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# Influence of tungsten on the NH<sub>3</sub>-SCR activity of MnWO<sub>x</sub>/TiO<sub>2</sub> catalysts†

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A series of bulk MnWO<sub>x</sub> and supported MnWO<sub>x</sub>/TiO<sub>2</sub> catalysts with MnWO<sub>4</sub> structure were prepared via self-propagating high-temperature synthesis (SHS), co-precipitation and impregnation methods. The catalysts were characterized using X-ray diffraction (XRD), N<sub>2</sub> adsorption/desorption, hydrogen-temperature programmed reduction (H<sub>2</sub>-TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The performance of MnWO<sub>x</sub> and MnWO<sub>x</sub>/TiO<sub>2</sub> and the relation between the tungsten and manganese oxide species in MnWO<sub>x</sub> and MnWO<sub>x</sub>/TiO<sub>2</sub> catalysts were investigated. The supported MnWO<sub>x</sub>/TiO<sub>2</sub> catalysts exhibited the activity improvement of the SCR reaction via the promotion of tungsten. The XRD pattern and the TEM images revealed that the presence of tungsten induces the formation of a MnWO<sub>4</sub> oxide phase, thus weakening the interaction between MnO<sub>2</sub> and TiO<sub>2</sub>, which is favorable for the specific surface area of MnWO<sub>x</sub>/TiO<sub>2</sub>. The MnWO<sub>4</sub> phase also has a positive effect for the activity and N<sub>2</sub> selectivity of MnWO<sub>x</sub>/TiO<sub>2</sub> in the high temperature range. In a feed gas that contains 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol% O<sub>2</sub> and N<sub>2</sub> as the balance gas, Mn<sub>2</sub>WO<sub>4</sub>/TiO<sub>2</sub>-SHS shows the best deNO<sub>x</sub> performance and the NO<sub>x</sub> conversion reaches 100% in the temperature range of 130–300 °C under the reaction condition of 30 000 h<sup>-1</sup>.

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## 1. Introduction

NH<sub>3</sub>-SCR is a well-established technology for the removal of nitrogen oxides from stationary and mobile emission sources.<sup>1–3</sup> V<sub>2</sub>O<sub>5</sub> based catalysts have also been proven to be very suitable catalysts for the NH<sub>3</sub>-SCR process in the temperature window of 350–400 °C.<sup>4–7</sup> Unfortunately, the temperature of exit flue gas is often lower than the work temperature range; this means there is a lot of excess energy cost when the V<sub>2</sub>O<sub>5</sub> based catalysts are used. Finding another catalyst system that can work under the temperature of exit flue gas is thereby attractive for many researchers' interest. Many single and mixed transition oxides system have been developed, such as Mn-,<sup>8–10</sup> Fe-<sup>11,12</sup> and Ce-based catalysts.<sup>13,14</sup> MnO<sub>2</sub> based catalysts have been substantially investigated, which are famous for the high activity and poor poison resistance at low temperature range.<sup>15–17</sup>

In the V<sub>2</sub>O<sub>5</sub> and CeO<sub>2</sub> based catalysts, tungsten is usually used as a promoter and stabilizer. WO<sub>3</sub> can widen the work temperature window and raise the SO<sub>2</sub> resistance by inhibiting the initial sintering of TiO<sub>2</sub>, increasing the amount of Lewis acid over catalyst, improving the electron transfer of the catalyst, facilitating the formation of reduced V<sub>2</sub>O<sub>5</sub>, and directly providing the active sites<sup>18–21</sup> The promotion effect also have

been adopted to improve the performance of MnO<sub>2</sub> based catalysts.<sup>22–24</sup> Casapu *et al.*<sup>25</sup> screened the doped MnO<sub>x</sub>-CeO<sub>2</sub> catalysts and found that an even stronger suppression of N<sub>2</sub>O formation was obtained with MnWCe system, but this catalyst also showed a very low ammonia oxidation activity. Xu *et al.*<sup>26</sup> studied the tungsten modified MnO<sub>x</sub>-CeO<sub>2</sub>/ZrO<sub>2</sub> monolith catalysts and found that MnO<sub>x</sub>-CeO<sub>2</sub>/10% WO<sub>3</sub>-ZrO<sub>2</sub> had the best textural properties and the most adsorbed sites of NH<sub>3</sub> or NO species. The NO<sub>x</sub> conversion was more than 80% in the temperature range of 150 to 380 °C at the gas hourly space velocity of 10 000 h<sup>-1</sup>. Meanwhile, Peng *et al.*<sup>27</sup> doped CeW catalyst with manganese and found MnCeW system exhibited more activity for NO<sub>x</sub> conversion than the CeW catalyst below 200 °C. The addition of tungsten to Mn/Ce/Ti resulting in the Mn/Ce/W/Ti catalyst also showed excellent NO<sub>x</sub> conversion in the 120–200 °C and SO<sub>2</sub> resistance.<sup>28</sup> These results illuminated the promoting effect of tungsten to the MnO<sub>2</sub> based catalysts. Further, Liu *et al.* first considered the MnWO<sub>x</sub> as the main active phase and got high deNO<sub>x</sub> efficiency from 60 to 250 °C.<sup>29</sup> Sun *et al.*<sup>30</sup> then prepared a series of W<sub>α</sub>Mn<sub>1-α</sub>O<sub>x</sub> Catalysts via coprecipitation method. W<sub>0.33</sub>Mn<sub>0.66</sub>O<sub>x</sub> catalyst with amorphous or poorly crystalline Mn and W species showed the highest NH<sub>3</sub>-SCR activity within a broad temperature range of 230–470 °C. Our group also prepared a Mn<sub>x</sub>W<sub>0.05</sub>Ti<sub>0.95-x</sub>O<sub>2-δ</sub> catalyst with self-propagating high-temperature synthesis method and obtained a high activity in the range of 200–400 °C. In different, an uncertain crystal phase was observed on the TEM image, which might be helpful for the activity of the MnWTi catalyst.<sup>31</sup>

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In this paper, to discuss the promoting function of tungsten and MnWO<sub>4</sub> phase on the properties of MnO<sub>2</sub> based catalysts, a series of bulk and supported MnWO<sub>x</sub> catalysts were prepared by self-propagating high-temperature synthesis (SHS), co-precipitation (CP) and impregnation (IMP) methods, and their catalytic activity in NH<sub>3</sub>-SCR reaction were tested.

## 2. Experimental

### 2.1 Catalyst preparation

The MnWO<sub>x</sub> catalysts were mainly prepared by self-propagating high-temperature synthesis, co-precipitation and impregnation method. The general preparation steps are as follows: for the bulk MnWO<sub>x</sub> catalysts *via* self-propagating high-temperature synthesis, stoichiometric molar amount of manganous nitrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) and ammonium tungstate hydrate ((NH<sub>4</sub>)<sub>10</sub>·W<sub>12</sub>O<sub>41</sub>·xH<sub>2</sub>O) was dissolved in the de-ioned water respectively. The total amount of precursor metal-salts is 0.01 mol. 0.1 mol of glycine (CH<sub>2</sub>NH<sub>2</sub>COOH) was then added into the precursor solution as a fuel. Then, the mixed solution was stirred, heated and concentrated to form proper homogeneity till it burnt. Then, the solid was transferred into a clean crucible and moved into a muffle kept at the constant temperature for 2 h for the aging of the target catalyst. Under the same conditions, the mixed Mn–W oxides catalysts with different molar ratio of Mn to W (labeled as Mn<sub>a</sub>WO<sub>x</sub> later) were dispersed on the surface of TiO<sub>2</sub> (anatase, htnano Co., Ltd). The loading amount of active components is kept at 20 wt%. The Mn<sub>2</sub>WO<sub>x</sub> and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub> catalysts with typical MnWO<sub>4</sub> phase were also prepared by co-precipitation and impregnation method. The detailed steps can be seen in elsewhere.<sup>32</sup> As a reference, MnO<sub>2</sub>, WO<sub>3</sub>, WO<sub>3</sub>/TiO<sub>2</sub> (20 wt% WO<sub>3</sub>), MnO<sub>2</sub>/TiO<sub>2</sub> (20 wt% MnO<sub>2</sub>) samples were also prepared *via* self-propagating high-temperature synthesis.

### 2.2 Catalyst characterization

N<sub>2</sub> adsorption/desorption isotherms of the catalysts were measured at –196 °C using a physical adsorption apparatus (3Flex, Micromeritics) to calculate BET surface area of the catalysts. Prior to measurement, all samples were degassed at 280 °C for 10 h to remove the impurities in the porous structure.

The XRD patterns of the samples were checked using an ARL SCINTAG X'TRA X-ray diffractometer (Shimadzu) equipped with CuKα radiation. XRD patterns were recorded in the 2θ range of 10° to 80° with a scan step size of 0.02°.

Transmission electron microscopy (TEM) images of the catalysts were taken on a Tecnai G2 F30 S-Twin electron microscope operating at an accelerating voltage of 300 kV. The dispersion of the elemental composition and the semi-quantitative determination of the Ti, Mn, W, and O ratio were detected by the energy dispersive X-ray spectrometer (EDX) at the same time.

The hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) profiles of the catalysts were recorded by a chemisorber (Chem2910, Finesorb). Each sample (*ca.* 100 mg) were pre-treated at 200 °C for 2 h in Ar flow before reduction process. Subsequently, the sample was heated from 100 °C to 950 °C in 5

vol% H<sub>2</sub>/95 vol% Ar flow, at a rate of 30 ml min<sup>–1</sup> with a heating rate of 10 °C min<sup>–1</sup>.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface atomic state and form of catalyst with Al target and Kα radiation, operating at 15 kV voltage and C 1s = 284.8 eV for calibration (Kratos AXIS Ultra DLD). The concentrations of Mn, W, Ti and O on catalyst surface were calculated from the peak areas ratios of the samples.

### 2.3 Catalytic tests

The activity evaluation of the catalysts was carried out in a fixed-bed quartz reactor with an inner diameter of 8 mm. The reaction conditions were as follows: 0.5 g of catalyst (20–60 mesh, 1 ml), 500 ppm NO, 500 ppm NH<sub>3</sub>, 5 vol% O<sub>2</sub>, N<sub>2</sub> as the balance gas, the total gas flow rate was 500 ml min<sup>–1</sup>, and the corresponding gas hourly space velocity (GHSV) was 30 000 h<sup>–1</sup>. The catalyst bed temperature was increased gradually and kept at each reaction temperature for half an hour to ensure the stabilization of the reaction. The composition of the feed gases were monitored continuously online using Teledyne T200H/M chemiluminescent NO<sub>x</sub> analyzer and gas chromatograph (Thermo Trace 1300 equipped with Porapak Q column). NO<sub>x</sub> conversion and N<sub>2</sub> selectivity are calculated as follows: NO<sub>x</sub> conversion (%) = ([NO<sub>x</sub>]<sub>in</sub> – [NO<sub>x</sub>]<sub>out</sub>)/[NO<sub>x</sub>]<sub>in</sub>, N<sub>2</sub> selectivity (%) = (([NO]<sub>in</sub> + [NH<sub>3</sub>]<sub>in</sub>) – [NO<sub>2</sub>]<sub>out</sub> – 2[N<sub>2</sub>O]<sub>out</sub>)/([NO]<sub>in</sub> + [NH<sub>3</sub>]<sub>in</sub>).

## 3. Results and discussions

### 3.1 Synthesis and characterization of the bulk and supported MnWO<sub>x</sub> catalysts

**3.1.1 Textual properties of the bulk and supported MnWO<sub>x</sub> catalysts.** Table 1 lists the textual properties of the bulk MnWO<sub>x</sub> catalysts. WO<sub>3</sub> almost has no surface area, which explains its poor catalytic activity. With the increment of Mn : W ratio, the surface area continually increases. MnO<sub>2</sub> has the largest surface area of 30 m<sup>2</sup> g<sup>–1</sup>. It seems that the existence of tungsten has a negative effect on the surface areas of the MnWO<sub>x</sub> catalysts by self-propagating high-temperature synthesis. The lower surface area of the MnWO<sub>x</sub> catalysts than the MnO<sub>2</sub> partially explains their worse activities than MnO<sub>2</sub> in low temperature range.

Table 2 lists part of the textual properties of the TiO<sub>2</sub> with supported MnWO<sub>x</sub> catalysts. Compared to the bulk MnWO<sub>x</sub>, the variation of surface area of these samples shows a different way. The Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS keeps the largest surface area of 142 m<sup>2</sup>

Table 1 Textual properties of the bulk MnWO<sub>x</sub> catalysts

Samples	BET surface area (m <sup>2</sup> g <sup>–1</sup> )	Pore volume (cm <sup>3</sup> g <sup>–1</sup> )	Average pore diameter (nm)
WO <sub>3</sub> -SHS	0	—	—
MnWO <sub>x</sub> -SHS	5	—	—
Mn <sub>2</sub> WO <sub>x</sub> -SHS	6	0.0421	28.7
Mn <sub>5</sub> WO <sub>x</sub> -SHS	15	0.0704	18.3
Mn <sub>10</sub> WO <sub>x</sub> -SHS	25	0.156	24.6
MnO <sub>2</sub> -SHS	30	0.178	23.5

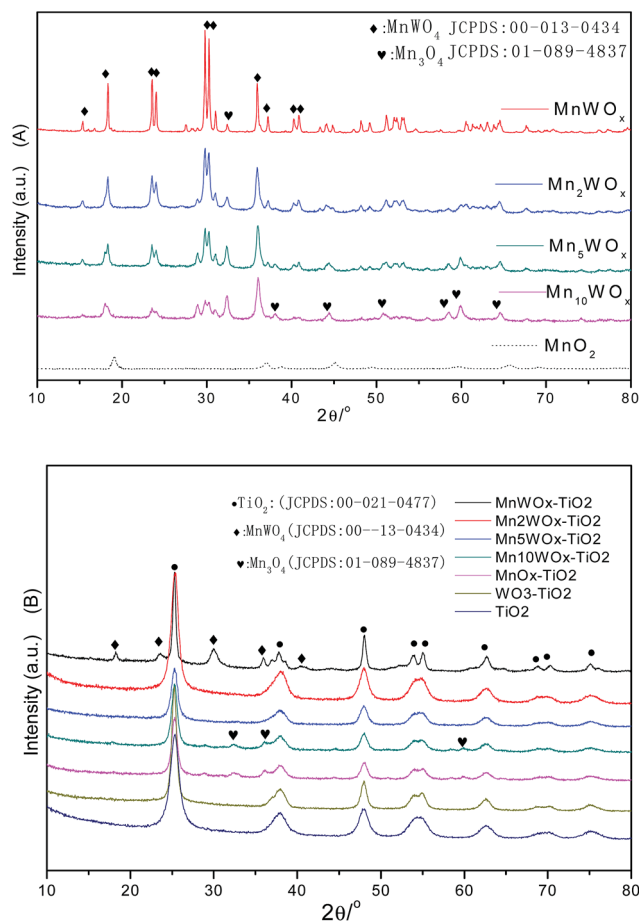


Table 2 Textual properties of the supported MnWO<sub>x</sub> catalysts

Samples	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)
WO <sub>3</sub> /TiO <sub>2</sub> -SHS	109	0.212	7.8
MnO <sub>2</sub> /TiO <sub>2</sub> -SHS	85	0.194	9.0
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	142	0.217	6.1
TiO <sub>2</sub>	184	0.296	6.4

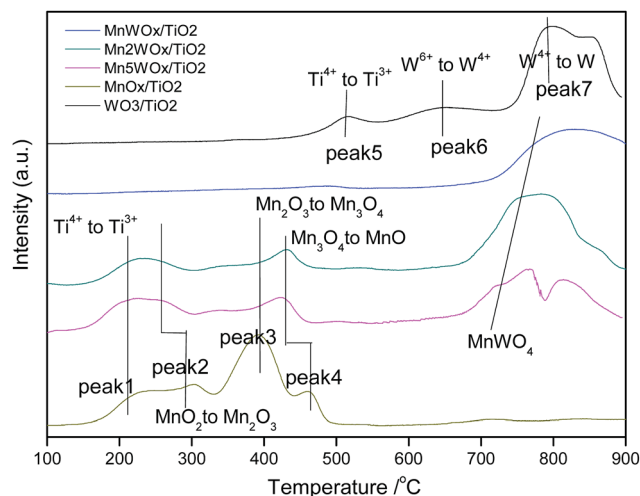
g<sup>-1</sup>; while the MnO<sub>2</sub>/TiO<sub>2</sub>-SHS only has 85 m<sup>2</sup> g<sup>-1</sup> of BET surface area, which is even smaller than 109 m<sup>2</sup> g<sup>-1</sup> of WO<sub>3</sub>/TiO<sub>2</sub>-SHS. The results means that the existence of W can alleviate the decrement of TiO<sub>2</sub> surface area, and increase the BET surface area of MnWO<sub>x</sub>/TiO<sub>2</sub>-SHS. Further, the decrement of average pore diameter of Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS indicates that the Mn<sub>2</sub>WO<sub>x</sub> species are well dispersed in the pore structure of TiO<sub>2</sub>, which will be favorable for the activity.

**3.1.2 XRD patterns of the MnWO<sub>x</sub> catalysts.** Fig. 1 displays the XRD patterns of the bulk and supported MnWO<sub>x</sub> catalysts. The bulk MnWO<sub>x</sub> samples do not have characteristic peaks of MnO<sub>2</sub>. Instead, they mainly present the typical characteristic peaks of monoclinic structure phase of MnWO<sub>4</sub>.<sup>32</sup> A little part of Mn<sub>3</sub>O<sub>4</sub> also can be found on the pattern of MnWO<sub>x</sub> sample. The

Fig. 1 XRD patterns of bulk and supported MnWO<sub>x</sub> catalysts.

peaks intensity of Mn<sub>3</sub>O<sub>4</sub> and MnWO<sub>4</sub> gradually enhance with the increment of Mn : W ratio. It means that the main species were the MnWO<sub>4</sub> and the Mn<sub>3</sub>O<sub>4</sub> on the bulk MnWO<sub>x</sub>. The general valence of manganese in MnWO<sub>x</sub> catalysts has been suppressed to be about +2/+3. In Fig. 1B, the TiO<sub>2</sub> with supported WO<sub>3</sub> (WO<sub>3</sub>/TiO<sub>2</sub>) sample only presented the characteristic peaks of anatase TiO<sub>2</sub>. The MnO<sub>2</sub>/TiO<sub>2</sub> and Mn<sub>10</sub>WO<sub>x</sub>/TiO<sub>2</sub> presents the characteristic peaks of Mn<sub>3</sub>O<sub>4</sub> and anatase TiO<sub>2</sub>. The MnWO<sub>x</sub>/TiO<sub>2</sub> presents the characteristic peaks of MnWO<sub>4</sub> and anatase TiO<sub>2</sub>. However, the characteristic peaks of MnWO<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> disappeared together on the patterns of Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub> and Mn<sub>5</sub>WO<sub>x</sub>/TiO<sub>2</sub>, which can be ensured that the active species were well dispersed on the TiO<sub>2</sub>. The above results suggested that the coexistence of MnWO<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> weaken the intensity of characteristic peaks and caused the disappearances of MnWO<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> on the patterns of Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub> and Mn<sub>5</sub>WO<sub>x</sub>/TiO<sub>2</sub>. For the MnWO<sub>x</sub> catalysts, MnWO<sub>4</sub> phase seemed to play an important role in NH<sub>3</sub>-SCR reaction.

**3.1.3 H<sub>2</sub>-TPR of TiO<sub>2</sub> with supported MnWO<sub>x</sub> samples with self-propagating high-temperature synthesis.** The NH<sub>3</sub>-SCR activity of MnWO<sub>x</sub> has a strong relation with the redox properties in the SCR reaction. H<sub>2</sub>-TPR was performed to identify the active species on the MnWO<sub>x</sub> catalysts. Fig. 2 displays the profiles of different supported MnWO<sub>x</sub>/TiO<sub>2</sub> samples and quantitative results are summarized in Tables S1 and S2.† It is known that the reduction of manganese oxides is influenced by the support properties, dopants, the preparation method as well as the reduction conditions.<sup>33</sup> Here, the profiles seems to be some complicated. In general, for the supported MnWO<sub>x</sub>/TiO<sub>2</sub> samples with SHS method, the profile can be divided into two reduction bands. In the lower temperature range of 200–500 °C, the reduction peaks are mainly originated from different MnO<sub>x</sub> species; in the higher temperature range of 600–900 °C, the reduction peaks are from different WO<sub>x</sub> species.<sup>34,35</sup> For the four reduction peaks in 200–500 °C on the MnO<sub>2</sub>/TiO<sub>2</sub> profile, the peaks at about 300, 400 and 460 °C can be attributed to the reduction of MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> to

Fig. 2 H<sub>2</sub>-TPR profiles of different TiO<sub>2</sub> with supported MnWO<sub>x</sub> samples with different Mn : W ratio and preparation methods.

MnO, respectively. Besides that, the peak at 220 °C is from the reduction of part  $Ti^{4+}$  to  $Ti^{3+}$ , which have interaction with manganese oxides.<sup>33</sup> The reduction profiles of  $Mn_xWO_x/TiO_2$ -SHS are clearly different from  $MnO_2/TiO_2$ . The reduction peaks of manganese oxides are almost diminished on the  $MnWO_x/TiO_2$ -SHS, which indicates that all the manganese species are well interacted with the tungsten and form the  $MnWO_x$  structure. The reduction peaks in 200–500 °C appear again on the  $Mn_2WO_x/TiO_2$ -SHS and  $Mn_5WO_x/TiO_2$ -SHS, indicates that excess manganese oxides are existed on the samples other than  $MnWO_x$ . The reduction peak sites move to the lower temperature attitude, and the peak intensity of  $Mn_2O_3$  to  $Mn_3O_4$  clearly decreases. Under this conditions, it seems that the  $MnO_2$  species are easy to be reduced and the large part of  $MnO_2$  can be directly reduced to MnO.

Another main reduction band distributed in 600–900 °C is probably from tungsten oxides,  $MnWO_4$  species and titanium oxides.<sup>36,37</sup> For  $WO_3/TiO_2$  sample, the reduction peaks at 520 °C, 650 °C and 800 °C are most probably from part of  $Ti^{4+}$  to  $Ti^{3+}$ ,  $W^{6+}$  to  $W^{4+}$  and  $W^{4+}$  to  $W^0$ .<sup>38,39</sup> When manganese is added, the two peaks at 520 °C and 650 °C diminished on the  $Mn_xWO_x/TiO_2$ -SHS profiles. The diminishing of peak at 520 °C might indicate the excellent dispersion of  $MnWO_4$  on the surface of  $TiO_2$  support; the diminishing of peak at 650 °C represents that there is no single  $WO_3$  species left. The only peak around 790 °C should be from  $MnWO_4$  structure, and it can be inferred that the  $Mn^{4+}$  and  $W^{6+}$  in  $MnWO_4$  structure needs a high temperature to be reduced. With the manganese content increases, the reduction temperature seems to be decreased.

**3.1.4 TEM of the bulk  $MnWO_x$  and supported  $MnWO_x/TiO_2$  samples by self-propagating high-temperature synthesis.** TEM images can distinguish the existence of the crystal structures in some areas. Fig. 3 displays the TEM images of the bulk and supported  $MnWO_x$  catalysts with different preparation methods. Co-precipitation method gets the homogenous particles with typical regular nano-rod shapes of  $MnWO_4$  structure in Fig. 3a. The ordered lattice fringes in Fig. 3b confirm that the particles have a typical  $MnWO_4$  crystal structure. 0.487 nm and 0.379 nm lattice spacing belongs to crystal face (100) and face (011) of  $MnWO_4$ .<sup>40</sup> On the  $Mn_2WO_x$ -SHS, the uniform lattice fringes with 0.483 nm of face (100) and 0.245 nm of face (200) can be seen in Fig. 3d. The rectangular shaped electron diffraction pattern also can confirm the  $MnWO_4$  structure. The agglomeration of particles clearly happens on the sample, which causes the poor specific area and poor  $NH_3$ -SCR activity.

For the two supported samples,  $MnWO_x$  species are uniformly distributed on the surfaces of the two samples in the shape of about 1 nm diameter nanoparticles, which are shown as the little black dots in Fig. 3f and h. Partly due to the little sizes of the nanoparticles,  $MnWO_4$  phase is hard to be distinguished on the images. The main change is come from the  $TiO_2$  support. It looks like that the  $TiO_2$  support has grown into large plates *via* impregnation method (Fig. 3e). The specific surface area of  $Mn_2WO_x/TiO_2$ -IMP is thereby severely influenced and decreases from 184  $m^2 g^{-1}$  to 56  $m^2 g^{-1}$ , which may cause the activity decreases. Meanwhile, the self-propagating high-

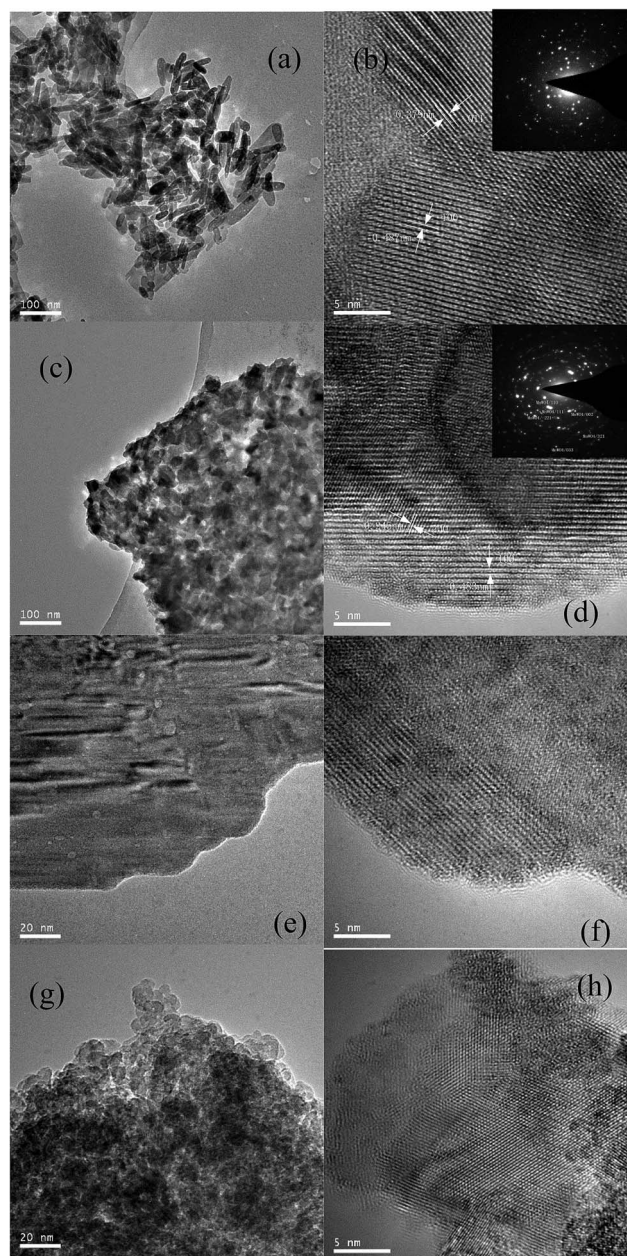


Fig. 3 TEM images of the bulk and supported  $MnWO_x$  catalysts with different preparation methods. (a), (b):  $Mn_2WO_x$ -CP; (c), (d):  $Mn_2WO_x$ -SHS; (e), (f):  $Mn_2WO_x/TiO_2$ -IMP; (g), (h)  $Mn_2WO_x/TiO_2$ -SHS.

temperature synthesis method keeps the structure of  $TiO_2$  support much better and more  $MnWO_x$  species nanoparticles can be formed and seen on the surface.

**3.1.5 Characterization of the bulk and supported  $MnWO_x$  samples by XPS method.** Oxidation states and atomic concentrations of manganese can reflect the properties of manganese species over the series of catalysts. XPS have been conducted for the  $MnWO_x$ -CP,  $MnWO_x/TiO_2$ -IMP,  $Mn_2WO_x$ -SHS and  $Mn_2WO_x/TiO_2$ -SHS. All binding energies presented have been adjusted *via* the C 1s peak standardized at 284.8 eV. The XPS spectra of Mn 2p are shown in Fig. 4. Two XPS peaks of Mn 2p appear at about 641.8 and 653.8 eV belonging to Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$



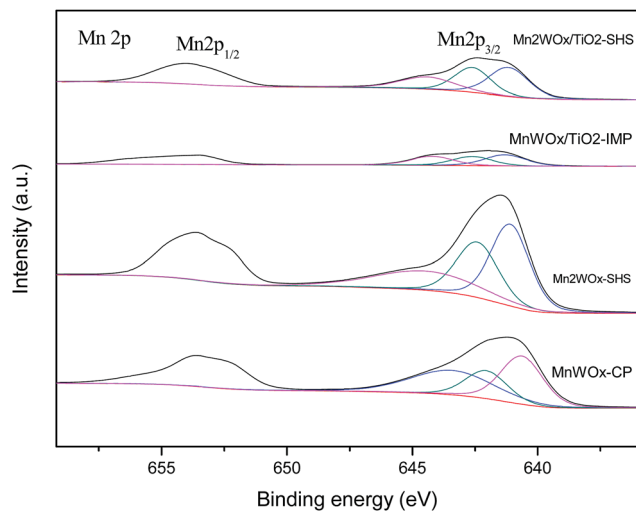


Fig. 4 Mn 2p XPS spectra of MnWO<sub>x</sub>-CP, MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP, Mn<sub>2</sub>WO<sub>x</sub>-SHS and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS.

respectively. The Mn 2p<sub>3/2</sub> spectra of all catalysts can be fitted into three sub-bands by Gaussian deconvolution. The peaks at 640.6–641.4 eV can be attributed to Mn<sup>3+</sup>, the peaks at 642.0–642.6 eV to Mn<sup>4+</sup>, and the peaks at 643.4–644.5 eV to Mn<sup>2+</sup>.<sup>28,29,41,42</sup> According to quantitative results in the Table 3, the Mn<sup>3+</sup> and Mn<sup>2+</sup> ions took the main part of manganese species. The average valence of manganese has been drawn to be +2.8, +3.0, +3.0 and +3.2 on the four catalysts. Among the four catalysts, the average valence of manganese is the lowest and the composition of Mn<sup>2+</sup> is the highest, which suggests the valence restriction from the formation of MnWO<sub>4</sub> phase.

Oxygen species plays an important role in the NH<sub>3</sub>-SCR activity. The O 1s XPS of Mn<sub>a</sub>WO<sub>x</sub> and Mn<sub>a</sub>WO<sub>x</sub>/TiO<sub>x</sub> are thereby displayed in Fig. 5, and the characteristic peaks are deconvoluted by Gaussian fitting method. The sub-bands at 528.9–530.4 eV can be attributed to the lattice O<sup>2-</sup> (denoted as O<sub>β</sub>); the sub-bands with higher binding energy at 531.0–531.5 eV to surface absorbed oxygen (denoted as O<sub>α</sub>) such as O<sub>2</sub><sup>2-</sup> and O<sup>-</sup> belonging to defect-oxide or hydroxyl-like group, and the binding energy at 532.3–533.2 eV can be assigned to chemisorbed water (denoted as O<sub>α'</sub>).<sup>43–46</sup> The surface absorbed O<sub>α</sub> is usually regarded as more reactive in oxidation reactions due to its higher mobility than lattice O<sup>2-</sup>, which is also beneficial to the NO oxidation to NO<sub>2</sub> thus facilitating the “fast SCR” process. The ratios of O<sub>α</sub>, O<sub>β</sub> and O<sub>α'</sub> on four catalysts are calculated and listed in Table 4. The bulk MnWO<sub>x</sub> and Mn<sub>2</sub>WO<sub>x</sub> catalysts have

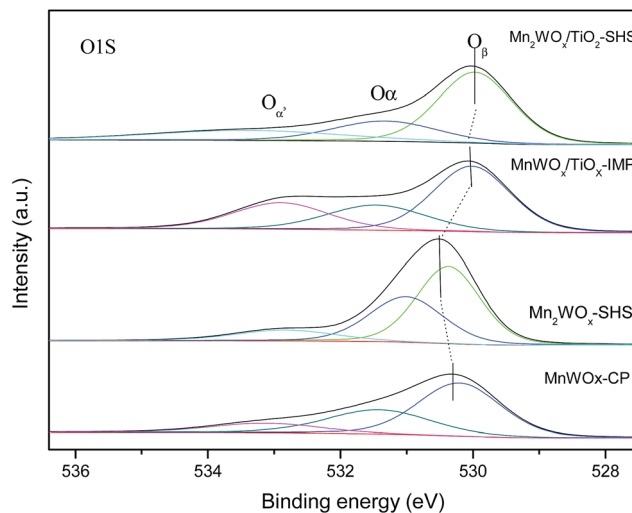


Fig. 5 O 1s XPS spectra of MnWO<sub>x</sub>-CP, MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP, Mn<sub>2</sub>WO<sub>x</sub>-SHS and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS.

Table 4 Quantitative results of O 1s XPS spectra of MnWO<sub>x</sub>-CP, MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP, Mn<sub>2</sub>WO<sub>x</sub>-SHS and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS

Samples	O <sub>β</sub>		O <sub>α</sub>		O <sub>α'</sub>	
	BE (eV)	Per.%	BE (eV)	Per.%	BE (eV)	Per.%
MnWO <sub>x</sub> -CP	530.2	55.20	531.4	31.78	533.1	13.02
Mn <sub>2</sub> WO <sub>x</sub> -SHS	530.4	41.06	531.0	34.72	532.8	24.22
MnWO <sub>x</sub> /TiO <sub>2</sub> -IMP	530.0	47.68	531.5	26.75	532.9	25.57
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	528.9	57.67	531.2	24.65	532.3	17.68

high O<sub>α</sub> ratios of 31.78% and 34.72% respectively, which means that the Mn<sub>a</sub>WO<sub>x</sub> mixed oxides may have a high response to the NH<sub>3</sub>-SCR reaction. The poor performance in Fig. 6 may be caused by the poor BET surface area. When the specific surface area is increased by TiO<sub>2</sub> supporting, Mn<sub>a</sub>WO<sub>x</sub>/TiO<sub>2</sub> then shows the high activity in NH<sub>3</sub>-SCR reaction.

### 3.2 Catalytic activity of the bulk and supported MnWO<sub>x</sub> catalysts

Fig. 6A displayed the activities of the bulk MnWO<sub>x</sub> catalysts with different Mn : W ratio by self-propagating high-temperature synthesis. Due to the poor specific surface area, the bulk WO<sub>3</sub> did not show the NH<sub>3</sub>-SCR activity obviously; while the bulk

Table 3 Quantitative results of Mn 2p XPS spectra of MnWO<sub>x</sub>-CP, MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP, Mn<sub>2</sub>WO<sub>x</sub>-SHS and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS

Samples	Mn <sup>4+</sup>		Mn <sup>3+</sup>		Mn <sup>2+</sup>		Average valence
	BE (eV)	Per.%	BE (eV)	Per.%	BE (eV)	Per.%	
MnWO <sub>x</sub> -CP	642.0	22.32	640.6	38.85	643.4	38.83	2.8
Mn <sub>2</sub> WO <sub>x</sub> -SHS	642.4	31.08	641.1	42.38	644.5	26.54	3.0
MnWO <sub>x</sub> /TiO <sub>2</sub> -IMP	642.6	30.26	641.3	38.17	644.2	31.57	3.0
Mn <sub>2</sub> WO <sub>x</sub> /TiO <sub>2</sub> -SHS	642.6	33.26	641.1	42.37	644.4	24.37	3.1



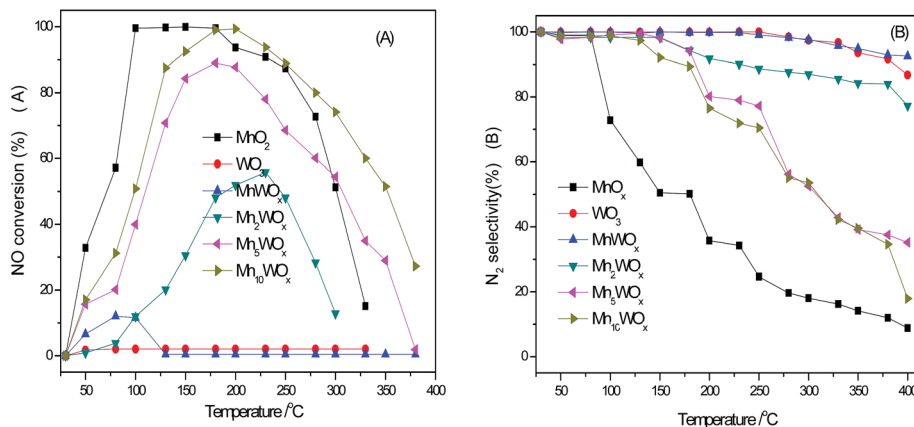


Fig. 6 (A) NO conversion and (B)  $N_2$  selectivity over bulk  $MnO_2$ ,  $WO_3$  and  $MnWO_x$  catalysts. Reaction conditions:  $[NO] = [NH_3] = 500$  ppm,  $[O_2] = 5$  vol%,  $N_2$  balance gas and GHSV =  $30\,000\ h^{-1}$ .

$MnO_2$  with the largest specific surface area among all the bulk samples showed the best performance in the lower temperature range. 100%  $NO_x$  conversion had been achieved in the range of 100–180 °C. When the W and Mn coexist and form the series of  $Mn_nWO_x$  catalysts, the activity catalysts undergone a series of change.  $Mn_1WO_x$  only showed poor activity in the range of 50–120 °C.  $Mn_2WO_x$  displayed higher activity in the temperature range of 100–300 °C. With the continuous increment of Mn content, the activity of  $Mn_nWO_x$  did not surpass the bulk  $MnO_2$  in the low temperature, some of  $Mn_nWO_x$  samples with high Mn : W ratio behaved better performance in the high temperature range. The  $Mn_{10}WO_x$  exhibited the higher activity than the bulk  $MnO_2$  when the reaction temperature is above 200 °C.

The  $N_2$  selectivities of bulk  $MnWO_x$  catalysts with different Mn : W ratio are presented in Fig. 6B. It can be seen that tungsten has a clearly effect of  $MnWO_x$  on the  $N_2$  selectivity, especially in the high temperature range. The  $N_2$  selectivity of bulk  $MnO_2$  decreases to be about 20% when the temperature rise to 200 °C. While with the decrease of Mn : W ratio, *i.e.*, the increases of W content, the  $N_2$  selectivity of  $Mn_nWO_x$  is more and more improved. On the  $MnWO_x$  with 1 : 1 ratio, the  $N_2$  selectivity of has almost reached 100%, the insertion of tungsten into  $Mn_nWO_x$  favours the increase in the activity and  $N_2$  selectivity. Supported  $MnWO_x/TiO_2$  catalysts with high specific surface area were then prepared and the activities were tested under the same reaction conditions. As shown in Fig. 7A and B, the supporting of  $MnO_2$  did not improve the activity of  $MnO_2/TiO_2$ . The 100%  $NO_x$  conversion window (working window) was still in the range of 100–180 °C. Meanwhile, the  $Mn_nWO_x/TiO_2$  catalysts showed much better performance than the bulk  $Mn_nWO_x$  samples and single  $MnO_2$  catalysts. Except  $Mn_1WO_x/TiO_2$ , all the other  $Mn_nWO_x/TiO_2$  catalysts presented the 100%  $NO_x$  conversion temperature window. The temperature window of the  $Mn_{1.5}WO_x/TiO_2$  was 180–240 °C; The  $Mn_2WO_x/TiO_2$  was 130–300 °C, and the window of  $Mn_5WO_x/TiO_2$  and  $Mn_{10}WO_x/TiO_2$  was in the same range of 130–240 °C.

$N_2$  selectivity of the supported  $MnWO_x$  catalysts are also been improved from Fig. 7C and D. The appearance of  $N_2$  selectivity decrease is retarded to high temperature attitude,

and the decrease degree is alleviated with the Mn : W ratio decreasing. On the  $Mn_nWO_x/TiO_2$  with Mn : W ratio of 1 and 2,  $N_2O$  is only formed above 200 °C and the  $N_2$  selectivity of  $Mn_{1-2}WO_x/TiO_2$  catalysts keep above 80% during the course.

The results show that the addition of tungsten can improve the activity and  $N_2$  selectivity of supported  $MnO_2$  based catalysts, especially in the higher temperature range. Though the  $Mn_1WO_x/TiO_2$  does not achieve the 100%  $NO_x$  conversion, it shows much better activity than the  $MnO_2/TiO_2$  when the temperature is above 250 °C. When the Mn : W ratio increases to 2 : 1, the performance of  $Mn_nWO_x/TiO_2$  will be better than  $MnO_2/TiO_2$ . It is the  $Mn_2WO_x/TiO_2$  that fetches the best performance among all the  $Mn_nWO_x/TiO_2$  samples. Considering the XRD pattern and BET surface areas, the existence of tungsten have shown two effects on the  $TiO_2$  supported  $Mn_nWO_x$  catalysts. The first is that the tungsten can alleviate the specific surface area loss of  $TiO_2$  support. The BET surface area of  $Mn_2WO_x/TiO_2$ -SHS is clearly bigger than  $WO_3/TiO_2$  and  $MnO_2/TiO_2$ , which is favorable for the catalytic activity in  $NH_3$ -SCR reaction. The second effect may be that the tungsten can interact with manganese oxide and form the  $MnWO_4$  phase with manganese oxides, which is even favorable for the catalytic activity.

### 3.3 Activity of $Mn_2WO_x$ -CP, $Mn_1WO_x/TiO_2$ -IMP and $Mn_2WO_x/TiO_2$ -IMP catalysts

The above results show that tungsten addition can improve  $NH_3$ -SCR activities of  $MnWO_x$  catalysts. To discuss the mechanism of the addition of tungsten, especially the  $MnWO_4$  phase on the catalytic activity. Co-precipitation and impregnation method, which have been reported to be able to get  $MnWO_x$  catalysts with typical  $MnWO_4$  phase,<sup>32</sup> were used to prepare a bulk  $Mn_2WO_x$  (labeled as  $Mn_2WO_x$ -CP) and the  $TiO_2$  supported  $MnWO_x$  and  $Mn_2WO_x$  (labeled as  $MnWO_x/TiO_2$ -IMP and  $Mn_2WO_x/TiO_2$ -IMP). The BET surface areas of  $Mn_2WO_x$ -CP,  $MnWO_x/TiO_2$ -IMP and  $Mn_2WO_x/TiO_2$ -IMP are 26, 52 and 56  $m^2\ g^{-1}$  respectively. The XRD patterns in Fig. 8 show that both  $Mn_2WO_x$ -CP and  $Mn_2WO_x/TiO_2$ -IMP both have typical



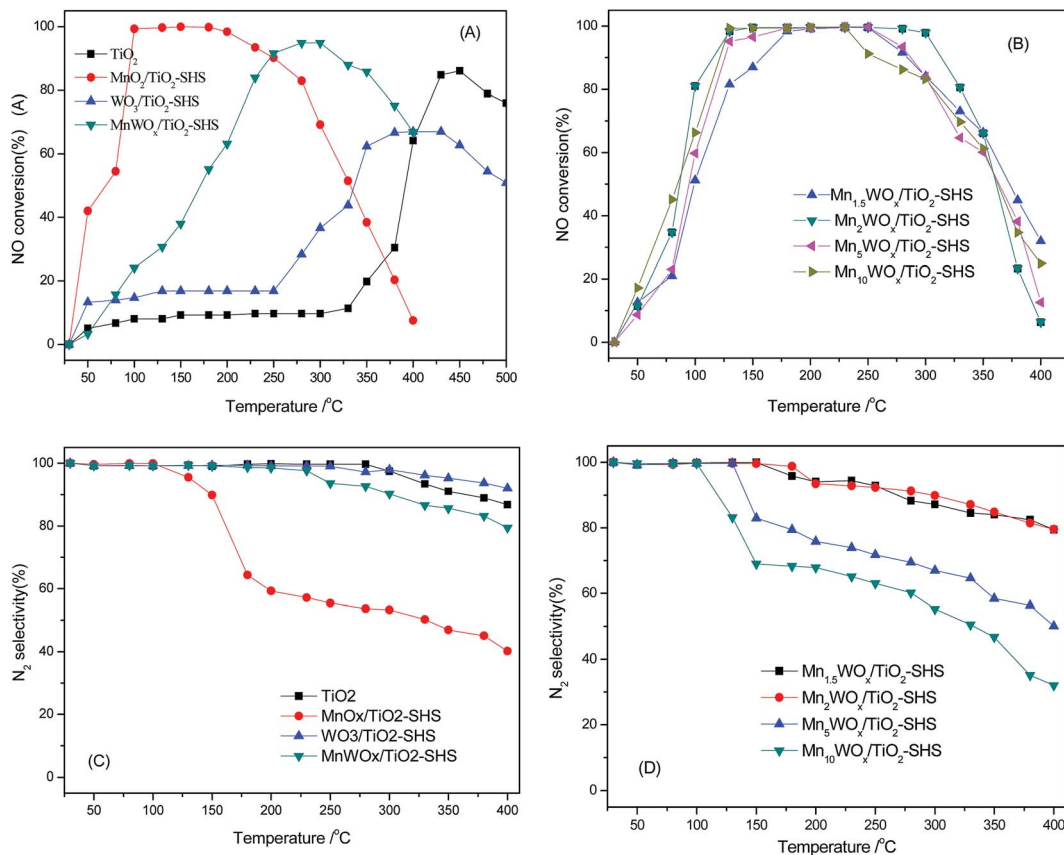


Fig. 7 (A), (B) NO conversion and (C), (D) N<sub>2</sub> activity over supported Mn<sub>3</sub>WO<sub>x</sub>/TiO<sub>2</sub>, MnO<sub>2</sub> and WO<sub>3</sub> via self-propagating high-temperature synthesis. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5 vol%, N<sub>2</sub> balance gas and GHSV = 30 000 h<sup>-1</sup>.

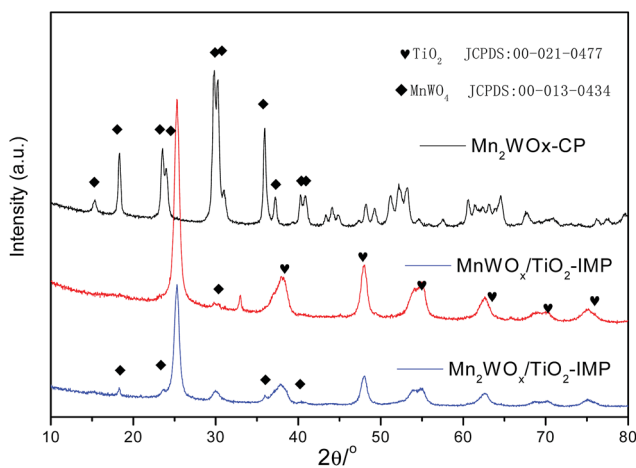


Fig. 8 XRD patterns of Mn<sub>2</sub>WO<sub>x</sub>-CP and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-IMP.

characteristic peaks of MnWO<sub>4</sub> without other impurity phase observed. Otherwise, MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP also have MnWO<sub>4</sub> structure.

As shown in Fig. 9A, the above three samples exhibit distinctive catalytic performances, compared to the samples with self-propagating high-temperature synthesis method, the main function temperature range of Mn<sub>2</sub>WO<sub>x</sub>-CP, MnWO<sub>x</sub>/

TiO<sub>2</sub>-IMP and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-IMP seemed to move to the high temperature attitude clearly. The NO<sub>x</sub> conversion over Mn<sub>2</sub>WO<sub>x</sub>-CP continually increased till 430 °C, where it reached the maximum of 52.9%. For the two supported samples, the active temperature window of MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP was in the range of 230–350 °C, where it can convert more than 94% NO. The deNO<sub>x</sub> performance of MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP was better than MnWO<sub>x</sub>/TiO<sub>2</sub>-SHS. The activity window of Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-IMP is similar to MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP, which the NO<sub>x</sub> conversion can reach 100% in the range of 250–350 °C. But the window width was some narrower than that of Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS, and moved about 50 °C towards high attitude. Considering the working windows of the two samples, it seems that the working window of MnWO<sub>x</sub>/TiO<sub>2</sub> catalysts can be broadened as wide as 130–350 °C (or even high<sup>31</sup>) by fine tuning or combing of different preparation methods. It also can be inferred that the MnWO<sub>4</sub> should have some positive effect on the activity of MnWO<sub>x</sub> catalysts, especially for the activity of MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP in the high temperature range.

The plot of N<sub>2</sub> product selectivity over above three catalysts as a function of temperature is shown in Fig. 9B. Mn<sub>2</sub>WO<sub>x</sub>-CP showed an excellent N<sub>2</sub> selectivity than MnWO<sub>x</sub>/TiO<sub>2</sub>-IMP and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS under the range of 250 °C. In contrast, Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-IMP and Mn<sub>2</sub>WO<sub>x</sub>/TiO<sub>2</sub>-SHS show a better N<sub>2</sub> selectivity than Mn<sub>2</sub>WO<sub>x</sub>-CP when the temperature is high than



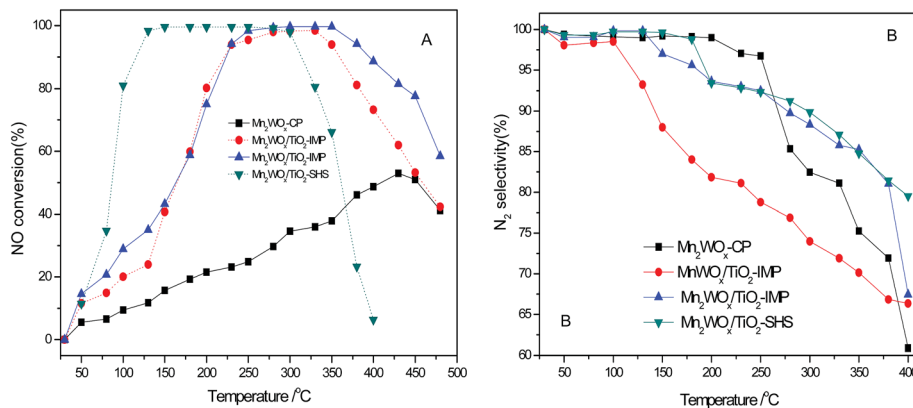


Fig. 9 (A) NO conversion and (B)  $N_2$  selectivity over bulk and supported  $Mn_2WO_x/TiO_2$  with different methods. Reaction conditions:  $[NO] = [NH_3] = 500$  ppm,  $[O_2] = 5$  vol%,  $N_2$  balance gas and  $GHSV = 30\,000\ h^{-1}$ .

280 °C. It confirms that the improvement of  $N_2$  selectivity is associated with existence of  $MnWO_4$  and dispersion on the surface of carrier.

## 4. Conclusions

A series of bulk  $MnWO_x$  and supported  $MnWO_x/TiO_2$  catalysts have been prepared by self-propagating high-temperature synthesis, impregnation and co-precipitation method to discuss the effect and mechanism of tungsten on the manganese oxide based catalysts. The tungsten can interact with manganese oxide, thus weaken the interaction between tungsten and titanium or manganese and titanium, alleviate the specific surface area loss of  $TiO_2$  support, and improve the  $NH_3$ -SCR activity of  $MnWO_x/TiO_2$  catalysts. The tungsten and manganese also can form a  $MnWO_4$  crystal structure, which might be favorable for the activity and  $N_2$  selectivity in the high temperature range (above 260 °C). How the  $MnWO_4$  works needs to be further investigated. Both self-propagating high-temperature synthesis and impregnation can get uniformly distributed  $MnWO_x$  nanoparticles, while the  $TiO_2$  support structure is more influenced by impregnation.

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