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ARTICLE

## Promotional effect of iron oxide on the catalytic properties of Fe-MnO<sub>x</sub>/TiO<sub>2</sub> (Anatase) Catalysts for the SCR reaction at low temperatures

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The surface interaction of iron-improved MnO<sub>x</sub>/TiO<sub>2</sub> (anatase) catalyst for the selective catalytic reduction of nitric oxide was studied by detailed experiments. It was found that iron improved the catalyst by regulating the polymerization degree and the dispersion of Mn oxide species supported on the anatase surface, which was the key factor for both of the SCR activity and the N<sub>2</sub> selectivity. The increased NO conversion was caused by higher Mn oxide dispersion while the selectivity evaluation showed that N<sub>2</sub>O formation on MnO<sub>x</sub>/TiO<sub>2</sub> catalyst was much higher than that on the iron-improved catalyst. Isotopic labelled experiments of <sup>15</sup>NH<sub>3</sub> with NO indicated that NH was the key species for N<sub>2</sub>O generation. NH was easily to be generated on MnO<sub>x</sub>/TiO<sub>2</sub> without iron, which had higher oxidability than iron-improved catalyst, as identified by the temperature programmed reduction of H<sub>2</sub> experiments.

### Introduction

Nitric oxide (NO) is one of the major air pollutants in atmospheric environment that cause acidic rain, photochemical smog, ozone depletion, greenhouse effect, *etc.*<sup>1</sup> Therefore, elimination of NO is a practical research topic with imperious demands.<sup>1-6</sup> Recently, manganese oxide (MnO<sub>x</sub>)-based catalysts have attracted much attention in this area because of their unique activities in the selective catalytic reduction (SCR) of NO with NH<sub>3</sub> to harmless N<sub>2</sub> at low temperature.<sup>2-4</sup> Previous studies have shown that among the anatase-supported MnO<sub>x</sub> catalysts prepared through different methods, MnO<sub>x</sub>/TiO<sub>2</sub>, prepared through the sol-gel method, exhibited higher activities than others that were fabricated through wet-impregnations or co-precipitations.<sup>3</sup> However, the major defect of these NO elimination technologies is the generation of N<sub>2</sub>O, which is the product of the insufficient reduction of NO and the oxidation of NH<sub>3</sub>.

During the investigations in the field, iron has been found to be an effective element to improve the catalytic properties.<sup>4-6</sup> In 2003, Yang *et al.* reported that impregnated the Fe-MnO<sub>x</sub>/TiO<sub>2</sub>

catalysts not only have elevated activities for NO-SCR, but also obviously restricted N<sub>2</sub>O generation, and they attributed these promoting effects to the lower crystallinity of manganese oxide induced by iron oxide.<sup>4h</sup> Wu *et al.* then proposed that the addition of iron resulted in the amorphous MnO<sub>x</sub> instead of the crystalline, leading to higher SCR activity of Fe-MnO<sub>x</sub>/TiO<sub>2</sub> catalyst.<sup>4g</sup> Recently, Dong *et al.* found that addition of surfactant cationic surfactant cetyltrimethyl ammonium bromide (CTAB) could suppress the transformation of anatase to rutile in Fe-MnO<sub>x</sub>/TiO<sub>2</sub> catalyst and obviously increase its SCR activity.<sup>4d</sup> Since MnO<sub>x</sub> was the active component for the low-temperature SCR, previous reports have also pointed out that its dispersion state on supporters was the key factor for SCR performance and Smirniotis *et al.* has proposed that the aggregation morphology of MnO<sub>x</sub> affected the catalyst activity much<sup>5</sup> while Blik group's work disclosed that aggregated MnO<sub>x</sub> species accelerated N<sub>2</sub>O generation.<sup>6</sup> But there are still several basic mechanism problems unresolved in the field and the relationships of iron with the MnO<sub>x</sub> dispersion state as well as the catalyst activity and the reaction selectivity are still unclear. Our group aimed to develop green technologies with industrially applicable potential.<sup>7</sup> In order to reveal the intrinsic effects of iron promoter in the Fe-MnO<sub>x</sub>/TiO<sub>2</sub> catalysts for further development, we have investigated the surface interaction among Fe-MnO<sub>x</sub>/TiO<sub>2</sub>. The experimental results have shown that iron improved the catalyst by regulating the polymerization degree and the dispersion of MnO<sub>x</sub> species supported on the anatase surface, which was the key factor for both of the SCR activity and the N<sub>2</sub> selectivity. Herein, we wish to report our findings.

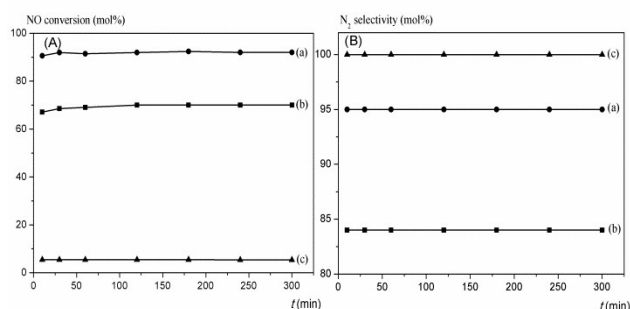
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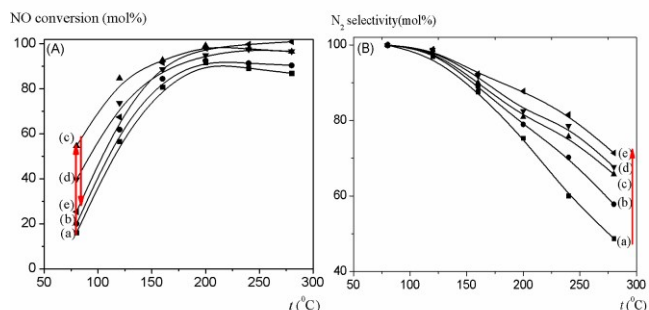
## Results and Discussion

We initially tested the catalytic activities of Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>, MnO<sub>x</sub>/TiO<sub>2</sub> and FeO<sub>x</sub>/TiO<sub>2</sub> in SCR. As shown in Figure 1, the reactions proceeded quickly and reached a steady-state within 30 min. In comparison, the catalyst Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub> obviously showed much higher activity than simple MnO<sub>x</sub>/TiO<sub>2</sub> (Figure 1A, curves *a* vs. *b*) and the NO conversion reached 88 % at the highest value. But the catalyst FeO<sub>x</sub>/TiO<sub>2</sub> was almost ineffective and the related NO conversions were just around 5 mol % (Figure 1A, curve *c*). The addition of iron also improved the N<sub>2</sub> selectivity of the SCR of NO (Figure 1B, curves *a* vs. *b*). Obviously, the iron component in the Fe-MnO<sub>x</sub>/TiO<sub>2</sub> catalysts acted as a promoter for the catalytic active component of MnO<sub>x</sub> supported on anatase.



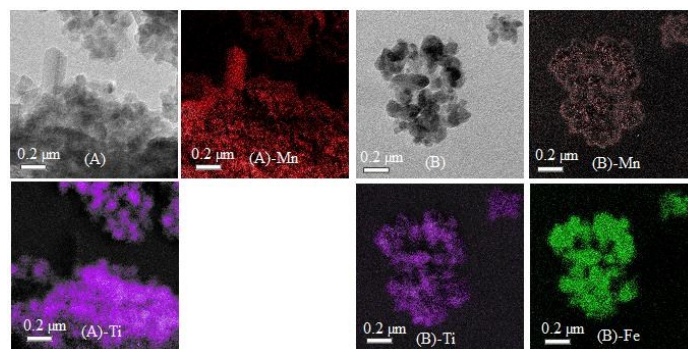
**Figure 1** Catalyst activity test at 160 °C with GHSV at  $1.0 \times 10^5$  h<sup>-1</sup>: (a) Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>; (b) MnO<sub>x</sub>/TiO<sub>2</sub>; (c) FeO<sub>x</sub>/TiO<sub>2</sub><sup>8</sup>

To further disclose the role of iron in catalyst, a series of Fe-MnO<sub>x</sub>/TiO<sub>2</sub> catalysts with different Fe/Ti ratio were then evaluated. As shown in Figure 2(A), for all catalysts, the NO conversions rose along with the reaction temperature, and reached a maximum at around 200 °C. Addition of iron benefited the NO conversion and the Fe(0.5)-MnO<sub>x</sub>/TiO<sub>2</sub> was screened out to be the best catalyst (curve *c*). It was obvious that the iron-doped catalysts improved the reaction much at low temperature (80-160 °C), while no more than 10 mol% of the NO conversion was enhanced at high temperature (200-280 °C). Figure 2(B) disclosed that the N<sub>2</sub> selectivity was enhanced along with the Fe/Ti ratio increasing. Thus, it is obvious that the addition of iron not only enhanced that catalyst activity, but also restrained N<sub>2</sub>O generation and increased N<sub>2</sub> selectivity.



**Figure 2** Catalyst evaluation in 30 min with GHSV at  $1.0 \times 10^5$  h<sup>-1</sup>: (a) MnO<sub>x</sub>/TiO<sub>2</sub>; (b) Fe(0.25)-MnO<sub>x</sub>/TiO<sub>2</sub>; (c) Fe(0.5)-MnO<sub>x</sub>/TiO<sub>2</sub>; (d) Fe(0.75)-MnO<sub>x</sub>/TiO<sub>2</sub>; (e) Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>.

The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) results indicated that the addition of iron resulted in much looser morphology of the catalyst material (Figure 3, Figure S3). In TEM and SEM images, the MnO<sub>x</sub>/TiO<sub>2</sub> behaved as an aggregated massive solid (Figure 3A, Figure S3b), but for Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>, the material was segregated in much smaller pieces with looser morphology (Figure 3B, Figure S3d). Further electron diffraction spectra (EDS) mapping technologies illustrated that both iron and manganese distributed uniformly in TiO<sub>2</sub> and the addition of iron undoubtedly avoided the aggregation of manganese oxide crystalline (Figure 3B-Mn vs. 3A-Mn).



**Figure 3** TEM image and element mapping of (A) MnO<sub>x</sub>/TiO<sub>2</sub>, (B) Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub><sup>9</sup>

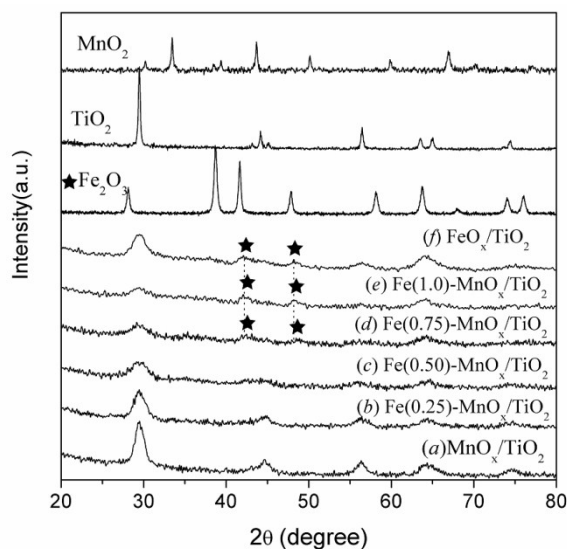
Table 1 calculated the TiO<sub>2</sub> crystallite size (D) at the Ti (101) lattice plane (29.4°) through Debye-Scherrer method. It was shown that the addition of iron and manganese led to smaller TiO<sub>2</sub> crystallite size, possibly because of its inhibitory effect for TiO<sub>2</sub> crystalline particle growth (Table 1, entries 2-6 vs. 1). The phenomena was well consistent with the references, which reported that the incorporation of Mn<sup>4+</sup> and Fe<sup>3+</sup> into the lattice restrained the growth of TiO<sub>2</sub>.<sup>10</sup> It was interesting that although the TiO<sub>2</sub> sizes were gradually reduced with the increase of iron content, the surface area of the catalyst got its peak when Fe/Mn ratio reached 0.5 and the highest rate constant and turn over frequency (TOF) for NO conversion at 80 °C were also achieved at this Fe/Mn value (Table 1, entry 4 vs. 2-3 and 5-6). In order to explain the phenomenon, X-ray powder diffraction (XRD) analyses of the catalysts were performed. As shown in the XRD spectra (Figure 4), no MnO<sub>2</sub> signal (2θ = 33.3 43.7 50.1 66.7°) was observed in the MnO<sub>x</sub>/TiO<sub>2</sub> catalysts, indicating that MnO<sub>x</sub> should be highly dispersed or exist in amorphous state. The crystalline Fe<sub>2</sub>O<sub>3</sub> peak emerged when the Fe/Mn ratio was more than 0.5, and the BET surface area began to decrease. Besides, the addition of iron also affected the total amounts of acidic sites on catalyst surface (Table 1), which increased first by the enhanced catalyst dispersion but decreased then due to the Fe<sub>2</sub>O<sub>3</sub> crystalline covering. The total acidity on catalyst surface is known to be the key point for the adsorption of NH<sub>3</sub>, which is crucial for the selective reduction of NO. The peaks of desorption around 200 °C were assigned to the chemical adsorbed NH<sub>3</sub> on Lewis acid sites caused by MnO<sub>x</sub> species (Figure S5), the adsorbed NH<sub>3</sub> species on MnO<sub>x</sub> can then react with gaseous NO to give N<sub>2</sub> formation through the Eley-Rideal mechanism at low temperatures.<sup>11,12</sup> Among

tested catalysts, Fe(0.5)-Mn/TiO<sub>2</sub> had the highest total acidity, as calculated from NH<sub>3</sub>-temperature programmed desorption (TPD) results (Figure 5), and thus behaved the best catalytic activity for NO elimination (Table 1, entry 4).

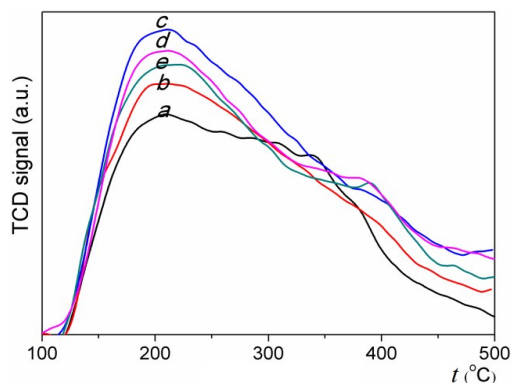
**Table 1** Physicochemical Properties of the Catalysts

entry	cat. <sup>a</sup>	D <sup>b</sup>	A <sup>c</sup>	t.a. <sup>d</sup>	Mn/Ti <sup>e</sup>	k <sup>f</sup>	TOF <sup>g</sup>
1	TiO <sub>2</sub>	150	56	-	-	-	-
2	(I)	80	143.8	2.86	0.36	6.03	0.67
3	(II)	56	190.8	2.94	0.38	6.64	1.07
4	(III)	53	200.0	3.21	0.42	25	3.08
5	(IV)	38	154.2	3.04	0.49	23	2.53
6	(V)	n.d. <sup>h</sup>	149.7	2.75	0.51	15	1.74

<sup>a</sup> Catalyst: (I) MnO<sub>x</sub>/TiO<sub>2</sub>, (II) Fe(0.25)-MnO<sub>x</sub>/TiO<sub>2</sub>, (III) Fe(0.5)-MnO<sub>x</sub>/TiO<sub>2</sub>, (IV) Fe(0.75)-MnO<sub>x</sub>/TiO<sub>2</sub>, (V) Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>. <sup>b</sup> Crystalline size of TiO<sub>2</sub> by D<sub>(101)</sub> (Å). <sup>c</sup> BET surface area (m<sup>2</sup>/g). <sup>d</sup> Total NH<sub>3</sub>-TPD peak area (a.u.). <sup>e</sup> Molar ratio of Mn/Ti on catalyst surface detected by XPS. <sup>f</sup> Rate constant for NO conversion at 80 °C (mol·m<sup>-2</sup>·s<sup>-1</sup>×10<sup>-8</sup>). <sup>g</sup> Turn over frequency for NO conversion at 80 °C (s<sup>-1</sup>×10<sup>-4</sup>). <sup>h</sup> No obvious crystalline TiO<sub>2</sub> detected.

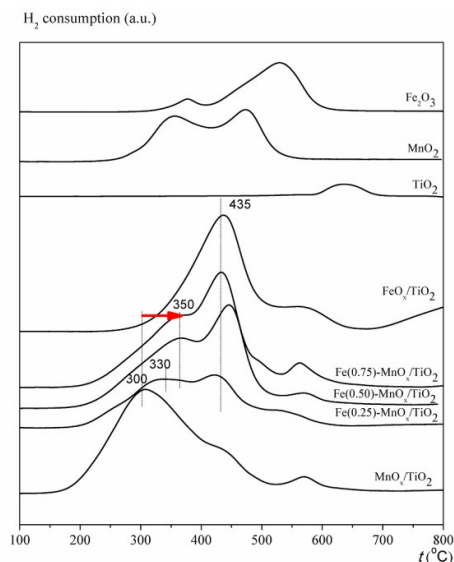


**Figure 4** XRD analysis of the catalysts.<sup>11</sup>



**Figure 5** NH<sub>3</sub>-TPD profile of the catalysts (a) MnO<sub>x</sub>/TiO<sub>2</sub>; (b) Fe(0.25)-MnO<sub>x</sub>/TiO<sub>2</sub>; (c) Fe(0.5)-MnO<sub>x</sub>/TiO<sub>2</sub>; (d) Fe(0.75)-MnO<sub>x</sub>/TiO<sub>2</sub>; (e) Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>

The X-ray photoelectron spectroscopy (XPS) experiments were also used to investigate the chemical state of catalyst surface components. As shown in Figure S4,<sup>9</sup> the valence of Ti in the supporter did not change and the peaks around 457.6 and 463.4 eV were in correspondence to the signals of Ti2p3/2 and Ti2p1/2, which were characteristic peaks of Ti<sup>4+</sup>. The additive iron mainly existed as Fe<sup>3+</sup>, which was indicated by the overwhelming peak at 711.9 eV.<sup>10</sup> The valences of manganese were not affected by the addition of iron, and Mn<sup>4+</sup> was the major species. Besides the lattice oxygen (O1s, 529.5 eV), the materials also contained absorbed oxygen, which was clearly characterized by the O1s signal at 531.0 eV. The Mn/Ti ratios on catalyst surfaces were then calculated according to the XPS analysis results (Table 1). It was very clear that the addition of iron led to the increase of Mn/Ti ratio on surface, which benefited the SCR of NO. But the sustained growing trend of Mn/Ti was not completely in agreement with the reaction rate constant and TOF, which reached the highest value with Fe(0.5)-MnO<sub>x</sub>/TiO<sub>2</sub> (Table 1, entry 4). Therefore, it was suggested that the catalyst activity was also related with the dispersed state of MnO<sub>x</sub> on surface.



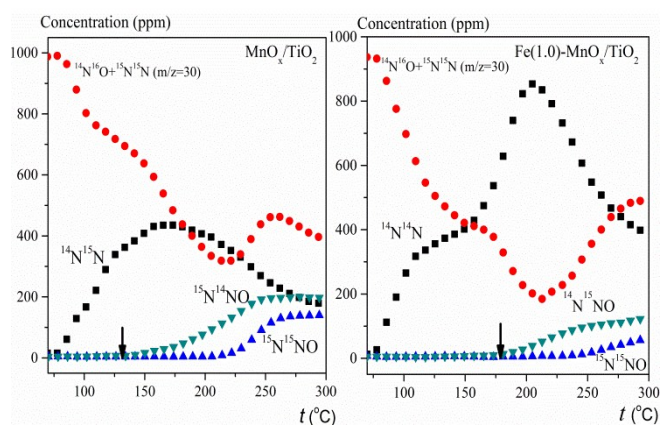
**Figure 6** The H<sub>2</sub>-TPR results of the catalysts

Temperature-programmed reduction (TPR) experiments with H<sub>2</sub> were then taken to confirm the MnO<sub>x</sub> dispersion state on catalyst surface. As shown in Figure 6, there were two reduction peaks of H<sub>2</sub> consumption for MnO<sub>x</sub>/TiO<sub>2</sub> catalyst: the broad peak around 200-500 °C indicated the reduction of Mn<sup>4+</sup> to Mn<sup>2+</sup>, while the peak at 580 °C was the characteristic for the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> (curve a). The addition of iron led to a new peak around 430 °C, which was suggested to be the signal of the Fe<sub>2</sub>O<sub>3</sub> reduction on TiO<sub>2</sub> surface (curves b-e). Obviously, the characteristic peak for MnO<sub>x</sub> reduction shifted to higher temperature along with the increase of iron content (curves b-e vs. a), which indicated the decrease of its reducibility. It has been well-known that the highly dispersed MnO<sub>x</sub> species has lower reducibility than aggregated MnO<sub>x</sub> species.<sup>13-14</sup> Thus, from the above TPR results, it could be concluded that the addition of iron led to the formation of highly dispersed MnO<sub>x</sub>



species on TiO<sub>2</sub>. Among dispersed MnO<sub>x</sub> species, the oligomers were more activated than the highly dispersed insular MnO<sub>x</sub> for NO reduction.<sup>13</sup> Hence, the observed rate constants and TOF of the reactions were improved after the addition of iron, which might lead to the MnO<sub>x</sub> oligomers at the first step (Table 1, entries 2-4). But the excess iron led to the highly dispersed insular MnO<sub>x</sub> species, which resulted in the lower catalytic activity for NO reduction,<sup>12</sup> as shown in Table 1, entries 4-6.

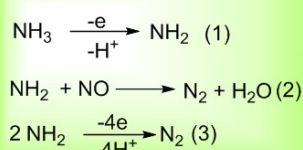
The mechanisms for the generation of N<sub>2</sub>O were our next concern. Thus, isotopic-labeled temperature-programmed surface reaction (TPSR) experiments using <sup>14</sup>NO and <sup>15</sup>NH<sub>3</sub> were then employed to provide essential hints. As depicted in Figure 7, in the reactions catalyzed by MnO<sub>x</sub>/TiO<sub>2</sub>, <sup>15</sup>N<sup>14</sup>NO was detected when the TPSR temperature reached 145 °C, indicating that the generation of N<sub>2</sub>O from the reaction of NH<sub>3</sub> with NO started at this temperature. The oxidation of NH<sub>3</sub> by air began at 225 °C, where the characteristic <sup>15</sup>N<sup>15</sup>NO signal was observed. But for the reactions using Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub> catalyst, the generation of <sup>14</sup>N<sup>15</sup>NO and <sup>15</sup>N<sup>15</sup>NO both needed higher temperature, which were at 180 °C and 240 °C respectively. Besides, the *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFT) also indicated that the addition of Fe restrained N<sub>2</sub>O generation. As shown in Figure S5,<sup>9</sup> for MnO<sub>x</sub>/TiO<sub>2</sub>, the characteristic peak of N<sub>2</sub>O emerged at 160 °C; But for Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub>, no N<sub>2</sub>O signal was observed at the temperature lower than 200 °C.



**Figure 7** Isotopic-labeled TPSR experimental results for the reaction of <sup>14</sup>NO with <sup>15</sup>NH<sub>3</sub>.<sup>15</sup>

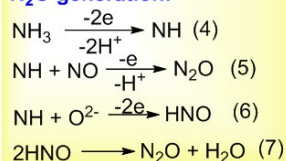
The reported works have illustrated that the NH<sub>3</sub> oxidation procedures affected the selectivity of the NO elimination reactions:<sup>4d, 16</sup> The oxidation of NH<sub>3</sub> afforded NH<sub>2</sub> (eq. 1), which led to N<sub>2</sub> through the reaction with NO (eq. 2) or dimerization (eq. 3). But the deep oxidation of NH<sub>3</sub> might generate NH (eq. 4), which led to undesired byproduct N<sub>2</sub>O through the reaction with NO (eq. 5) or O<sub>2</sub> (eqs. 6-7).<sup>4d, 16</sup>

#### N<sub>2</sub> generation:

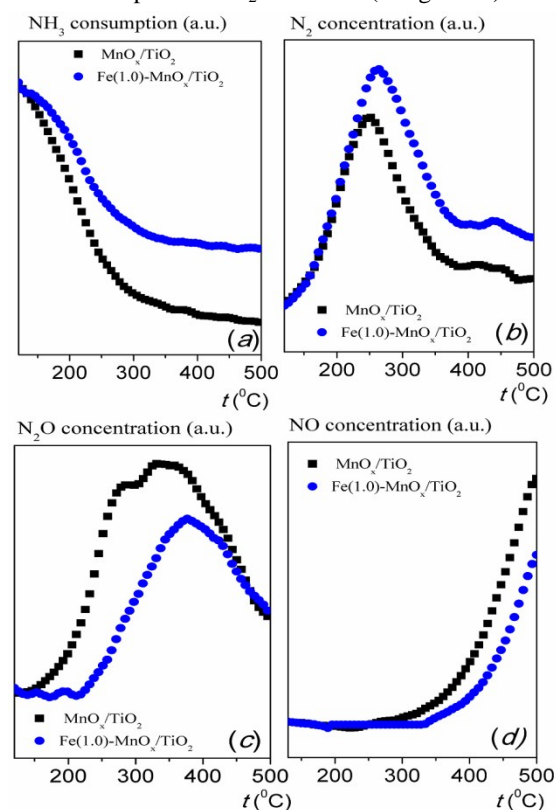


vs

#### N<sub>2</sub>O generation:



Therefore, the selectivity of the reaction might be controlled by the catalyst oxidability versus NH<sub>3</sub>. The results of TPR experiments with H<sub>2</sub> showed that the addition of iron led to dispersed MnO<sub>x</sub> species (Figure 6), which had low oxidability and thus avoided the generation of N<sub>2</sub>O.<sup>6</sup> The TPSR experiments for the reaction of NH<sub>3</sub> with O<sub>2</sub> on the catalyst surface further supported our hypothesis. As shown in Figure 8, the NH<sub>3</sub> consumptions on Fe(1.0)-MnO<sub>x</sub>/TiO<sub>2</sub> were obviously lower than that on MnO<sub>x</sub>/TiO<sub>2</sub> (Image a), indicating the much lower catalytic activity for NH<sub>3</sub> oxidation, which resulted in the high N<sub>2</sub> selectivity (Image b) and restrained the generation of over oxidation products N<sub>2</sub>O and NO (Images c-d).



**Figure 8.** TPSR experimental results for the reaction of NH<sub>3</sub> with O<sub>2</sub> (Reaction conditions: 2000 ppm NH<sub>3</sub>, 4 vol.% O<sub>2</sub> balanced by Ar, GHSV = 1.0 × 10<sup>5</sup> h<sup>-1</sup>)

## Experimental Section

### Catalyst Preparation

The Fe-MnO<sub>x</sub>/TiO<sub>2</sub> catalysts were prepared by sol-gel method: 48 ml butyl titanate was added into a vigorously stirred aqueous solution containing 126 ml *n*-butanol, 14 ml acetic acid, 12 ml deionized water and required amount of ferric nitrate and manganese nitrate (Mn/Ti molar ratio = 0.4, Fe/Mn molar ratio = 0.0 ~ 1.0). The obtained gel was aged for 24 h and dried at 110 °C, then calcined at 500 °C in air for 4 h. The prepared samples were crushed and sieved to 20-40 mesh. For comparison, MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> catalysts prepared by decomposition of the corresponding nitrates under air at 300 °C and 500 °C for 4h, respectively.

### Catalytic Characterization

Transmission electron microscopy (TEM) and electron diffraction spectra (EDS) were used to investigate the microstructure and the element dispersion of the catalyst with JEM-2010 UHR transmission electron microscope (TEM) operated at 200 KV.

Scanning electron microscope (SEM) experiments were performed with a Hitachi S-4800 electron microscope. The samples were vapor-deposited with gold before observation.

X-ray diffraction (XRD) studies were performed on a Bruker D8 ADVANCE Powder X-ray diffractometer equipped with Co K $\alpha$  radiation ( $\lambda = 1.7026 \text{ \AA}$ ). The X-ray tube was operated at 40 kV and 40 mA.

The surface areas of samples were determined by the BET isotherms of N<sub>2</sub> adsorption at -196 °C using a Micromeritics ASAP 2020 instrument with an auto-controlled system. 0.1g of catalyst was degassed at 300 °C for 2h before each measurement.

Ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) was performed in a quartz U-tube reactor, and 0.1 g catalyst powders were pretreated with argon flow (40 ml/min) at 500 °C for 1 h, and purged at 100 °C for 0.5 h, then heated from 100 to 500 °C at a heating rate of 10 °C /min. The desorbed NH<sub>3</sub> signal was measured by a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) measurement was carried out using Multilab 2000 XPS system with a monochromatic Mg K $\alpha$  source and a charge neutralizer. All the binding energy were referenced to the surface contaminated carbon (C1s=284.6 eV).

Hydrogen Temperature Programmed Reduction (H<sub>2</sub>-TPR) were performed in a quartz U-tube reactor, and 0.05 g catalyst were reduced without pretreatment. The H<sub>2</sub> consumption signal was detected by a thermal conductivity detector (TCD).

Isotopic labeled <sup>15</sup>NH<sub>3</sub>+<sup>14</sup>NO+O<sub>2</sub> Temperature programmed reaction were performed in a quartz U-tube reactor. 0.1 g of catalysts were pretreated in argon flow at 500 °C for 30min. Then, the catalysts were switched to argon flow containing 1000 ppm <sup>14</sup>NO, 1100ppm <sup>15</sup>NH<sub>3</sub> with 4 vol. % O<sub>2</sub> and heated from 100-500 °C at the heating rate of 10 °C/min. The signals of <sup>14</sup>NO (m/z=30), <sup>14</sup>N<sub>2</sub>O (m/z=44), <sup>14</sup>N<sup>15</sup>NO (m/z=45), <sup>15</sup>N<sup>15</sup>NO (m/z=46) and <sup>14</sup>N<sup>15</sup>N (m/z=29), <sup>14</sup>N<sup>14</sup>N (m/z=28) were measured by a quadrupole mass spectrometer.

*In situ* DRIFT spectra of absorbed and oxidized species of NH<sub>3</sub> were collected on a Nicolet 5700 FTIR instrument (4 cm<sup>-1</sup> resolution) equipped with a gas flow system. Before measurement, the catalysts were pretreated for in N<sub>2</sub> flow for 0.5 h at 300 °C. After cooling to room temperature, the samples were exposed to NH<sub>3</sub> (1 vol. %)/N<sub>2</sub> for 0.5 h and purged by pure N<sub>2</sub> for 0.5 h. Then, the samples were heated to 300 °C with a linear heating rate (10 °C /min) in N<sub>2</sub>+O<sub>2</sub> (1 vol. %) flow. The final DRIFT-IR spectra were recorded at different temperatures with subtraction of corresponding background spectra.

NH<sub>3</sub>+O<sub>2</sub> temperature-programmed surface reaction (TPSR) were performed in a quartz U-tube reactor, 0.1 g catalysts were pretreated in argon flow at 500 °C for 1 h. Then the catalysts were switched to argon flow containing 2000 ppm of NH<sub>3</sub>, 4 vol. % O<sub>2</sub> and heated from 100 to 500 °C at a heating rate of 10 °C/min. The signals of NO (m/z=30), NH<sub>3</sub> (m/z=17), N<sub>2</sub>O (m/z=46) and N<sub>2</sub> (m/z=28) were measured by a quadrupole mass spectrometer.

### Catalytic Performance test

Selective catalytic reduction (SCR) of NO by NH<sub>3</sub> was carried out in a fixed-bed U-tube glass reactor (i. d. 6 mm) with 0.1g catalyst samples. The inlet concentrations of reactants were 1000 ppm NO<sub>x</sub>, 1100 ppm NH<sub>3</sub> and 4 % vol. O<sub>2</sub> and N<sub>2</sub> was the remainder. The catalytic reaction was carried out at 80-280 °C and 0.1 Mpa with a total flow rate of 3.1 ml s<sup>-1</sup> (ambient conditions). The temperature of the catalyst was measured and controlled by means of a K-Type thermocouple (o.d.= 0.5 mm) attached closely to the catalyst bed. The NO (m/z = 30) and N<sub>2</sub>O (m/z = 46) concentrations before and after reaction were determined by using a Quadrupole mass spectrometer (DycorDymaxion DM300M, AMETEK). Because the NO<sub>2</sub> gas was not found both of inlet and outlet reaction gas under the above SCR reaction conditions over MnO<sub>x</sub>/TiO<sub>2</sub> catalyst activity test, the definitions used for NO conversion and N<sub>2</sub> selectivity are as follows:

$$\text{NO conversion} = 100 \times \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}}$$

$$\text{N}_2 \text{ selectivity} = 100 \times \left(1 - \frac{2[\text{N}_2\text{O}]}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}\right)$$

While working in excess oxygen and with NH<sub>3</sub>/NO (molar ratio)  $\geq 1$ , the NO conversion rate for the SCR process can be supposed to first order reaction model in NO. The rate constant  $k$  based on the specific surface area of sample was calculated according to the expression below:

$$k = -\frac{F_{\text{in}}}{m \times S} \ln(1 - x)$$

The NO turnover frequencies (NO TOFs) were calculated assuming a first-order reaction rate and according to the expression below:

$$\text{NOTOF}_S = \frac{F_{\text{in}} - F_{\text{out}}}{M_{\text{site}}}$$

Where  $k$  is the rate constant based on BET surface area of sample (mol·m<sup>-2</sup>·s<sup>-1</sup>), NO TOFs is defined as the number of moles of NO converted per mole of active sites per second (mol<sub>NO converted</sub>/(mol<sub>site</sub>·s)),  $F$  is the molar NO feed rate (mol s<sup>-1</sup>),  $m$  is the catalyst mass (g),  $S$  is the specific surface area of catalyst sample (m<sup>2</sup> g<sup>-1</sup>),  $x$  is the fractional NO conversion,  $M_{\text{site}}$  is the moles of catalytically active manganese species calculated by assuming all Mn component is catalytically active.

### Conclusions

In conclusion, iron improved the catalyst by regulating the polymerization degree and dispersion state of MnO<sub>x</sub> on its surface: The addition of iron led to the dispersed oligomerized MnO<sub>x</sub>, which enhanced the total acidity on catalyst surface and thus improved its activity. The oligomerized MnO<sub>x</sub> had lower oxidability versus NH<sub>3</sub> than the original polymerized one, and could restrain the deeply oxidized species NH, which was the key intermediate to generate the undesired byproduct N<sub>2</sub>O. The excess iron addition led to the highly dispersed insular Mn

species with reduced oxidability, which benefited the SCR selectivity, but decreased the catalyst activity. Although this mechanism remains to be fully clarified and alternative processes may also exist, the conclusion should be the most likely mechanism based on the above experimental findings and the related literatures.

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