

[Communication]

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以 ZrO_2-TiO_2 为载体的整体式锰基催化剂应用于低温 NH_3 -SCR 反应

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摘要: 以 MnO_2 为活性组分, Fe_2O_3 为助剂, 制备了以 TiO_2 及 ZrO_2-TiO_2 为载体的整体式催化剂. 考察了它们在不同温度焙烧后应用于富氧条件下, NH_3 选择性催化还原(NH_3 -SCR)氮氧化物的低温反应性能和高温稳定性. 用 X 射线衍射(XRD)实验、比表面积测定(BET)、储氧性能测定(OSC)及程序升温还原(H_2 -TPR)等方法对催化剂进行了表征. 结果表明, 以 ZrO_2-TiO_2 为载体的催化剂具有很好的高温热稳定性, 并具有较高的比表面积和储氧能力, 同时具有较强的氧化能力. 催化剂的活性测试结果表明, 以 ZrO_2-TiO_2 为载体的整体式锰基催化剂明显地提高了 NH_3 -SCR 反应的低温活性, 具有良好的应用前景.

关键词: ZrO_2-TiO_2 ; 低温 NH_3 -SCR; NO ; NH_3 ; 整体式催化剂

中图分类号: O643

Monolith Manganese-Based Catalyst Supported on ZrO_2-TiO_2 for NH_3 -SCR Reaction at Low Temperature

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Abstract: Monolith catalysts were prepared using TiO_2 and ZrO_2-TiO_2 as supports with MnO_2 as active component and Fe_2O_3 as promoter. The catalytic activities at low temperature and stability at high temperature for selective catalytic reduction of NO_x with NH_3 (NH_3 -SCR) in the presence of excessive O_2 were studied after the catalysts calcined at different temperatures. The catalysts were characterized by X-ray diffraction (XRD), specific surface area measurements (BET), oxygen storage capacity (OSC), and temperature programmed reduction (H_2 -TPR). The results indicated that the catalyst supported on ZrO_2-TiO_2 had excellent stability at high temperature, and possessed high specific surface area and oxygen storage capacity, and had strong redox property. The results of the catalytic activities indicated that the monolith manganese-based catalyst using ZrO_2-TiO_2 as support had evidently improved the activity of NH_3 -SCR reaction at low temperature, and it showed great potential for practical application.

Key Words: ZrO_2-TiO_2 ; Low-temperature NH_3 -SCR; NO ; NH_3 ; Monolith catalyst

Nowadays, the selective catalytic reduction (SCR) of NO_x with NH_3 in the presence of excessive O_2 has generally been recognized as the most effective and widely commercialized removal technology of NO_x ^[1]. The commercial catalyst for this process is $V_2O_5/WO_3/TiO_2$ catalyst; however, this catalyst is active within a narrow temperature window of 300–400 °C, consequently, it is necessary to local the SCR unit upstream of the desulfurizer and electrostatic precipitator to avoid re-heating of the flue gas from

stationary sources. Therefore, there is increasing interest in developing low-temperature catalysts capable of working downstream of the particle removal equipment and the desulfuration device of flue gases without the need for re-heating the gas. As for the automotive diesel engines, the exhaust temperatures are generally low (120–350 °C), but the highest exhaust temperatures are typically at about 800 °C^[1]; so it is necessary to develop novel catalyst which works well at low-temperature and has good

Received: February 18, 2008; Revised: April 23, 2008; Published on Web: May 16, 2008.

English edition available online at www.sciencedirect.com

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国家自然科学基金(20273043)和国家自然科学基金重点项目(20333030)资助

stability at high temperature.

Some catalysts containing transition metals (Mn, Cu, Cr, Co, Fe, V, Ni) have been investigated for the low-temperature SCR reaction in recent years^[2], and it was found that the metal manganese has perfect catalytic activity. A series of unitary compounds including TiO₂, Al₂O₃, SiO₂, as well as active carbon have been studied as the support of the low temperature SCR catalyst^[3-7]. TiO₂ has good performance and resistance to sulfur poisoning^[1,3]. Recently, Qi *et al.*^[8] reported that manganese-iron oxide supported on TiO₂ was highly active for low-temperature SCR of NO with NH₃ with 100% selectivity to N₂ at a high space velocity. However, compared with the small specific surface area and poor thermal stability of TiO₂, the binary compounds ZrO₂-TiO₂ display larger specific surface area and stronger surface acidity^[9], and is also resistant to sulfur poisoning^[10]; moreover, the Mn-based catalyst in low temperature NH₃-SCR reaction using binary compounds as support has not been found in the published reports, and the reports about the monolith catalyst for low-temperature SCR are very limited. In the experiments, the monolith catalyst with manganese-iron oxide as active component supported on ZrO₂-TiO₂ was attempted for low-temperature SCR reaction.

1 Experimental

1.1 Preparation of carrier materials and catalysts

Carrier materials TiO₂ (T) and ZrO₂-TiO₂ (ZT) were prepared by the co-precipitation method from the corresponding chemicals, namely, TiOSO₄·2H₂O (CR) and Zr(NO₃)₄·3H₂O (AR) at appropriate ratios, and calcined at 500 °C for 3 h. Fe (10%, *w*)-Mn (10%, *w*)-based transition metals from the corresponding chemicals, namely, Fe(NO₃)₃·9H₂O (AR) and Mn(NO₃)₂ (AR) were supported on TiO₂ and ZrO₂-TiO₂ by incipient wetness and calcined at 500 or 800 °C for 3 h, and the as-prepared catalysts were coated on honeycomb cordierites and calcined at 500 °C for 3 h in air.

1.2 Catalytic activity measurements

The catalytic activity measurement was carried out in a fixed-bed continuous flow microreactor. The concentration of the gas was monitored online by a five-component analyzer FGA-4015 (made in Foshan, China) before and after the gas passed the microreactor. The compositions of feed gas were as follows: 0.1% NO, 0.1% NH₃, 3% O₂, balance Ar. The total flow rate was 420 mL·min⁻¹, and the gas hourly space velocity (GHSV) was 10000 h⁻¹.

1.3 Characterization of the catalysts

The XRD analysis was determined on Japan science D/max-rA diffractometer. Using Cu K_α radiation (λ=0.15406 nm). The tube voltage and current were 40 kV and 100 mA, respectively. X-ray spectra were measured from 2θ=20° to 2θ=70°. BET surface area measurements were made on a ZXF-05 automatic surface analyzer (Chemical Industrial Academe of Northwest, China). The oxygen storage capacity (OSC) was measured by oxygen impulse adsorption technique, which was performed in self-

made experimental equipment. The temperature programmed reduction (TPR) experiment in hydrogen was performed in a self-made experimental equipment. The reduction of H₂ was determined by a thermal conductivity detector at a heating rate of 10 °C·min⁻¹ and a temperature range from 100 to 800 °C.

2 Results and discussion

2.1 Results of catalytic activities

The results of catalytic activities are shown in Fig.1 (Mn-Fe/T5: Mn-Fe/TiO₂ calcined at 500 °C; Mn-Fe/T8: Mn-Fe/TiO₂ calcined at 800 °C; Mn-Fe/ZT5: Mn-Fe/ZrO₂-TiO₂ calcined at 500 °C; Mn-Fe/ZT8: Mn-Fe/ZrO₂-TiO₂ calcined at 800 °C). It can be seen that catalyst Mn-Fe/ZT5 has the widest reaction window and the biggest NO conversion (nearly 100% at 240 °C). The light-off temperature of the catalyst Mn-Fe/ZT5 is 118 °C, which is much lower than that of the catalyst Mn-Fe/T5 (150 °C). When the catalysts were calcined at high temperature (800 °C), the light-off temperature of the catalyst Mn-Fe/ZT8 is also at 133 °C, even lower than that of Mn-Fe/T5 calcined at 500 °C; however, Mn-Fe/T8 has the lowest activity when calcined at 800 °C. It is clear that ZrO₂-TiO₂ has promoted both the activity and the thermal stability of the catalyst, and the experimental results are better than that of the other monolith manganese-based catalysts of SCR in the published report^[11].

The activities of the best catalyst Mn-Fe/ZT5 at different GHSVs have been detected, and the results are shown in Fig.2. According to Fig.2, when the GHSV of the reaction is increased, the light-off temperature, the reaction window, and the biggest NO conversion of Mn-Fe/ZT5 are decreased. When the GHSV is at 10000, 20000, 36000, and 55000 h⁻¹, the light-off temperature is at 118, 138, 152, and 182 °C; and the biggest NO conversion is 99.5%, 94%, 88%, and 78%, respectively. It is shown that the catalytic activities of Mn-Fe/ZT5 are still good even at higher GHSV (55000 h⁻¹).

Water vapor is one of the main components in flue gases and often leads to catalyst deactivation. The effect of H₂O on the

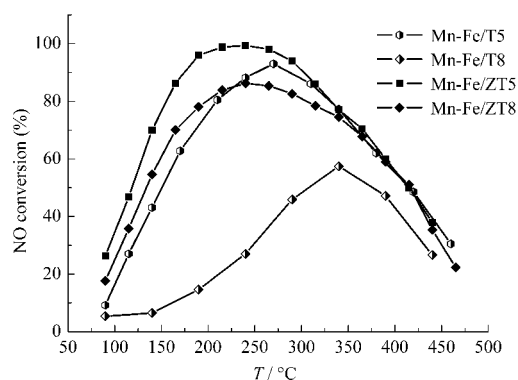


Fig.1 Catalytic activities of different catalysts in the NH₃-SCR reaction

Mn-Fe/T5: Mn-Fe/TiO₂ calcined at 500 °C; Mn-Fe/T8: Mn-Fe/TiO₂ calcined at 800 °C; Mn-Fe/ZT5: Mn-Fe/ZrO₂-TiO₂ calcined at 500 °C; Mn-Fe/ZT8: Mn-Fe/ZrO₂-TiO₂ calcined at 800 °C

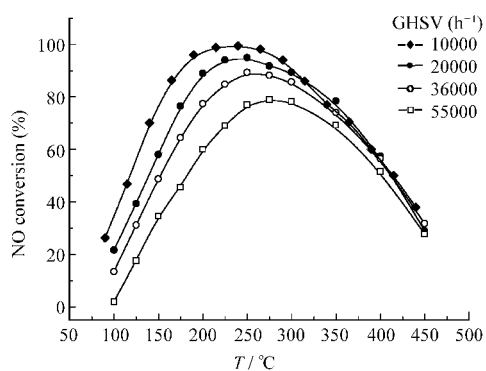


Fig.2 Activities of catalyst Mn-Fe/ZT5 at different GHSVs

SCR activities of Mn-Fe/ZT5 is further studied, and the results are shown in Fig.3. It can be seen that when 10% H₂O is added to the reaction gas, the conversion of NO decreased slightly from 99% to 95% in 89 min. After cutting off the H₂O, the activity was restored to its original level in 98 min. This indicates that the influence of H₂O on the SCR activities of catalyst Mn-Fe/ZT5 is not serious and reversible.

2.2 XRD results of the catalysts

Fig.4 shows the XRD patterns of the catalysts Mn-Fe/TiO₂ and Mn-Fe/ZrO₂-TiO₂ calcined at 500 and 800 °C, respectively. According to Fig.4(A), catalyst Mn-Fe/T5 is obviously presented as anatase after calcination at 500 °C. No visible manganese and iron oxide phases can be observed; it is because the loadings of these two metals are too low to be detected^[8,12], indicating that they are dispersed uniformly. When the calcination temperature is raised to 800 °C, Mn-Fe/T8 is obviously presented as rutile, and the diffraction peak of Fe₂O₃ emerges, showing that iron oxide has been sintered. However, manganese oxide can not be observed, suggesting that iron oxide can easily be sintered compared to manganese at high temperature. The XRD results show that Mn-Fe/T5 is presented as anatase and Mn-Fe/T8 is presented as rutile, so the catalytic activity of Mn-Fe/T5 is better than that of Mn-Fe/T8 due to their different textural properties (Table 1).

According to Fig.4(B), no anatase peak can be seen over the catalyst Mn-Fe/ZT5, only a wide peak can be observed after calcination at 500 °C. So Mn-Fe/ZT5 is presented as low crys-

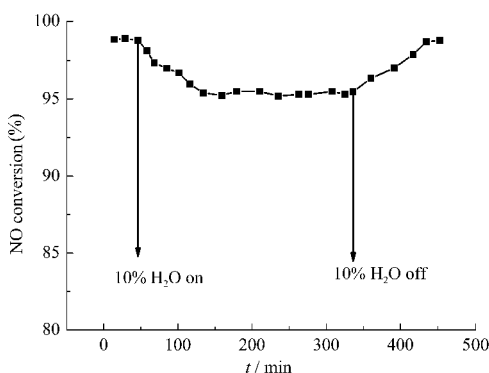


Fig.3 Effects of H₂O on the activities of Mn-Fe/ZT5

reaction conditions: 0.1% NO, 0.1% NH₃, 3% O₂, 10% H₂O, balance Ar; total flow rate: 420 mL·min⁻¹; GHSV: 10000 h⁻¹; T=250 °C

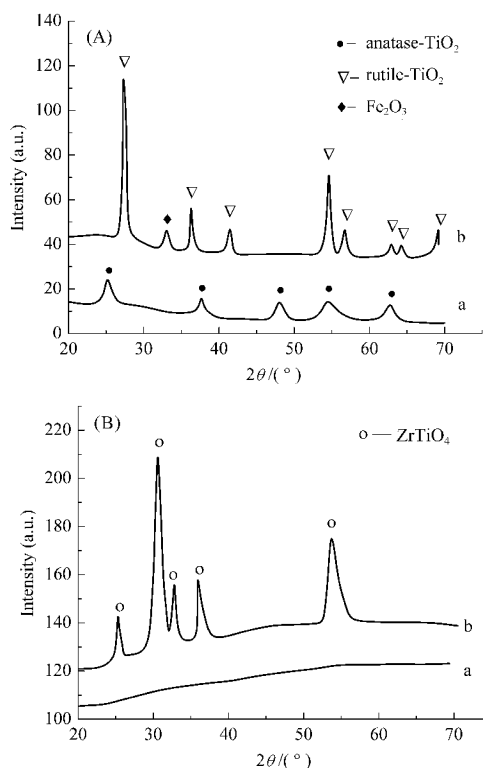


Fig.4 XRD patterns of Mn-Fe/TiO₂ (A) and Mn-Fe/ZrO₂-TiO₂ (B) calcined at 500 °C (a) and 800 °C (b)

talline (amorphous). The diffraction peaks of manganese and iron oxides cannot be seen either. When the calcination temperature is raised to 800 °C, no rutile can be seen over Mn-Fe/ZT8, and it is presented as ZrTiO₄. However, the diffraction peaks of manganese and iron oxides cannot be observed even when they are calcined at 800 °C, indicating that there are strong interactions between the two metal oxides^[8] on ZrO₂-TiO₂, and the results indicate that Mn-Fe/ZrO₂-TiO₂ has good stability when calcined at high temperature.

2.3 BET surface area measurements of the catalysts

The BET surface areas and pore volumes of the catalysts calcined at different temperatures are listed in Table 1. According to Table 1, the surface areas and pore volumes of the catalysts calcined at 500 °C are evidently larger than that of catalysts calcined at 800 °C. At each temperature, Mn-Fe/ZT has higher surface area and pore volume than Mn-Fe/T. The results indicate that the addition of ZrO₂ into TiO₂ increases both the surface area and pore volumes of the catalysts. According to the XRD re-

Table 1 Surface area (S_{BET}), total pore volume (V), and oxygen storage capacity (OSC) of the catalysts calcined at different temperatures

| Sample | T/°C | | | | | |
|----------|---|-------|-------------------------------------|------|--|-------|
| | 500 | 800 | 500 | 800 | 500 | 800 |
| | $S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$ | | $V/(\text{mL} \cdot \text{g}^{-1})$ | | $\text{OSC}/(\mu\text{mol} \cdot \text{g}^{-1})$ | |
| Mn-Fe/T | 30.75 | 0.321 | 0.06 | 0.01 | 383.9 | 26.09 |
| Mn-Fe/ZT | 175.4 | 10.67 | 0.25 | 0.08 | 459.9 | 294.5 |

Mn-Fe/T: Mn-Fe/TiO₂; Mn-Fe/ZT: Mn-Fe/ZrO₂-TiO₂

sults, Mn-Fe/ZT is presented as amorphous after calcination at 500 °C, and thus, it has high surface areas and pore volume; Mn-Fe/ZT calcined at 800 °C is presented as ZrTiO₄, and therefore, the surface area and pore volume become small. Mn-Fe/T is presented as anatase at 500 °C and as rutile at 800 °C, and the surface area and pore volume become very small at high temperature. From the results of BET and the tests of catalytic activities, it can be seen that, in this reaction system, the surface area and pore volume of the catalysts have some influences on the catalytic activity; however, they are not the most important factors that influence the activity.

2.4 Results of OSC of catalysts

The results of oxygen storage capacity (OSC) are listed in Table 1. It is worth noting that the addition of ZrO₂ into TiO₂ increases oxygen storage capacity of the catalysts at each temperature, especially at 800 °C. It has been proved that CeO₂ possesses some OSC; however, when ZrO₂, which nearly has no OSC, is added into CeO₂, the OSC is increased obviously, because the microcosmic structure of CeO₂ has been changed, so the mobility of the oxygen is improved^[13]. In the experiments, the addition of ZrO₂ into TiO₂ has changed the microcosmic structure of the support, and leads to different interactions between the Mn-Fe and the support; so the mobility of the oxygen may be changed and the OSC is increased. It is ordinarily regarded that when some NO₂ takes part in the SCR reaction, the SCR reaction will be much faster^[14], that is, when some NO is oxidized to NO₂, the SCR reaction rate will be increased considerably. Although the reaction system is in the presence of excessive O₂ and the oxidation of NO ($\text{NO} + 1/2\text{O}_2 \rightarrow \text{NO}_2$) can be realized in the view of thermodynamics, however, it is an exothermic reaction and difficult to be carried out at high temperature^[15]. The addition of ZrO₂ into TiO₂ has increased OSC of the catalysts, and the oxygen species could be changed when they were stored in oxygen storage material and then released to the system^[16]. It is easier for NO to react with the active O₂ to form NO₂. So the catalytic activity is enhanced^[17].

2.5 Results of H₂-TPR of catalysts

According to Fig.5, two evident hydrogen consumption peaks can be seen on the catalysts Mn-Fe/T5, Mn-Fe/ZT5, and Mn-Fe/ZT8 in the temperature range of 200–540 °C. Because the reduction temperature of Fe⁴⁺→Fe³⁺ is close to that of Mn⁴⁺→Mn³⁺, so the first reduction peak before 400 °C maybe assigned to the reduction of both Fe⁴⁺→Fe³⁺ and Mn⁴⁺→Mn³⁺; moreover, the reduction temperature of Mn³⁺→Mn²⁺ is also close to that of Fe³⁺→Fe²⁺, so the second peak around 400–540 °C can be regarded as the reduction of both Mn³⁺→Mn²⁺ and Fe³⁺→Fe²⁺^[18,19]. Unlike the first three catalysts, the reduction peak of Mn-Fe/T8 disappears in the temperature range of 200–400 °C, and the reduction peaks present in the temperature range of 400–800 °C, indicating that there exists strong interaction between the active component and rutile TiO₂^[20]. It can be seen that the redox ability of the Mn-Fe/T8 is the worst. However, from the results of TPR, the redox properties of these catalysts decrease in the order: Mn-Fe/

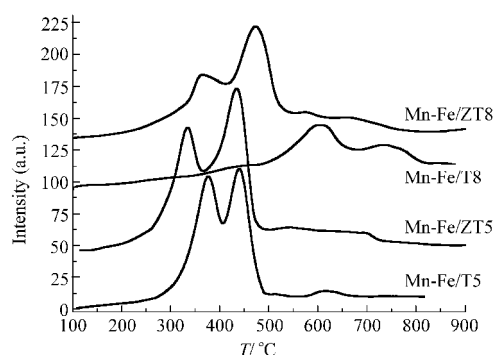


Fig.5 H₂-TPR results of the catalysts

ZT5>Mn-Fe/T5>Mn-Fe/ZT8>Mn-Fe/T8. The results are in agreement with both the OSC measurements and catalytic activity measurements.

It is ordinarily regarded that, in NH₃-SCR reaction, NH₃ was primarily adsorbed on the catalyst surface either on Brønsted acid site^[21] or on Lewis acid site^[22], and then is partially oxidized and dehydrogenated to be combined with NO to form NH₃NO^[21] or NH₂NO(ads)^[22] and decomposed to N₂ and H₂O. So it is a crucial step for NH₃ to be partially oxidized. Lietti *et al.*^[23,24] pointed out repeatedly that the activity of SCR reaction was closely related to the redox property of catalyst surface. In addition, the strong redox property may enhance the rate of the oxidation of NO to NO₂ and promote the activity of the reaction^[25]. So in the experiments, the redox ability of the catalyst should be the primary reason which influences the catalytic activity.

3 Conclusions

The study revealed that manganese-based catalyst supported on ZrO₂-TiO₂ had stronger redox property and possessed more OSC than the catalyst supported on TiO₂. It evidently improved stability of catalyst at high temperature and had good activity of SCR at low temperature.

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