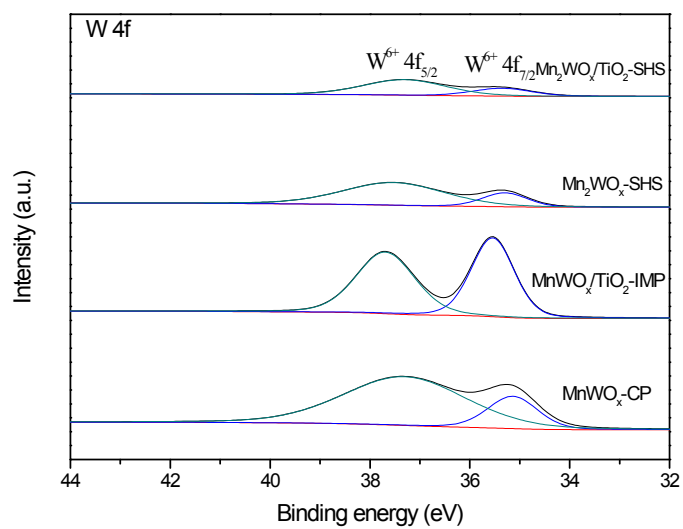


Fig.S2 W4f XPS spectra of  $MnWO_x$ -CP,  $MnWO_x/TiO_2$ -IMP,  $Mn_2WO_x$ -SHS and  $Mn_2WO_x/TiO_2$ -SHS

The resistance to  $\text{SO}_2$  and  $\text{H}_2\text{O}$  is an important property besides the activity for catalysts. The  $\text{H}_2\text{O}$  and  $\text{SO}_2$  in exhaust fumes can induce the deactivation and poisoning of catalyst. Therefore, the influence of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  on NO conversion by  $\text{Mn}_2\text{WO}_x/\text{TiO}_2\text{-SHS}$  at 200 °C and 260 °C was investigated. 10 vol%  $\text{H}_2\text{O}$  was added to the system, the  $\text{NO}_x$  conversion of  $\text{Mn}_2\text{WO}_x/\text{TiO}_2\text{-SHS}$  showed a notable deactivation on NO reduction at 200 °C. However, NO conversion slightly decreased from 99% to 98% at 260 °C. After 3.5h(200 °C) or 8h(260 °C), when  $\text{H}_2\text{O}$  was removed from the flue gas, NO conversion nearly recovered to original levels. This result indicated that the decrease in activity brought about by  $\text{H}_2\text{O}$  might be caused by its competitive adsorption between with  $\text{NH}_3$  and  $\text{NO}_x$  on the active sites over the catalyst surface.

In the presence of 100ppm  $\text{SO}_2$  at 200 °C and 260 °C, the NO conversion of  $\text{Mn}_2\text{WO}_x/\text{TiO}_2\text{-SHS}$  decreased from the initial 100% to 72% in 3.5 h and 100% to 80% in 8h respectively. After the removal of  $\text{SO}_2$ , NO conversion over  $\text{Mn}_2\text{WO}_x/\text{TiO}_2\text{-SHS}$  partly recovered to 80% and 85%. The coexistence of 100 ppm  $\text{SO}_2$  and 5 vol.%  $\text{H}_2\text{O}$  notably induced decrease of NO conversion at both 200 °C and 260 °C. After switching off  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , the NO conversion was recovered with a sharp increase from 65% to 70% and 70% to 80%. It can be speculated that some ammonium sulfates or ammonium bisulfate may be formed by the reaction between  $\text{SO}_2$  and the reactants ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$ ) and the formed sulfates can occupy the active sites or deposit on the surface of the catalyst.

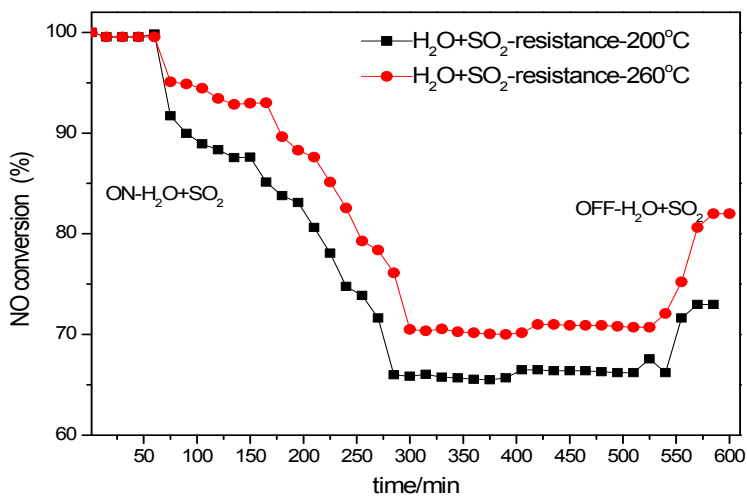
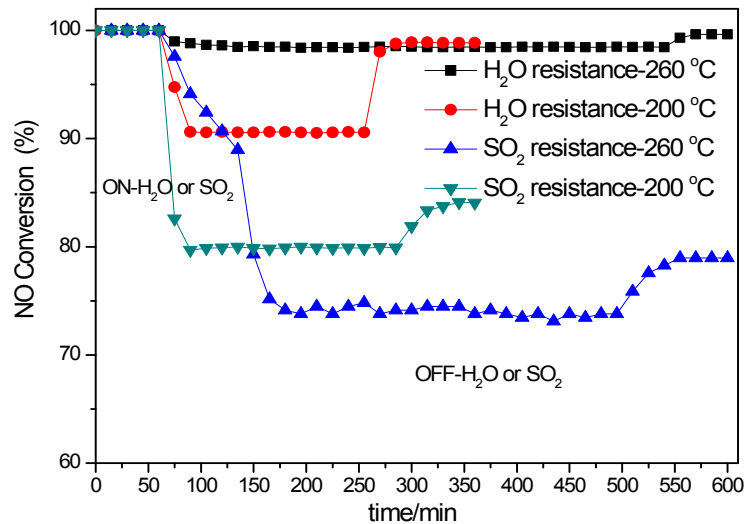


Fig.S3 The H<sub>2</sub>O and SO<sub>2</sub> resistance of Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS

Reaction conditions: H<sub>2</sub>O=10% or SO<sub>2</sub>=100ppm, GHSV=30000h<sup>-1</sup>

In order to investigate the effects of W species in Mn<sub>a</sub>WO<sub>x</sub>/TiO<sub>2</sub> catalyst, the separate NH<sub>3</sub> oxidation (NH<sub>3</sub> + O<sub>2</sub>) experiments were also carried out (Fig.S4). The NH<sub>3</sub> oxidation ability may directly affect NH<sub>3</sub>-SCR activity in the high temperature range. The NH<sub>3</sub> oxidation ability of MnWO<sub>x</sub>/TiO<sub>2</sub> is obviously lower than that of



$\text{MnO}_x/\text{TiO}_2$ , increasing the ratio of Mn/W results in the increase of the  $\text{NH}_3$  oxidation ability, which means that a suitable addition of W could inhibit the unselective oxidation of  $\text{NH}_3$  and thus promote the high temperature activity. Considering the XRD pattern and SCR activity, the  $\text{MnWO}_x/\text{TiO}_2$  only presents the characteristic peaks of  $\text{MnWO}_4$  and  $\text{TiO}_2$ , but the  $\text{MnWO}_4$  and  $\text{Mn}_3\text{O}_4$  disappears together on the patterns of  $\text{Mn}_2\text{WO}_x/\text{TiO}_2$  and  $\text{Mn}_5\text{WO}_x/\text{TiO}_2$ . The results suggest that the existence of  $\text{MnWO}_4$  crystalline phase may be beneficial to the enhancement of  $\text{N}_2$  selectivity in  $\text{NH}_3$ -SCR reaction. When the ratio of Mn/W exceed 1, amorphous  $\text{Mn}_3\text{O}_4$  destroy the existence of  $\text{MnWO}_4$  crystalline phase, resulting in weaker  $\text{NH}_3$  adsorption and higher  $\text{NH}_3$  unselective oxidation.

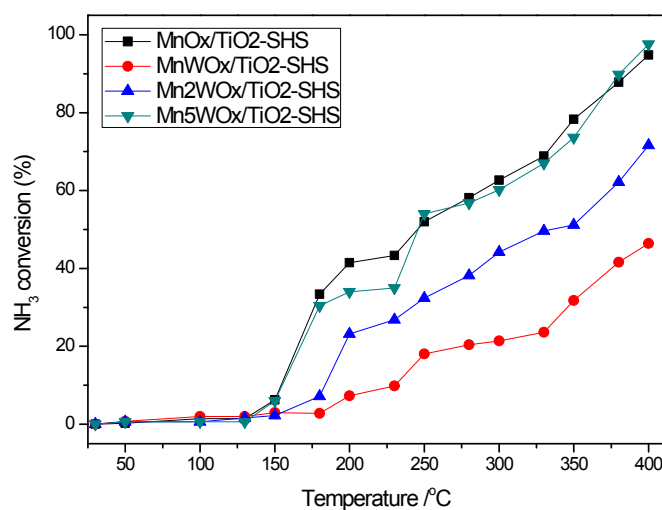


Fig.S4  $\text{NH}_3$  conversions during separate  $\text{NH}_3$  oxidation reaction over  $\text{MnO}_x/\text{TiO}_2$  and  $\text{Mn}_a\text{WO}_x/\text{TiO}_2$  catalysts. Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 500$  ppm,  $[\text{O}_2] = 5$  vol.%,  $\text{N}_2$  balance and GHSV  $30,000 \text{ h}^{-1}$ .

The  $\text{NO}_2$  production in the separate  $\text{NO}$  oxidation reaction over  $\text{Mn}_a\text{WO}_x/\text{TiO}_2$  is obviously higher than that over bulk  $\text{Mn}_a\text{WO}_x$  in the low temperature

range of 50- 200 °C. However, considering XPS analysis in Fig.9 and Table4, surface absorbed  $O_a$  ratio of bulk  $Mn_aWO_x$  is higher than the supported catalysts. The results indicate that some other important changes (such as the existence and increase of  $MnWO_4$  crystallite, and surface acid sites) but not the changes of  $O_a$  ratio induced by the addition of carrier caused the enhancement of low temperature NO oxidation ability. However, the inhibited high temperature oxidation of  $NH_3$  over  $Mn_2WO_x/TiO_2-SHS$  might be also associated with the low  $O_a$  ratio besides the influence of  $MnWO_4$  crystalline phase.

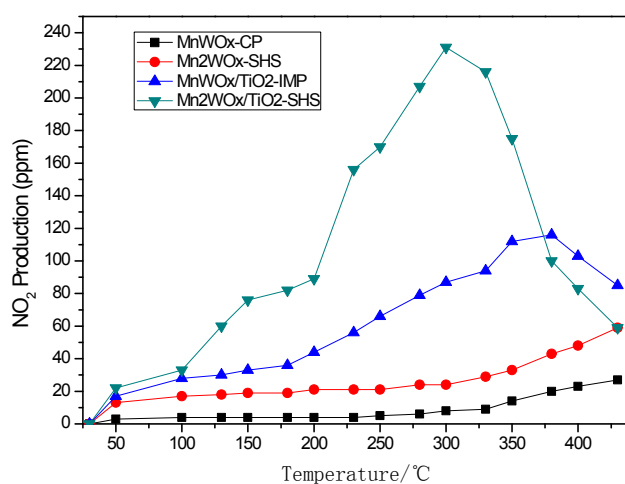


Fig.S5 NO conversions during separate NO oxidation reaction over  $Mn_aWO_x$  and  $Mn_aWO_x/TiO_2$  catalysts. Reaction conditions:  $[NO] = [NH_3] = 500$  ppm,  $[O_2] = 5$  vol.%,  $N_2$  balance and GHSV  $30,000 h^{-1}$ .