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Article

Influence of the TiO₂ crystalline phase of MnO_x/TiO₂ catalysts for NO oxidation

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ARTICLE INFO

Article history:

Received 21 August 2013

Accepted 23 September 2013

Published 20 January 2014

Keywords:

Nitrogen oxide oxidation

Manganese oxide

Titanium dioxide

Crystalline phase

Pollution control

ABSTRACT

Mn-based catalysts impregnated on TiO₂ with different crystalline phases (rutile (R), anatase (A), and P25 (P)) were studied for the oxidation of NO to NO₂. 10%MnO_x/TiO₂(P) was the most active catalyst, giving 83% of NO conversion at 300 °C and a GHSV of 20000 h⁻¹. The catalyst activities were in the order MnO_x/TiO₂(P) > MnO_x/TiO₂(A) > MnO_x/TiO₂(R). The catalysts were characterized by X-ray diffraction, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, H₂ temperature-programmed reduction, and O₂ temperature-programmed desorption. Compared to anatase and rutile, P25 gave better dispersion of MnO_x on the support surface, suppressed the agglomeration of catalyst particles, and also produced more Mn₂O₃, which was more active for the oxidation of NO. In addition, P25 enhanced the reduction of MnO_x, especially for Mn₂O₃, and the formation of easily desorbed O₂⁻ generated from the Mn³⁺–O bond.

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1. Introduction

Nitrogen oxides (NO_x) emitted from fossil fuel combustion are major air pollutants that cause many environmental and human health hazards, including acid rain, photochemical smog, ozone depletion, and the greenhouse effect [1]. Currently, the most widely used method for NO_x removal in flue gas is selective catalytic reduction (SCR) with a V-W-Ti catalyst. This technology has high efficiency and stability for NO_x removal, but there still exist many problems, e.g., high reaction temperature (300–400 °C) needed has limited its application. The requirement to add ammonia or urea increased system complexity and operation cost, and there is the possibility of secondary pollution caused by ammonia slip [2].

Extensive research has been conducted to solve these problems. Recently, NO catalytic oxidation (SCO) has begun to attract more attention. Over 90% of NO_x formed in combustion is NO, and SCO is a process to convert most of the NO in flue gas

to NO₂, which is chemically more active and easier to capture in a later stage. This technology has two main applications: (1) as an intermediate step for the SCR reaction to improve the reaction rate and utilization of ammonia [3–5]; (2) because NO₂ is more water soluble than NO, it is possible to vary out the simultaneous adsorption of SO_x and NO_x in the flue gas desulfurization plant [6,7].

In early research, Pt-based catalysts were shown to have good performance for the SCO [8–10], but its high cost and easy poisoning by SO₂ and H₂O have limited its commercial application. Recently, it was demonstrated that transition metal oxides possess good catalytic activity in NO oxidation [11–14]. Among these, Mn-based catalysts are receiving more attention because of their high catalytic activities, low prices, and environmental friendliness. Their multivalent chemical states and porous physical structures make MnO_x a good candidate catalyst for NO oxidation. The performance of both unsupported and supported Mn-based catalysts have been investigated, including

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DOI: 10.1016/S1872-2067(12)60726-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 1, January 2014

Mn-Co-Ce-O_x [15,16], Mn-Ce [17] Mn/Ti [14,18,19,20], Mn-Co/Ti [21], Mn/AC, Mn/C [22], and Fe-Mn/Ti [18], as well as the effects of different experimental conditions. Compared to unsupported catalysts, the supported one can improve its thermal stability and the dispersion of the active sites [23]. The nature of the support has a significant impact on the performance of the catalyst.

Existing research on supported Mn-based catalysts for NO oxidation has mainly focused on TiO₂ supported MnO_x, which was demonstrated to give high catalytic performance. It is well known that the crystal phase of the TiO₂ affects catalyst activity [24], but its role in the NO catalytic oxidation has not been reported yet. In this paper, Mn catalysts supported on TiO₂ with three different crystalline phases were prepared to investigate the influence of the TiO₂ crystalline phase on the activity of MnO_x/TiO₂ for NO catalytic oxidation. The catalysts were characterized by N₂ adsorption-desorption measurement, field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), H₂ temperature-programmed reduction (H₂-TPR), and O₂ temperature-programmed desorption (O₂-TPD) to understand the interactions between MnO_x and TiO₂.

2. Experimental

2.1. Catalyst preparation

All chemicals used were analytical reagent. Commercial nanosized TiO₂ was used in this study. A 25 nm-anatase TiO₂ and 25 nm-rutile TiO₂ were supplied by Aladdin Industrial Inc. of China, and the 25 nm mixed crystal Type P25 TiO₂ (20% rutile and 80% anatase) was provided by Evonik Degussa GmbH of Germany.

TiO₂-supported 10 wt% Mn catalysts were prepared by the impregnation method. An appropriate amount of Mn(CH₃COO)₂·4H₂O (Aladdin Industrial Inc.) was dissolved in 150 ml deionized water and heated to and kept at 80 °C. After TiO₂ of the correct mass was added into the solution, water was slowly evaporated with electromagnetic stirring. The paste obtained was dried at 110 °C overnight, then crushed and sieved to obtain 40–60 mesh particles. Finally, the sample was calcined in air at 400 °C for 6 h. The Mn catalysts supported on P25 TiO₂, anatase TiO₂, and rutile TiO₂ were labeled MnO_x/TiO₂(P), MnO_x/TiO₂(A), and MnO_x/TiO₂(R), respectively.

2.2. Catalytic activity tests

NO catalytic oxidation measurement was carried out in a fixed-bed reactor (quartz tube, inner diameter 33 mm). The gas flow was controlled by a mass flow meter. The reaction temperature was controlled by a programmed electric furnace. The reactor inlet gas composition was 0.05% NO, 6% O₂, and N₂ balance. The total gas flow rate was controlled at 1.5 L/min. Catalyst activities were tested at 100–400 °C and GHSV of 20000 h⁻¹. Catalyst (5.0 g) was used in a typical test. The concentrations of NO and NO₂ at the reactor outlet were monitored by a Fourier transform infrared spectroscopy (FT-IR) gas ana-

lyzer (Nexus 670). Because the inlet and outlet concentrations of NO_x in all experiments were recorded after equilibrium reached, NO conversion was calculated from the ratio of outlet concentration of NO₂ and the sum of outlet concentrations of NO and NO.

2.3. Catalyst characterization

A variety of characterization methods were used to study the physiochemical properties of the MnO_x/TiO₂ catalysts. N₂ adsorption-desorption measurement were carried out on a Micromeritics ASAP2010 automated N₂ adsorption analyzer. The specific surface area of samples was calculated by the BET method, and the pore volume and pore diameter were measured by the BJH method. A JEOL S-4800 FESEM was used to investigate the surface morphology of catalysts. XRD was used to characterize the crystalline phase of the sample using a German Bruker D8 Advance diffractometer with Cu radiation source, scanning range of 10° to 90° (2θ), and a step size of 0.05°. XPS was used to analyze the atomic concentrations and Mn valence state on the catalyst surface on a British EscaLab 250Xi X-ray diffractometer using Al K_α (1486.6 eV, pass energy 30.0 eV) radiation as the excitation source. H₂-TPR and O₂-TPD were carried out on a CHEMISORB 2720 chemisorption analyzer with a thermal conductivity detector (TCD). Catalyst (100 mg) was used in the test. For the H₂-TPR analysis, the sample was pretreated at 250 °C for 30 min under N₂ (30 mL/min), and then cooled to room temperature before reduction by 5% H₂/Ar (20 mL/min), and the temperature was increased from room temperature to 800 °C (10 °C/min). For the O₂-TPD analysis, the sample was pretreated first at 250 °C for 30 min under N₂ (30 mL/min). After cooling to room temperature, N₂ was switch to high purity O₂ until adsorbed to saturation, and then the gas was switched to He (20 mL/min). When the TCD signal was stable, the temperature was increased from room temperature to 1000 °C (10 °C/min).

3. Results and discussion

3.1. Catalytic activity

Figure 1 shows the NO conversion on the series MnO_x/TiO₂. For reference, the activity of unsupported MnO_x calcined from Mn(CH₃COO)₂·4H₂O under air at 400 °C for 6 h is also presented. The sequence of catalyst activities for NO catalytic oxidation was MnO_x/TiO₂(P) > MnO_x/TiO₂(A) > MnO_x > MnO_x/TiO₂(R). MnO_x/TiO₂(P) gave the highest catalytic activity with the NO conversion of 83%. MnO_x/TiO₂(P) and MnO_x/TiO₂(A) had the same maximum activity temperature of 300 °C. For MnO_x and MnO_x/TiO₂(R), the maximum temperature was 350 °C. This indicates that P25 TiO₂ and anatase TiO₂ significantly enhanced the low temperature NO catalytic oxidation activity of MnO_x, while rutile TiO₂ seemed to have no catalytic activity promotion at all. The lower catalytic activity of MnO_x/TiO₂(R) compared to MnO_x may be due to the relatively low MnO_x loading. Thus, it could be concluded that, compared to rutile TiO₂, anatase TiO₂ can better interact with MnO_x on the catalyst surface,

Fig. 1. NO conversion over different MnO_x/TiO₂ catalysts. Reaction conditions: 0.05% NO, 6% O₂, and N₂ balance, GHSV = 20000 h⁻¹.

while a small amount of rutile TiO₂ in P25 TiO₂ further promoted this interaction.

3.2. Textural properties of the supports and catalysts

The specific surface area, pore volume, and pore diameter of the MnO_x/TiO₂ catalysts and supports are shown in Table 1. The data showed that anatase TiO₂ had the largest surface area and pore volume. The larger surface area and pore volume of the support provided more gas-catalyst contact and more active sites, thus improving the catalytic activity. Compared to the pristine supports, after loading MnO_x on the surface of the three types of TiO₂, the surface area of MnO_x/TiO₂(A) and MnO_x/TiO₂(R) were reduced by 16.3% and 26.3%, respectively. The pore volumes were also much reduced. In contrast, the specific surface area of MnO_x/TiO₂(P) was only reduced slightly from 46.3 to 45.3 m²/g, while the pore volume remained almost the same. This indicates that MnO_x was better dispersed on P25 TiO₂. The pore sizes of the three catalysts did not change much compared to those of the pristine supports, indicating that the change in specific surface area was mainly due to blockage of the pores.

The morphology of the catalyst surface was observed by SEM. As shown in Fig. 2, the surface of MnO_x/TiO₂(P) was rough and catalyst particles were distributed evenly without agglomeration, indicating that MnO_x existed in a highly dispersed phase on the TiO₂(P) surface after calcination, as implied in Table 1. The catalyst particles of MnO_x/TiO₂(A) appeared to be much agglomerated, resulting in a smaller specific surface area and pore volume. For the MnO_x/TiO₂(R) catalyst, no obvious

Table 1

Textural properties of the supports and MnO_x/TiO₂ catalysts.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
TiO ₂ (P)	46.3	0.13	11.43
TiO ₂ (A)	93.9	0.27	11.44
TiO ₂ (R)	23.2	0.06	9.55
MnO _x /TiO ₂ (P)	45.3	0.13	11.11
MnO _x /TiO ₂ (A)	78.6	0.21	10.48
MnO _x /TiO ₂ (R)	17.4	0.05	10.56

Fig. 2. SEM images of different samples. (a) TiO₂(P); (b) MnO_x/TiO₂(P); (c) TiO₂(A); (d) MnO_x/TiO₂(A); (e) TiO₂(R); (f) MnO_x/TiO₂(R).

agglomeration was found on the surface, but more bulk adhesion could be seen. The uneven distribution of MnO_x reduced the specific surface area and pore volume of the TiO₂(R) supported catalyst. Based on BET and SEM results, it can be concluded that the small amount of rutile TiO₂ contained in P25 TiO₂ prevented agglomeration of catalyst particles and improved the dispersion of MnO_x on the TiO₂ surface.

3.3. XRD results

The XRD patterns of the MnO_x/TiO₂ catalysts and their supports are illustrated in Fig. 3. The peaks corresponding to the crystalline phases of all three TiO₂ supports were clearly observed. After MnO_x was loaded, their peak position and inten-

Fig. 3. XRD patterns for the MnO_x/TiO₂ catalysts and supports.

sity did not change. No peak corresponding to MnO_x was detected over any $\text{MnO}_x/\text{TiO}_2$ sample. The monolayer surface coverage is defined as the maximum amount of MnO_x on the TiO_2 support [25]. From the bond length of $\text{M}-\text{O}$ in Mn_2O_3 , the nominal quantity of Mn needed to cover the TiO_2 surface as a monolayer was calculated to 0.0532 wt% per m^2 of the support [26]. It was estimated that the Mn loading at monolayer coverage is 6.6 wt% for all the samples. As no MnO_x was identified on the TiO_2 surfaces with 10% Mn loading, MnO_x was distributed homogeneously on the support surface as an amorphous phase or low crystallinity grains, or there was a relatively high proportion of Mn_2O_3 in the MnO_x loaded on the TiO_2 surface because Mn_2O_3 is highly amorphous in nature [27].

3.4. XPS results

The Mn atomic concentration and Mn/Ti ratio measured by XPS are shown in Table 2. The ratio of Mn/Ti is a measurement of the dispersion of MnO_x on the surface of TiO_2 [25]. Although the nominal Mn loadings in all the catalysts were the same, their Mn/Ti ratios on the catalyst surface were different. $\text{MnO}_x/\text{TiO}_2(\text{P})$ has the lowest Mn/Ti ratio of 0.20, $\text{MnO}_x/\text{TiO}_2(\text{A})$ has a Mn/Ti ratio of 0.22 and $\text{MnO}_x/\text{TiO}_2(\text{R})$ has the highest ratio of 0.83. This revealed again that MnO_x on the last catalyst existed in a highly dispersed phase and was intercalated with TiO_2 lattice, which agreed well with the BET, SEM, and XRD results. P25 TiO_2 has a lower specific surface area and Mn/Ti ratio compared to $\text{TiO}_2(\text{A})$, signifying that MnO_x interacted stronger with P25 TiO_2 . The high Mn atomic concentration and Mn/Ti ratio on $\text{TiO}_2(\text{R})$ surface may be due to two reasons: one is the low specific surface area and pore volume of $\text{TiO}_2(\text{R})$, and the other is the weak interaction between $\text{TiO}_2(\text{R})$ and MnO_x , which only allowed MnO_x to cover the $\text{TiO}_2(\text{R})$ surface as isolated species that do not interact with the support. According to the XRD results, no MnO_x crystalline phase was present on the $\text{TiO}_2(\text{R})$ surface, indicating that its MnO_x existed in the form of polymeric or microcrystalline crystallites, rather than in monolayer form. This observation is consistent with the results reported in the literature [25].

Figure 4 shows the Mn 2p XPS spectra of the surface of the $\text{MnO}_x/\text{TiO}_2$ catalysts. It can be deduced from the asymmetry of the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ profiles that MnO_x existed in two states, MnO_2 and Mn_2O_3 . The peak at lower binding energy (641.3–641.7 eV) was attributed to Mn^{3+} [28], and the peak at higher binding energy (642.2–643 eV) was attributed to Mn^{4+} [29]. The proportion of Mn^{3+} to Mn is shown in Table 2. The relatively high proportion of Mn_2O_3 verified the XRD results. The confirmation of the two different oxidation states of MnO_x by XPS indicated a possible mechanism of NO oxidation on the

Fig. 4. Mn $2p_{3/2}$ XPS spectra of the $\text{MnO}_x/\text{TiO}_2$ catalysts.

$\text{MnO}_x/\text{TiO}_2$ catalysts. Previous studies have shown that the activity of MnO_x is significantly influenced by the oxidation states and crystalline phases [30], and for the oxidation of NO, Mn_2O_3 has a higher catalytic activity than MnO_2 [20,31]. In the reaction of CO oxidation, Cimino et al. [32] attributed the higher catalytic activity of Mn^{3+} to the relatively weak $\text{Mn}^{3+}-\text{O}$ bond. Similarly, it can be speculated here that the easy-to-break $\text{Mn}^{3+}-\text{O}$ bond promoted the formation and desorption of NO_2 . It was reported that the species of MnO_x present strongly depended on the properties of the support, and TiO_2 contributed to the formation of Mn_2O_3 and MnO_2 mixed oxides [33]. Among the three TiO_2 supports, Mn^{3+} was present as a higher proportion on the surface of P25 TiO_2 , suggesting that P25 TiO_2 was more conducive to the formation of Mn_2O_3 , which thus promoted the catalytic activity of MnO_x for NO oxidation.

For transitional metal oxides, how the oxygen combines with the metal ions affects much the catalyst activity. The O 1s XPS spectra of the three catalysts are shown in Fig. 5. All the O 1s profiles have three overlapping peaks. The first peak at 529.56–529.82 eV corresponded to lattice O or chemisorbed

Fig. 5. O 1s XPS spectra of the $\text{MnO}_x/\text{TiO}_2$ catalysts.

Table 2
XPS results of the $\text{MnO}_x/\text{TiO}_2$ catalysts.

Sample	Mn content (at %)	Mn/Ti atomic ratio	Mn^{3+}/Mn atomic ratio
$\text{MnO}_x/\text{TiO}_2(\text{P})$	4.81	0.20	0.48
$\text{MnO}_x/\text{TiO}_2(\text{A})$	4.60	0.22	0.37
$\text{MnO}_x/\text{TiO}_2(\text{R})$	7.97	0.83	0.42

atoms O^{2-} in the metal oxides [34,35], the second peak at 530.59–531.05 eV, corresponded to hydroxyl [35], and the third peak at 532.0–532.54 eV corresponded to oxygen in MnO_x [36]. Similar to the findings in the literature [34], lattice oxygen was the dominant oxygen species on the surface of P25 TiO_2 . The strong interaction between P25 TiO_2 and MnO_x may be the most important reason for improved MnO_x catalytic activity in NO oxidation. The hydroxyl oxygen content on the catalyst surface seemed to play a minor role in NO oxidation as no obvious relationship with catalyst activity was found.

3.5. H_2 -TPR results

H_2 -TPR was used to investigate the reducibility of MnO_x on the TiO_2 surface. H_2 consumption was compared using the areas of the TPR profiles (Fig. 6). $MnO_x/TiO_2(A)$ has a larger H_2 consumption than $MnO_x/TiO_2(R)$ and $MnO_x/TiO_2(P)$, indicating that the average valence state of Mn on anatase TiO_2 was the highest, which was consistent with the XPS results. All the three catalysts showed a two-step reduction process. The first peak was located between 300 and 400 °C, and the second peak was located at 400–600 °C, which agreed with the results reported in the literature [25,37]. MnO_x was reduced in the following sequence: $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ [38], and MnO reduction would not be seen under our experimental conditions [39]. Therefore, the low temperature reduction peak corresponded to the reduction of highly dispersed and easy reducible MnO_2 , and the high temperature peak corresponded to the reduction of Mn_2O_3 or bulk MnO_x phase [33]. MnO_2 loaded on the $TiO_2(A)$ and $TiO_2(P)$ had the same reduction temperature, which was lower than that of MnO_2 loaded on $TiO_2(R)$. This indicates that MnO_2 on $TiO_2(A)$ and $TiO_2(P)$ was more easily reduced. The reduction temperature of Mn_2O_3 correlated with the catalytic activity, i.e., the lowest Mn_2O_3 reduction temperature corresponded to the highest NO oxidation activity, implying that the crystalline phase of TiO_2 affected the reducibility of Mn_2O_3 significantly. It was concluded from the reducibility of MnO_x that $TiO_2(A)$ and $TiO_2(P)$ had a stronger interaction with MnO_x than $TiO_2(R)$ did. In the interaction with MnO_2 , $TiO_2(A)$ and $TiO_2(P)$ were similar, but with Mn_2O_3 , the interaction was in the order

of $TiO_2(P) > TiO_2(A) > TiO_2(R)$. The decrease in reduction temperature means the promotion of oxygen mobility [20], as discussed previously that Mn_2O_3 played a more important role in NO oxidation. Therefore, the better reducibility of MnO_x , especially Mn_2O_3 , on the surface of P25 TiO_2 explained why P25 TiO_2 gave the highest performance of the MnO_x catalyst for NO oxidation.

3.6. O_2 -TPD results

O_2 -TPD was used to investigate the oxygen species on the catalysts surface. As shown in Fig. 7, all the samples had a large capacity for the adsorption of oxygen species. A desorption peak appeared before 200 °C for all catalysts. As the temperature increased, all three catalysts showed oxygen desorption without obvious peaks. A second desorption peak appeared at 510 °C for $MnO_x/TiO_2(R)$ and 590 °C for $MnO_x/TiO_2(P)$ and $MnO_x/TiO_2(A)$. Above 700 °C, all the catalysts showed a third desorption peak at similar temperature. The first peak at low temperature corresponded to physically adsorbed or weakly chemisorbed O_2^- species. The peak areas were consistent with the specific surface areas of three catalysts. The high surface areas of $MnO_x/TiO_2(A)$ and $MnO_x/TiO_2(R)$ explained the slow desorption of weakly chemisorbed oxygen species. The second peak corresponded to strongly chemisorbed O_2^- species. The third peak corresponded to the chemically stable lattice oxygen in MnO_x and TiO_2 . Combining the maximum activity temperature and desorption temperature of the catalysts, it can be deduced that the strongly chemisorbed O_2^- as indicated by the second peak played an important role in the reaction. Compared to $MnO_x/TiO_2(A)$ and $MnO_x/TiO_2(P)$, the second peak of $MnO_x/TiO_2(R)$ was broader and weaker, indicating that chemisorbed O_2^- was different from those on the surfaces of $MnO_x/TiO_2(A)$ and $MnO_x/TiO_2(P)$. The former was generated from the interaction between MnO_x and O_2 , while the latter were generated from the interaction between MnO_x , TiO_2 , and O_2 . The relatively sharp peak also indicated that chemisorbed O_2^- species on the surface of $MnO_x/TiO_2(A)$ and $MnO_x/TiO_2(P)$ was more easily desorbed. Although $MnO_x/TiO_2(A)$ possessed a larger specific surface area than $MnO_x/TiO_2(P)$, the larger sec-

Fig. 6. H_2 -TPR profiles of MnO_x/TiO_2 catalysts.

Fig. 7. O_2 -TPD profiles of the MnO_x/TiO_2 catalysts.

ond peak of $\text{MnO}_x/\text{TiO}_2(\text{P})$ showed that P25 TiO_2 better enhanced the formation of chemisorbed O_2^- . During the reaction, easier desorption of O_2^- and a larger oxygen storage capacity were beneficial to the performance of the catalyst [21]. Combining the XRD, XPS, and H_2 -TPR results, it can be speculated that the oxygen corresponding to the second peak came from the relatively weak $\text{Mn}^{3+}\text{--O}$ bond. $\text{TiO}_2(\text{A})$ and $\text{TiO}_2(\text{P})$ were capable of enhancing the activity of the $\text{Mn}^{3+}\text{--O}$ bond, thus promoting the desorption of chemisorbed O_2^- . Obviously, the promotion by P25 TiO_2 was much stronger. The strong interaction between P25 TiO_2 and MnO_x promoted the formation of Mn_2O_3 . Furthermore, P25 TiO_2 improved the dispersion of MnO_x on its surface, which improved oxygen mobility accordingly [12].

Xu et al. [21] studied the reaction mechanism of NO oxidation on Mn-Co/Ti catalyst, which was confirmed by Wu et al. [20] on $\text{MnO}_x/\text{TiO}_2$. Xu et al. [21] found the formation of bridging nitrates and bidentate nitrates on the catalyst surface during the reaction, and they inferred the following reaction mechanism:

The generation of adsorbed NO_2 was faster than that of the nitrate species, and the NO_2 generated could be easily desorbed from the catalyst surface [20,21]. Thus, reaction (2) is the rate limiting step of the overall reaction. P25 TiO_2 favored the formation of easily desorbed O_2^- , and consequently increased the reaction rate and NO conversion.

4. Conclusions

The activity of Mn catalysts impregnated on TiO_2 with different phases was in the order $\text{MnO}_x/\text{TiO}_2(\text{P}) > \text{MnO}_x/\text{TiO}_2(\text{A}) > \text{MnO}_x/\text{TiO}_2(\text{R})$. The decrease in the specific surface area and pore volume of TiO_2 after impregnation were due to blockage of pores, and $\text{MnO}_x/\text{TiO}_2(\text{P})$ showed the smallest changes in specific surface area and pore volume. Compared to $\text{TiO}_2(\text{A})$ and $\text{TiO}_2(\text{R})$, $\text{TiO}_2(\text{P})$ gave a higher dispersion of MnO_x on the catalysts surface, reduced the agglomeration and adhesion of catalyst particles and produced more Mn_2O_3 species, which was more active for the oxidation of NO. In addition, $\text{TiO}_2(\text{P})$ en-

hanced the reduction of MnO_x , especially Mn_2O_3 , and the formation of easily desorbed O_2^- generated from the $\text{Mn}^{3+}\text{--O}$ bond. The chemisorbed O_2^- promoted the formation of intermediate nitrates, thus increasing NO conversion.

References

- [1] Părvulescu V I, Grange P, Delmon B. *Catal Today*, 1998, 46: 233
- [2] Skalska K, Miller J S, Ledakowicz S. *Sci Total Environ*, 2010, 408: 3976
- [3] Ruggeri M P, Grossale A, Nova I, Tronconi E, Jirglova H, Sobalik Z. *Catal Today*, 2012, 184: 107
- [4] Koebel M, Madia G, Raimondi F, Wokaun A. *J Catal*, 2002, 209: 159
- [5] Ruggeri M P, Nova I, Tronconi E. *Top Catal*, 2013, 56: 109
- [6] De Paiva J L, Kachan G C. *Chem Eng Process*, 2004, 43: 941
- [7] Wang Z H, Zhang X, Zhou Z J, Chen W Y, Zhou J H, Cen K F. *Energy Fuels*, 2012, 26: 5583
- [8] Zhao Y, Xu P Y, Fu D, Huang J J, Yu H H. *J Environ Sci*, 2006, 18: 281
- [9] Bhatia D, McCabe R W, Harold M P, Balakotaiah V. *J Catal*, 2009, 266: 106
- [10] Li L D, Shen Q, Cheng J, Hao Z P. *Appl Catal B*, 2010, 93: 259
- [11] Shiba K, Hinode H, Wakihara M. *React Kinet Catal Lett*, 1996, 58: 133
- [12] Yung M M, Holmgren E M, Ozkan U S. *J Catal*, 2007, 247: 356
- [13] Zhang J X, Zhang S L, Cai W, Zhong Q. *Appl Surf Sci*, 2013, 268: 535
- [14] Li L D, Qu L L, Cheng J, Li J J, Hao Z. *Appl Catal B*, 2009, 88: 224
- [15] Li K, Tang X L, Yi H H, Ning P, Song J H, Wang J G. *Ind Eng Chem Res*, 2011, 50: 11023
- [16] Li K, Tang X L, Yi H H, Ning P, Kang D J, Wang C. *Chem Eng J*, 2012, 192: 99
- [17] Qi G S, Yang R T. *J Catal*, 2003, 217: 434
- [18] Qi G S, Yang R T. *Appl Catal B*, 2003, 44: 217
- [19] Irfan M F, Goo J H, Kim S D. *Appl Catal B*, 2008, 78: 267
- [20] Wu Z B, Tang N, Xiao L, Liu Y, Wang H Q. *J Colloid Interface Sci*, 2010, 352: 143
- [21] Xu W Q, Zhao J, Wang H R, Zhu T Y, Li P, Jing P F. *Acta Phys-Chim Sin* (徐文青, 赵俊, 王海蕊, 朱廷钰, 李鹏, 荆鹏飞. 物理化学学报), 2013, 29: 385
- [22] Tang X L, Hao J M, Yi H H, Li J H. *Catal Today*, 2007, 126: 406
- [23] Pinna F. *Catal Today*, 1998, 41: 129
- [24] Li G Q, Liu C Y, Liu Y. *Appl Surf Sci*, 2006, 253: 2481
- [25] Ettireddy P R, Ettireddy N, Mamedov S, Boolchand P, Smirniotis P G. *Appl Catal B*, 2007, 76: 123
- [26] Gallardo-Amores J M, Armaroli T, Ramis G, Finocchietti E, Busca G. *Appl Catal B*, 1999, 22: 249

Graphical Abstract

Chin. J. Catal., 2014, 35: 120–126 doi: 10.1016/S1872-2067(12)60726-8

Influence of the TiO_2 crystalline phase of $\text{MnO}_x/\text{TiO}_2$ catalysts for NO oxidation

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Mn-based catalyst supported on P25 TiO_2 was more active for NO oxidation than those supported on anatase and rutile TiO_2 , achieving 83% of NO conversion at 300 °C and 20000 h^{-1} of GHSV.

- [27] Stobbe E R, De Boer B A, Geus J W. *Catal Today*, 1999, 47: 161
- [28] Morales M R, Barbero B P, Cadus L E. *Appl Catal B*, 2006, 67: 229
- [29] Delimaris D, Ioannides T. *Appl Catal B*, 2008, 84: 303
- [30] Tang X L, Hao J M, Xu W G, Li J H. *Catal Commun*, 2007, 8: 329
- [31] Atribak I, Bueno-López A, García-García A, Navarro P, Frías D, Montes M. *Appl Catal B*, 2010, 93: 267
- [32] Cimino A, Indovina V. *J Catal*, 1974, 33: 493
- [33] Sultana A, Sasaki M, Hamada H. *Catal Today*, 2012, 185: 284
- [34] Smirniotis P G, Sreekanth P M, Peña D A, Jenkins R G. *Ind Eng Chem Res*, 2006, 45: 6436
- [35] Park E, Chin S, Jeong J, Jurng J. *Microporous Mesoporous Mater*, 2012, 163: 96
- [36] Carja G, Kameshima Y, Okada K, Madhusoodana C D. *Appl Catal B*, 2007, 73: 60
- [37] Kapteijn F, Singoredjo L, Andreini A, Moulijn J A. *Appl Catal B*, 1994, 3: 173
- [38] Trawczyński J, Bielak B, Miśta W. *Appl Catal B*, 2005, 55: 277
- [39] Leith I R, Howden M G. *Appl Catal*, 1988, 37: 75

TiO₂晶相对MnO_x/TiO₂催化剂催化NO氧化性能的影响

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摘要: 以浸渍在不同晶相TiO₂ (金红石型(R)、锐钛矿型(A)和P25型(P))上的锰基催化剂为对象, 研究了TiO₂晶相对MnO_x/TiO₂催化剂催化NO氧化活性的影响。结果表明, MnO_x/TiO₂(P)催化剂活性最高, NO转化率在300 °C及GHSV = 20000 h⁻¹条件下可达83%。各催化剂活性顺序为MnO_x/TiO₂(P) > MnO_x/TiO₂(A) > MnO_x/TiO₂(R)。采用X射线粉末衍射、场发射扫描电子显微镜、X射线光电子能谱、H₂程序升温还原和O₂程序升温脱附等手段研究了TiO₂晶相影响MnO_x/TiO₂催化剂催化活性的作用机理。结果表明, 相比于A和R型TiO₂, P型TiO₂能够增加MnO_x在其表面的分散度并抑制催化剂颗粒的团聚和粘连, 且更有利于Mn₂O₃的生成, 而后者催化NO氧化活性比其它MnO_x更高; 此外, P型TiO₂可以增加MnO_x尤其是Mn₂O₃的还原性, 并可促进O₂⁻从M³⁺-O键的脱附。

关键词: 一氧化氮氧化; 锰氧化物; 二氧化钛; 晶型; 污染控制

收稿日期: 2013-08-21. 接受日期: 2013-09-23. 出版日期: 2014-01-20.

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本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).