 Influence of tungsten on the NH$_3$-SCR activity of MnWO$_x$/TiO$_2$ catalysts$^\dagger$

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A series of bulk MnWO$_x$ and supported MnWO$_x$/TiO$_2$ catalysts with MnWO$_4$ 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$_2$ adsorption/desorption, hydrogen-temperature programmed reduction (H$_2$-TPR), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The performance of MnWO$_x$ and MnWO$_x$/TiO$_2$ and the relation between the tungsten and manganese oxide species in MnWO$_x$ and MnWO$_x$/TiO$_2$ catalysts were investigated. The supported MnWO$_x$/TiO$_2$ 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$_x$ oxide phase, thus weakening the interaction between MnO$_2$ and TiO$_2$, which is favorable for the specific surface area of MnWO$_x$/TiO$_2$. The MnWO$_4$ phase also has a positive effect for the activity and N$_2$ selectivity of MnWO$_x$/TiO$_2$ in the high temperature range. In a feed gas that contains 500 ppm NO, 500 ppm NH$_3$, 5 vol% O$_2$ and N$_2$ as the balance gas, Mn$_2$WO$_x$/TiO$_2$-SHS shows the best deNO$_x$ performance and the NO$_x$ conversion reaches 100% in the temperature range of 130–300 °C under the reaction condition of 30 000 h$^{-1}$.

1. Introduction

NH$_3$-SCR is a well-established technology for the removal of nitrogen oxides from stationary and mobile emission sources.$^{1-3}$ V$_2$O$_5$ based catalysts have also been proven to be very suitable catalysts for the NH$_3$SCR process in the temperature window of 350–400 °C.$^{4,5}$ 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$_2$O$_5$ 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$^{+}$, Fe$^{11,12}$ and Ce-based catalysts.$^{13,14}$ MnO$_2$ based catalysts have been substantially investigated, which are famous for the high activity and poor poison resistance at low temperature range.$^{15,17}$

In the V$_2$O$_5$ and CeO$_2$ based catalysts, tungsten is usually used as a promoter and stabilizer. WO$_3$ can widen the work temperature window and raise the SO$_2$ resistance by inhibiting the initial sintering of TiO$_2$, increasing the amount of Lewis acid over catalyst, improving the electron transfer of the catalyst, facilitating the formation of reduced V$_2$O$_3$, and directly providing the active sites$^{18-21}$ The promotion effect also have been adopted to improve the performance of MnO$_2$ based catalysts.$^{22-24}$ Casapu et al.$^{25}$ screened the doped MnO$_x$-CeO$_2$ catalysts and found that an even stronger suppression of N$_2$O formation was obtained with MnWCe system, but this catalyst also showed a very low ammonia oxidation activity. Xu et al.$^{26}$ studied the tungsten modified MnO$_x$-CeO$_2$/ZrO$_2$ monolith catalysts and found that MnO$_x$-CeO$_2$/10% WO$_3$/ZrO$_2$ had the best textural properties and the most adsorbed sites of NH$_3$ or NO species. The NO$_x$ conversion was more than 80% in the temperature range of 150 to 380 °C at the gas hourly space velocity of 10 000 h$^{-1}$. Meanwhile, Peng et al.$^{27}$ doped CeW catalyst with manganese and found MnCeW system exhibited more activity for NO$_x$ conversion than the CeW catalyst below 200 °C. The addition of tungsten to Mn/Co/Ti resulting in the Mn/Ce/W/Ti catalyst also showed excellent NO$_x$ conversion in the 120–200 °C and SO$_2$ resistance.$^{28}$ These results illuminated the promoting effect of tungsten to the MnO$_2$ based catalysts. Further, Liu et al.$^{29}$ first considered the MnWO$_x$ as the main active phase and got high deNO$_x$ efficiency from 60 to 250 °C.$^{29}$ Sun et al.$^{30}$ then prepared a series of W$_x$Mn$_{1-x}$O$_4$ Catalysts via coprecipitation method. W$_{0.1}$Mn$_{0.6}$O$_2$ catalyst with amorphous or poorly crystalline Mn and W species showed the highest NH$_3$-SCR activity within a broad temperature range of 230–470 °C. Our group also prepared a Mn$_x$W$_{0.05}$Ti$_{0.95-n}$O$_2$ 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.$^{31}$

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In this paper, to discuss the promoting function of tungsten and MnWO₄ phase on the properties of MnO₂ based catalysts, a series of bulk and supported MnWO₄ catalysts were prepared by self-propagating high-temperature synthesis (SHS), coprecipitation (CP) and impregnation (IMP) methods, and their catalytic activity in NH₃-SCR reaction were tested.

2. Experimental

2.1 Catalyst preparation

The MnWO₄ 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 MnWO₄ catalysts via self-propagating high-temperature synthesis, stoichiometric molar amount of manganous nitrate (Mn(NO₃)₂·4H₂O) and ammonium tungstate [(NH₄)₂WO₄·xH₂O] was dissolved in the de-ioned water respectively. The total amount of precursor metal-salts is 0.01 mol. 0.1 mol of glycine (C₂H₄N₂COOH) 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 MnₓWO₄) later were dispersed on the surface of TiO₂ (anatase, htnano Co., Ltd). The loading amount of active components is kept at 20 wt%. The MnₓWO₄ and MnₓWO₄/TiO₂ catalysts with typical MnWO₄ phase were also prepared by coprecipitation and impregnation method. The detailed steps can be seen in elsewhere. As a reference, MnO₂, WO₃, WO₃/TiO₂ (20 wt% WO₃), MnO₂/TiO₂ (20 wt% MnO₂) samples were also prepared via self-propagating high-temperature synthesis.

2.2 Catalyst characterization

N₂ 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.

X-ray diffraction (XRD) patterns of the catalysts were recorded by a Siemens D5000 X-ray diffractometer. The 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 (H₂-TPR) profiles of the catalysts were recorded by a chemisorber (Chem2910, Finesorb). Each sample (ca. 100 mg) were pretreated 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% H₂/95 vol% Ar flow, at a rate of 30 ml min⁻¹ with a heating rate of 10 °C min⁻¹.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface atomic state and form of catalyst with Al target and Kz radiation, operating at 15 kV voltage and C 1 s = 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 NOx, 500 ppm NH₃, 5 vol% O₂, N₂ as the balance gas, the total gas flow rate was 500 ml min⁻¹, and the corresponding gas hourly space velocity (GHSV) was 30 000 h⁻¹. 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 NOx analyzer and gas chromatograph (Thermo Trace 1300 equipped with Porapak Q column). NOx conversion and N₂ selectivity are calculated as follows:

\[ \text{NOx conversion} = \frac{\text{[NO]in} - \text{[NO]out}}{\text{[NO]in}} \]

\[ \text{N₂ selectivity} = \frac{\text{[N₂]out} - 2\text{[N₂O]out}}{\text{[NO]in} + \text{[NH₃]in}} \]

3. Results and discussions

3.1 Synthesis and characterization of the bulk and supported MnWO₄ catalysts

3.1.1 Textual properties of the bulk and supported MnWO₄ catalysts. Table 1 lists the textual properties of the bulk MnWO₄ catalysts. WO₃ almost has no surface area, which explains its poor catalytic activity. With the increment of Mn : W ratio, the surface area continually increases. MnO₂ has the largest surface area of 30 m² g⁻¹. It seems that the existence of tungsten has a negative effect on the surface areas of the MnWO₄ catalysts by self-propagating high-temperature synthesis. The lower surface area of the MnWO₄ catalysts than the MnO₂ partially explains their worse activities than MnO₂ in low temperature range.

Table 2 lists part of the textual properties of the TiO₂ with supported MnWO₄ catalysts. Compared to the bulk MnWO₄, the variation of surface area of these samples shows a different way. The MnₓWO₄/TiO₂-SHS keeps the largest surface area of 142 m².

| Samples       | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Average pore diameter (nm) |
|---------------|----------------------------|-----------------------|----------------------------|
| WO₃-SHS       | 0                          | —                     | —                          |
| MnₓWO₄-SHS    | 5                          | —                     | —                          |
| MnₓWO₄/TiO₂-SHS | 6                          | 0.0421                | 28.7                       |
| MnₓWO₄/TiO₂-SHS | 15                         | 0.0704                | 18.3                       |
| MnₓWO₄/TiO₂-SHS | 25                         | 0.156                 | 24.6                       |
| MnO₂-SHS      | 30                         | 0.178                 | 23.5                       |
while the MnO2/TiO2-SHS only has 85 m² g⁻¹ of BET surface area, which is even smaller than 109 m² g⁻¹ of WO3/TiO2-SHS. The results means that the existence of W can alleviate the decrement of TiO2 surface area, and increase the BET surface area of MnWOₓ/TiO2-SHS. Further, the decrement of average pore diameter of Mn2WOₓ/TiO2-SHS indicates that the Mn2WOₓ species are well dispersed in the pore structure of TiO2, which will be favorable for the activity.

3.1.2 XRD patterns of the MnWOₓ catalysts. Fig. 1 displays the XRD patterns of the bulk and supported MnWOₓ catalysts. The bulk MnWOₓ samples do not have characteristic peaks of MnO2. Instead, they mainly present the typical characteristic peaks of monoclinic structure phase of MnWO4.32 A little part of Mn3O4 also can be found on the pattern of MnWOₓ sample. The peaks intensity of Mn3O4 and MnWO4 gradually enhance with the increment of Mn : W ratio. It means that the main species were the MnWO4 and the Mn3O4 on the bulk MnWOₓ. The general valence of manganese in MnWO₄ catalysts has been suppressed to be about +2/+3. In Fig. 1B, the TiO2 with supported WO3 (WO3/TiO2) sample only presented the characteristic peaks of anatase TiO2. The MnO2/TiO2 and Mn10WOₓ/TiO2 presents the characteristic peaks of MnO3 and anatase TiO2. The MnWOₓ/TiO2 presents the characteristic peaks of MnWO4 and anatase TiO2. However, the characteristic peaks of MnWO₄ and MnO3 disappeared together on the patterns of Mn2WOₓ/TiO2 and Mn5WOₓ/TiO2, which can be ensured that the active species were well dispersed on the TiO2. The above results suggested that the coexistence of MnWO4 and Mn3O4 weaken the intensity of characteristic peaks and caused the disappearances of MnWO4 and MnO3 on the patterns of Mn2WOₓ/TiO2 and Mn5WOₓ/TiO2. For the MnWOₓ catalysts, MnWO4 phase seemed to play an important role in NH3-SCR reaction.

3.1.3 H₂-TPR of TiO2 with supported MnWOₓ samples with self-propagating high-temperature synthesis. The NH3-SCR activity of MnWOₓ has a strong relation with the redox properties in the SCR reaction. H₂-TPR was performed to identify the active species on the MnWOₓ catalysts. Fig. 2 displays the profiles of different supported MnWOₓ/TiO2 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.33 Here, the profiles seems to be some complicated. In general, for the supported MnWOₓ/TiO2 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 MnO2 species; in the higher temperature range of 600–900 °C, the reduction peaks are from different WO3 species.14,15 For the four reduction peaks in 200–500 °C on the MnO2/TiO2 profile, the peaks at about 300, 400 and 460 °C can be attributed to the reduction of MnO2 to Mn2O3, Mn2O3 to Mn3O4 and Mn3O4 to

### Table 2  Textual properties of the supported MnWOₓ catalysts

| Samples           | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Average pore diameter (nm) |
|-------------------|--------------------------|-----------------------|-----------------------------|
| WO3/TiO2-SHS      | 109                      | 0.212                 | 7.8                         |
| MnO2/TiO2-SHS     | 85                       | 0.194                 | 9.0                         |
| Mn2WO4/TiO2-SHS   | 142                      | 0.217                 | 6.1                         |
| TiO2              | 184                      | 0.296                 | 6.4                         |
| WO3/TiO2          | 109                      | 0.212                 | 7.8                         |
| MnO2/TiO2         | 85                       | 0.194                 | 9.0                         |
| Mn2WO4/TiO2       | 142                      | 0.217                 | 6.1                         |
| TiO2              | 184                      | 0.296                 | 6.4                         |

![Fig. 1 XRD patterns of bulk and supported MnWOₓ catalysts.](image1)

![Fig. 2 H₂-TPR profiles of different TiO2 with supported MnWO₄ samples with different Mn : W ratio and preparation methods.](image2)
MnO₂, respectively. Besides that, the peak at 220 °C is from the reduction of part Ti⁴⁺ to Ti³⁺, which have interaction with manganese oxides. The reduction profiles of Mn₂WO₄/TiO₂-SHS are clearly different from MnO₂/TiO₂. The reduction peaks of manganese oxides are almost diminished on the Mn₂WO₄/TiO₂-SHS, which indicates that all the manganese species are well interacted with the tungsten and form the MnWO₄ structure. The reduction peaks in 200–500 °C appear again on the Mn₂WO₄/TiO₂-SHS and Mn₃WO₄/TiO₂-SHS, indicates that excess manganese oxides are existed on the samples other than Mn₂WO₄. The reduction peak sites move to the lower temperature attitude, and the peak intensity of Mn₂O₃ to Mn₃O₄ clearly decreases. Under this conditions, it seems that the MnO₂ species are easy to be reduced and the large part of MnO₂ can be directly reduced to MnO.

Another main reduction band distributed in 600–900 °C is probably from tungsten oxides, MnWO₄ species and titanium oxides. For WO₃/TiO₂ sample, the reduction peaks at 520 °C, 650 °C and 800 °C are most probably from part of Ti⁴⁺ to Ti³⁺, W⁶⁺ to W⁴⁺ and W⁴⁺ to W⁰. When manganese is added, the two peaks at 520 °C and 650 °C diminished on the Mn₂WO₄/TiO₂-SHS profiles. The diminishing of peak at 520 °C might indicate the excellent dispersion of MnWO₄ on the surface of TiO₂ support; the diminishing of peak at 650 °C represents that there is no single WO₃ species left. The only peak around 790 °C should be from MnWO₄ structure, and it can be inferred that the Mn⁴⁺ and W⁶⁺ in MnWO₄ 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 MnWO₄ and supported MnWO₄/TiO₂ 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 MnWO₄ catalysts with different preparation methods. Co-precipitation method gets the homogenous particles with typical regular nano-rod shapes of MnWO₄ structure in Fig. 3a. The ordered lattice fringes in Fig. 3b confirm that the particles have a typical MnWO₄ crystal structure. 0.487 nm and 0.379 nm lattice spacing belongs to crystal face (100) and face (011) of MnWO₄. On the Mn₃WO₄/TiO₂-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 Mn₂WO₄ structure. The agglomeration of particles clearly happens on the sample, which causes the poor specific area and poor NH₃-SCR activity.

For the two supported samples, MnWO₄ 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, MnWO₄ phase is hard to be distinguished on the images. The main change is come from the TiO₂ support. It looks like that the TiO₂ support has grown into large plates via impregnation method (Fig. 3e). The specific surface area of Mn₂WO₄/TiO₂-IMP is thereby severely influenced and decreases from 184 m² g⁻¹ to 56 m² g⁻¹, which may cause the activity decreases. Meanwhile, the self-propagating high-temperature synthesis method keeps the structure of TiO₂ support much better and more MnWO₄ species nanoparticles can be formed and seen on the surface.

3.1.5 Characterization of the bulk and supported MnWO₄ 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 MnWO₄/CP, Mn₃WO₄/TiO₂-IMP, Mn₃WO₄-SHS and Mn₂WO₄/TiO₂-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 2p₁/₂ and Mn 2p₃/₂.
respectively. The Mn 2p3/2 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 Mn3+, the peaks at 642.0–642.6 eV to Mn4+, and the peaks at 643.4–644.5 eV to Mn2+. According to quantitative results in the Table 3, the Mn3+ and Mn2+ 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 Mn2+ is the highest, which suggests the valence restriction from the formation of MnWO4 phase.

Oxygen species plays an important role in the NH3-SCR activity. The O 1s XPS of MnWOx and MnWOx/TiO2 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 O2− (denoted as O_b); the sub-bands with higher binding energy at 531.0–531.5 eV to surface absorbed oxygen (denoted as O_a) such as O2 or O− 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_a0). The surface absorbed O_a is usually regard as more reactive in oxidation reactions due to its higher mobility than lattice O2−, which is also beneficial to the NO oxidation to NO2 thus facilitating the “fast SCR” process. The ratios of O_a, O_b and O_a0 on four catalysts are calculated and listed in Table 4. The bulk MnWOx and Mn2WOx catalysts have high O_a ratios of 31.78% and 34.72% respectively, which means that the MnWOx mixed oxides may have a high response to the NH3-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 TiO2 supporting, Mn2WOx/TiO2 then shows the high activity in NH3-SCR reaction.

### 3.2 Catalytic activity of the bulk and supported MnWOx catalysts

Fig. 6A displayed the activities of the bulk MnWOx catalysts with different Mn : W ratio by self-propagating high-temperature synthesis. Due to the poor specific surface area, the bulk WO3 did not show the NH3-SCR activity obviously; while the bulk

### Table 3 Quantitative results of Mn 2p XPS spectra of MnWOx-CP, MnWOx/TiO2-IMP, Mn2WOx-SHS and Mn2WOx/TiO2-SHS

| Samples       | Mn3+  | Mn4+  | Mn2+  | Average valence |
|---------------|-------|-------|-------|-----------------|
| MnWOx-CP     | 642.0 | 22.32 | 640.6 | 2.8             |
| Mn2WOx-SHS   | 642.4 | 31.08 | 641.1 | 3.0             |
| MnWOx/TiO2-IMP | 642.6 | 30.26 | 641.3 | 3.0             |
| Mn2WOx/TiO2-SHS | 642.6 | 33.26 | 641.1 | 3.1             |

### Table 4 Quantitative results of O 1s XPS spectra of MnWOx-CP, MnWOx/TiO2-IMP, Mn2WOx-SHS and Mn2WOx/TiO2-SHS

| Samples       | O_b  | O_a  | O_a0 | BE (eV) | Per.% | BE (eV) | Per.% | BE (eV) | Per.% |
|---------------|------|------|------|---------|-------|---------|-------|---------|-------|
| MnWOx-CP     | 530.2| 55.20| 531.4| 31.78   | 533.1 | 13.02   |
| Mn2WOx-SHS   | 530.4| 41.06| 531.0| 34.72   | 532.8 | 24.22   |
| MnWOx/TiO2-IMP | 530.0| 47.68| 531.5| 26.75   | 532.9 | 25.57   |
| Mn2WOx/TiO2-SHS | 528.9| 57.67| 531.2| 24.65   | 532.3 | 17.68   |
MnO₂ with the largest specific surface area among all the bulk samples showed the best performance in the lower temperature range. 100% NO₃ conversion had been achieved in the range of 100–180 °C. When the W and Mn coexist and form the series of MnₓWO₄ catalysts, the activity catalysts undergo a series of change. MnₓWO₄ only showed poor activity in the range of 50–120 °C. MnₓWO₄ displayed higher activity in the temperature range of 100–300 °C. With the continuous increment of Mn content, the activity of MnₓWO₄ did not surpass the bulk MnO₂ in the low temperature, some of MnₓWO₄ samples with high Mn : W ratio behaved better performance in the high temperature range. The MnₓWO₄ exhibited the higher activity than the bulk MnO₂ when the reaction temperature is above 200 °C.

The N₂ selectivities of bulk MnₓWO₄ catalysts with different Mn : W ratio are presented in Fig. 6B. It can be seen that tungsten has a clearly effect of MnₓWO₄ on the N₂ selectivity, especially in the high temperature range. The N₂ selectivity of bulk MnO₂ 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 N₂ selectivity of MnₓWO₄ is more and more improved. On the MnₓWO₄ with 1 : 1 ratio, the N₂ selectivity of has almost reached 100%, the insertion of tungsten into MnₓWO₄ favours the increase in the activity and N₂ selectivity. Supported MnₓWO₄/TiO₂ 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 MnO₂ did not improve the activity of MnₓWO₄/TiO₂. The 100% NO₂ conversion window (working window) was still in the range of 100–180 °C. Meanwhile, the MnₓWO₄/TiO₂ catalysts showed much better performance than the bulk MnₓWO₄ samples and single MnO₂ catalysts. Except Mn₁WO₄/TiO₂, all the other MnₓWO₄/TiO₂ catalysts presented the 100% NO₂ conversion temperature window. The temperature window of the Mn₁ₓWO₄/TiO₂ was 180–240 °C; The Mn₂WO₄/TiO₂ was 130–300 °C, and the window of Mn₃WO₄/TiO₂ and Mn₁₀WO₄/TiO₂ was in the same range of 130–240 °C.

N₂ selectivity of the supported MnₓWO₄ catalysts are also been improved from Fig. 7C and D. The appearance of N₂ selectivity decrease is retarded to high temperature attitude, and the decrease degree is alleviated with the Mn : W ratio decreasing. On the MnₓWO₄/TiO₂ with Mn : W ratio of 1 and 2, N₂O is only formed above 200 °C and the N₂ selectivity of MnₓWO₄/TiO₂ catalysts keep above 80% during the course.

The results show that the addition of tungsten can improve the activity and N₂ selectivity of supported MnO₂ based catalysts, especially in the higher temperature range. Though the Mn₁WO₂/TiO₂ does not achieve the 100% NO₂ conversion, it shows much better activity than the Mn₂O₃/TiO₂ when the temperature is above 250 °C. When the Mn : W ratio increases to 2 : 1, the performance of MnₓWO₄/TiO₂ will be better than Mn₂O₃/TiO₂. It is the MnₓWO₄/TiO₂ that fetches the best performance among all the MnₓWO₄/TiO₂ samples. Considering the XRD pattern and BET surface areas, the existence of tungsten have shown two effects on the TiO₂ supported MnₓWO₄ catalysts. The first is that the tungsten can alleviate the specific surface area loss of TiO₂ support. The BET surface area of MnₓWO₄/TiO₂-SHS is clearly bigger than WO₃/TiO₂ and MnO₂/TiO₂, which is favorable for the catalytic activity in NH₃-SCR reaction. The second effect may be that the tungsten can interact with manganese oxide and form the MnWO₄ phase with manganese oxides, which is even favorable for the catalytic activity.

3.3 Activity of Mn₂WO₄-CP, Mn₅WO₄/TiO₂-IMP and Mn₁₀WO₄/TiO₂-IMP catalysts

The above results show that tungsten addition can improve NH₃-SCR activities of MnₓWO₄ catalysts. To discuss the mechanism of the addition of tungsten, especially the MnₓWO₄ phase on the catalytic activity. Co-precipitation and impregnation method, which have been reported to be able to get MnₓWO₄ catalysts with typical MnₓWO₄ phase,²² were used to prepare a bulk MnₓWO₄ (labeled as MnₓWO₄-CP) and the TiO₂ supported MnₓWO₄ and MnₓWO₄ (labeled as MnₓWO₄/TiO₂-IMP and MnₓWO₄/TiO₂-IMP). The BET surface areas of MnₓWO₄-CP, MnₓWO₄/TiO₂-IMP and MnₓWO₄/TiO₂-IMP are 26, 52 and 56 m² g⁻¹ respectively. The XRD patterns in Fig. 8 show that both MnₓWO₄-CP and MnₓWO₄/TiO₂-IMP both have typical
characteristic peaks of MnWO$_4$ without other impurity phase observed. Otherwise, MnWO$_x$/TiO$_2$-IMP also have MnWO$_4$ 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$_2$WO$_x$-CP, MnWO$_x$/TiO$_2$-IMP and Mn$_2$WO$_x$/TiO$_2$-IMP seemed to move to the high temperature attitude clearly. The NO$_x$ conversion over Mn$_2$WO$_x$-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$_x$/TiO$_2$-IMP was in the range of 230–350 °C, where it can convert more than 94% NO. The deNO$_x$ performance of MnWO$_x$/TiO$_2$-IMP was better than MnWO$_x$/TiO$_2$-SHS. The activity window of Mn$_2$WO$_x$/TiO$_2$-IMP is similar to MnWO$_x$/TiO$_2$-IMP, which the NO$_x$ conversion can reach 100% in the range of 250–350 °C. But the window width was some narrower than that of Mn$_2$WO$_x$/TiO$_2$-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$_x$/TiO$_2$ catalysts can be broadened as wide as 130–350 °C (or even higher) by fine tuning or combing of different preparation methods. It also can be inferred that the MnWO$_4$ should have some positive effect on the activity of MnWO$_x$ catalysts, especially for the activity of MnWO$_x$/TiO$_2$-IMP in the high temperature range.

The plot of N$_2$ product selectivity over above three catalysts as a function of temperature is shown in Fig. 7B. Mn$_2$WO$_x$-CP showed an excellent N$_2$ selectivity than MnWO$_x$/TiO$_2$-IMP and Mn$_2$WO$_x$/TiO$_2$-SHS under the range of 250 °C. In contrast, Mn$_2$WO$_x$/TiO$_2$-IMP and MnWO$_x$/TiO$_2$-SHS show a better N$_2$ selectivity than Mn$_2$WO$_x$-CP when the temperature is high than TiO$_2$-IMP and Mn$_2$WO$_x$/TiO$_2$-IMP.
280 °C. It confirms that the improvement of N2 selectivity is associated with existence of MnWO4 and dispersion on the surface of carrier.

4. Conclusions

A series of bulk MnWO4 and supported MnWO4/TiO2 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 TiO2 support, and improve the NH3-SCR activity of MnWO4/TiO2 catalysts. The tungsten and manganese also can form a MnWO4 crystal structure, which might be favorable for the activity and N2 selectivity in the high temperature range (above 260 °C). How the MnWO4 works needs to be further investigated. Both self-propagating high-temperature synthesis and impregnation can get uniformly distributed MnWO4 nanoparticles, while the TiO2 support structure is more influenced by impregnation.

Notes and references

1 M. Fu, C. Li, P. Lu, L. Qu, M. Zhang, Y. Zhou, M. Yu and Y. Fang, Catal. Sci. Technol., 2014, 4, 14–25.
2 F. Can, X. Courtois, S. Royer, G. Blanchard, S. Rousseau and D. Duprez, Catal. Today, 2012, 197, 144–157.
3 Z. Liu, J. Li and J. Hao, Chem. Eng. J., 2010, 165, 420–425.
4 G. Coudurier and J. C. Védrine, Catal. Today, 2000, 56, 415–430.
5 L. J. Alemany, F. Berti, G. Busca, G. Ramis, D. Robba, G. P. Toledo and M. Trombetta, Appl. Catal., B, 1996, 10, 299–311.
6 L. Lietti, I. Nova, G. Ramis, L. Dall’Acqua, G. Busca, E. Giamello, P. Forzatti and F. Bregani, J. Catal., 1999, 187, 419–435.
7 D. Ye, R. Qu, H. Song, X. Gao, Z. Luo, M. Ni and K. Cen, Chem. Eng. J., 2016, 283, 846–854.
8 S. Andreoli, F. A. Deorsola, C. Galletti and R. Pirone, Chem. Eng. J., 2015, 278, 174–182.
9 J. Xiang, L. Wang, F. Cao, K. Qian, S. Su, S. Hu, Y. Wang and L. Liu, Chem. Eng. J., 2016, 302, 570–676.
10 C. Liu, J. Shi, C. Gao and C. Niu, Appl. Catal., A, 2016, 25, 54–69.
11 X. Xiong, C. Wu, Q. Hu, Y. Wang, J. Jin, C. Lu and D. Guo, Chem. Eng. J., 2016, 286, 459–466.
12 R. Foo, T. Vazhnova, D. B. Lukyanov, P. Millington, J. Collier, R. Rajaram and S. Golunski, Appl. Catal., B, 2015, 162, 174–179.
13 D. W. Kwon, K. B. Nam and S. C. Hong, Appl. Catal., B, 2015, 166–167, 37–44.
14 Y. Peng, K. Li and J. Li, Appl. Catal., B, 2015, 140–141, 483–492.
15 D. K. Pappas, T. Boningari, P. Boolchand and P. G. Smirniotis, J. Catal., 2016, 334, 1–13.
16 Y. J. Kim, H. J. Kwon, I.-S. Nam, J. W. Choung, J. K. Kil, H. J. Kim, M. S. Cha and G. K. Yeo, Catal. Today, 2010, 151, 244–250.
17 S. M. Lee, K. H. Park and S. C. Hong, Chem. Eng. J., 2012, 195–196, 323–331.
18 S. Zhang and Q. Zhong, J. Mol. Catal. A: Chem., 2013, 373, 108–113.
19 Y. He, M. E. Ford, M. Zhu, Q. Liu, Z. Wu and I. E. Wachs, Appl. Catal., B, 2016, 188, 123–133.
20 Z. Li, J. Li, S. Liu, X. Ren, J. Ma, W. Su and Y. Peng, Catal. Today, 2015, 258, 11–16.
21 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, Appl. Catal., B, 2012, 115–116, 100–106.
22 Z. Ma, X. Wu, Y. Feng, Z. Si and D. Weng, Catal. Commun., 2015, 69, 188–192.
23 Z. Liu, Y. Liu, Y. Li, H. Su and L. Ma, Chem. Eng. J., 2016, 283, 1044–1050.
24 X. Wang, X. Li, Q. Zhao, W. Sun, M. Tade and S. Liu, Chem. Eng. J., 2016, 288, 216–222.
25 M. Casapu, O. Kröcher and M. Elesner, Appl. Catal., B, 2009, 88, 413–419.
26 H. Xu, Q. Zhang, C. Qiu, T. Lin, M. Gong and Y. Chen, Chem. Eng. Sci., 2012, 76, 120–128.
27 Y. Peng, Z. Liu, X. Niu, L. Zhou, C. Fu, H. Zhang, J. Li and W. Han, *Catal. Commun.*, 2012, **19**, 127–131.
28 D. W. Kwon, K. B. Nam and S. C. Hong, *Appl. Catal., A*, 2015, **497**, 160–166.
29 F. Liu, W. Shan, Z. Lian, L. Xie, W. Yang and H. He, *Catal. Sci. Technol.*, 2013, **3**, 2699–2707.
30 W. Sun, X. Li, Q. Zhao, M. Tade and S. Liu, *Energy Fuels*, 2016, **30**, 1810–1814.
31 Z. Kong, C. Wang, Z. Ding, Y. Chen and Z. Zhang, *Catal. Commun.*, 2015, **64**, 27–31.
32 J. Tang, J. Shen, N. Li and M. Ye, *J. Alloys Compd.*, 2016, **666**, 15–22.
33 P. R. Ettireddy, N. Ettireddy, S. Mamedov, P. Boolchand and P. G. Smirniotis, *Appl. Catal., B*, 2007, **76**, 123–134.
34 D. Fang, J. Xie, H. Hu, H. Yang, F. He and Z. Fu, *Chem. Eng. J.*, 2015, **271**, 23–30.
35 P. G. W. A. Kompio, A. Brückner, F. Hipler, G. Auer, E. Löfler and W. Grünert, *J. Catal.*, 2012, **286**, 237–247.
36 D. W. Kwon and S. C. Hong, *Appl. Surf. Sci.*, 2015, **356**, 181–190.
37 L. Chen, J. Li and M. Ge, *J. Phys. Chem. C*, 2009, **113**, 21177–21184.
38 C. Wang, S. Yang, H. Chang, Y. Peng and J. Li, *Chem. Eng. J.*, 2013, **225**, 520–527.
39 S. S. R. Putluru, L. Schill, A. Godiksen, R. Poreddy, S. Mossin, A. D. Jensen and R. Fehrmann, *Appl. Catal., B*, 2016, **183**, 282–290.
40 M. Mačzka, M. Ptak, M. Kurnatowska, L. Kępiński, P. Tomaszewski and J. Hanuza, *J. Solid State Chem.*, 2011, **184**, 2446–2457.
41 Y. Wan, W. Zhao, Y. Tang, L. Li, H. Wang, Y. Cui, J. Gou, Y. Li and J. Shi, *Appl. Catal., B*, 2014, **148–149**, 2114–2122.
42 Z. Lian, F. Liu, H. He, X. Shi, J. Mo and Z. Wu, *Chem. Eng. J.*, 2014, **250**, 390–398.
43 M. Kang, E. D. Park, J. M. Kim and J. E. Yie, *Appl. Catal., A*, 2007, **327**, 261–269.
44 J. Fang, X. Bi, D. Si, Z. Jiang and W. Huang, *Appl. Surf. Sci.*, 2007, **253**, 8952–8961.
45 W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Appl. Catal., B*, 2012, **115–116**, 100–106.
46 Z. Kong, C. Wang, Z. Ding, Y. Chen and Z. Zhang, *J. Fuel Chem. Technol.*, 2014, **42**, 1447–1454.