

[Communication]

www.whxb.pku.edu.cn

新型铁锰复合氧化物催化低温脱除 NO_x陈志航 李雪辉* 杨青 李华 高翔
江燕斌 王芙蓉 王乐夫

(华南理工大学化学与化工学院, 广东省绿色化学产品技术重点实验室, 广州 510640)

摘要: 采用溶胶-凝胶法合成了一系列铁锰复合氧化物催化剂, 利用 X 射线衍射(XRD)对催化剂的活性相态进行研究, 并考察了铁锰摩尔比及焙烧温度对催化性能的影响. 结果表明, 该催化剂体系在低温(80–220 °C)下选择性催化氨还原 NO_x 反应中显示出优异的活性. 其中 Fe(0.4)-MnO_x(500)(即摩尔比 $n(\text{Fe})/(n(\text{Fe})+n(\text{Mn}))=0.4$, 焙烧温度 500 °C)催化剂具有最佳低温催化活性, 在空速 30000 h⁻¹, 温度 80 °C 的条件下, NO_x 转化效率达到 90.6%, N₂ 选择性达 100%. Fe-MnO_x 复合氧化物催化剂中形成的 Fe₃Mn₃O₈ 晶相有利于促进 NO 氧化成 NO₂, 从而提高低温选择性催化还原的活性.

关键词: 铁锰复合氧化物; 低温; 选择性催化还原; NO_x; 氨

中图分类号: O643

Removal of NO_x Using Novel Fe-Mn Mixed-Oxide Catalysts at Low TemperatureCHEN Zhi-Hang LI Xue-Hui* YANG Qing LI Hua GAO Xiang JIANG Yan-Bin
WANG Fu-Rong WANG Le-Fu

(Guangdong Provincial Key Laboratory for Green Chemical Product Technology, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China)

Abstract: A series of novel Fe-Mn mixed-oxide catalysts were prepared by a sol-gel method. X-ray diffraction (XRD) was used to characterize the active phase and the effects of the $n(\text{Fe})/(n(\text{Fe})+n(\text{Mn}))$ molar ratio as well as the calcination temperature on the catalytic properties were investigated. This catalytic system had good selective catalytic reduction (SCR) properties for NO_x by ammonia at low temperatures (80–220 °C). We achieved 90.6% conversion of NO_x with 100% selectivity of N₂ on an Fe(0.4)-MnO_x mixed oxide (the molar ratio of $n(\text{Fe})/(n(\text{Fe})+n(\text{Mn}))=0.4$ and calcined at 500 °C) at 80 °C with a space velocity of 30000 h⁻¹. XRD characterization results showed that a new Fe₃Mn₃O₈ phase was generated for Fe-MnO_x. The oxidation activity of NO to NO₂ by O₂ on these Fe-MnO_x catalysts suggested that the existence of Fe₃Mn₃O₈ was beneficial for an increased oxidation rate of NO to NO₂, which improved the activity of low-temperature SCR.

Key Words: Fe-Mn mixed-oxide; Low temperature; Selective catalytic reduction; NO_x; NH₃

Selective catalytic reduction (SCR)^[1–4] plays a very important role in eliminating NO_x (nitrogen oxides, including NO, NO₂, and N₂O) emissions from stationary source (e.g. power plants). For instance, SCR of NO with NH₃ was used as a mature and high efficient technology for flue gas denitrification in power plants^[5,6].

The general reaction and main side reaction are as follows:



Typical commercialized catalysts for SCR of NO are V₂O₅-WO₃(MoO₃)/TiO₂^[7,8] which are the most studied and widely used

Received: December 21, 2008; Revised: January 19, 2009; Published on Web: February 25, 2009.

*Corresponding author. Email: cexhli@scut.edu.cn; Tel: +8620-87114707.

国家自然科学基金(20876063)和广东省自然科学基金(06025654)资助项目

commercial catalysts, and these kinds of catalysts should be operated optimally at about 350 °C. Commercial SCR system was divided into two main categories, one was the SCR device placed in the upstream of dust controllers, the other was in the downstream of dust controllers and before the desulfurization units where catalysts could work at the best temperature range. But in this section the catalysts were susceptible to deactivation from high concentrations of SO₂ and dust (e.g., K₂O, CaO, and As₂O₃), which shortened the service life of the catalyst. Another new one was placed downstream of dust controllers and desulfurization units to avoid above problems. Simultaneously, the temperature of flue gas dropped to below 200 °C after the desulfurization unit, then a large heat transfer unit need to be installed so that the flue gas temperature could adapt to traditional catalysts. Thus, developing highly active catalysts for low-temperature SCR (<200 °C) has obvious superiority and it becomes a research focus.

Many researches showed that elemental manganese played an important part at low temperature SCR process and some of its mixed-oxide catalysts had relatively higher activity, such as MnO_x^[9], MnO_x/TiO₂^[10], Fe-Mn/TiO₂^[11,12], CuO_x-MnO_x^[13], and MnO_x-CeO₂^[14]. Although results obtained are significant for further screening of catalysts, their optimal active temperature is relatively high above 150 °C, the selectivity, sulfur and water tolerance should be improved intensively as well. Qi *et al.*^[11] prepared 10% Fe-10% Mn/TiO₂ (*w*, mass fraction) catalyst by impregnation method and 78% of NO conversion was obtained at 80 °C (0.1% NO (φ , volume fraction, the same behind), 0.1% NH₃ and gas hourly space velocity (GHSV)=15000 h⁻¹); Long and his coworkers^[15] reported that the conversion of NO on Fe-Mn catalyst prepared by coprecipitation method was 74% at 80 °C (0.1% NO, 0.1% NH₃ and GHSV=15000 h⁻¹). In the presence of SO₂ and water, the NO conversion activity decreased significantly. In this communication, various Fe-Mn mixed-oxide catalysts were prepared by sol-gel method and applied for low temperature NO reduction with NH₃. The effect of molar ratio $n(\text{Fe})/(n(\text{Fe})+n(\text{Mn}))$ and calcination temperature on NO_x conversions and the structures of phase were studied.

1 Experimental

1.1 Catalyst preparation

2 mol·L⁻¹ citric acid (99.5%) aqueous solution acting as complexing agent was added to the mixture (98.5%) of ferric nitrate and manganese acetate (99.0%) salt with equal molar ratio of citric acid to metal (the total mole of elemental iron and manganese). The above mixture was stirred at room temperature for 1.0 h and then dried at 120 °C for 12 h, the resulting porous foam-like solid was then calcined at 600 °C for 5.0 h under atmosphere in muffle furnace. Finally, the samples were crushed and sieved to 60–100 mesh. So prepared catalyst is denoted as Fe(*y*)-MnO_x (*T*), where *y* represents the molar ratio $n(\text{Fe})/(n(\text{Fe})+n(\text{Mn}))$ and *T* denotes the calcinations temperature (°C), e.g., Fe(0.4)-MnO_x (500). Pure iron oxides (FeO_x) and manganese oxides (MnO_x) were prepared by the same procedure; mechanically mixed cata-

lyst, FeO_x-MnO_x, was prepared by the mixture of pure FeO_x and MnO_x with equal molar ratio of Fe to Mn and then calcined at 600 °C for 5.0 h.

1.2 Catalytic activity test

The SCR activity measurement was carried out in a fixed bed quartz reactor. About 2.7 g catalyst was used in each run. The typical reactant gas composition was as follows: 0.1% NO, 0.1% NH₃, 3% O₂, and balance N₂ or He (used for selectivity experiments). The total flow rate was 860 mL·min⁻¹ (under ambient conditions), thus, a very high GHSV referred to powder catalyst was obtained (30000 h⁻¹). The compositions of the feed gases and the effluent streams were monitored continuously using on-line sensors with emission monitors: gas analysis (SWG-300, MRU, Germany) for NO, NO₂, and O₂. Data were obtained with the average value in 10 min after the catalytic process was hold 30 min in steady state. The effluent streams were also analyzed by a gas chromatograph (4890D, HP, USA) at 60 °C with 0.5 nm molecular sieve column for N₂ and Porapak Q column for N₂O. From the concentration of the gases at steady state, the NO_x conversion ($\delta(\text{NO}_x)$) and N₂ selectivity ($S(\text{NO}_x)$) are calculated according to the following equations:

$$\delta(\text{NO}_x) = \frac{\varphi(\text{NO}_x)_{\text{in}} - \varphi(\text{NO}_x)_{\text{out}}}{\varphi(\text{NO}_x)_{\text{in}}} \times 100\% \quad (3)$$

$$S(\text{NO}_x) = \frac{\varphi(\text{N}_2)_{\text{out}}}{\varphi(\text{N}_2)_{\text{out}} + \varphi(\text{N}_2\text{O})_{\text{out}}} \times 100\% \quad (4)$$

$\varphi(\text{NO}_x) = \varphi(\text{NO}) + \varphi(\text{NO}_2)$, and the subscripts in and out indicated the inlet concentration and outlet concentration at steady state, respectively. The experiment of NO oxidation to NO₂ was performed in the fixed-bed quartz reactor. The reactant gas composition was as follows: 0.1% NO, 3% O₂, and balance N₂; the total flow rate was 860 mL·min⁻¹ (ambient conditions). About 2.7 g sample were used each run. NO conversion to NO₂ ($\delta(\text{NO})$) was calculated by using the following equation:

$$\delta(\text{NO}) = \frac{\varphi(\text{NO}_2)_{\text{out}} - \varphi(\text{NO})_{\text{out}}}{\varphi(\text{NO}_x)_{\text{in}}} \times 100\% \quad (5)$$

1.3 Characterization of catalysts

X-ray diffraction (XRD) patterns were obtained using a Auto X-ray diffractometer Rigaku (D/MAX-3A, Rigaku, Japan) with Cu K α radiation ($\lambda=0.15418$ nm). Intensity data were collected over a 2θ range of 5°–85° with a 0.05° step size and a counting time of 1.0 s per point. The XRD phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files.

2 Results and discussion

2.1 Activities of different catalysts and their X-ray diffraction analyses

The performances of pure FeO_x, MnO_x oxides, Fe(0.5)-MnO_x mixed-oxide catalysts and mechanically mixed FeO_x-MnO_x mixture catalyst for selective catalytic reduction of NO_x with NH₃ in the presence of excess oxygen are shown in Fig.1. Pure MnO_x catalyst owned a certain catalytic activity of 45.2% NO_x conversion under the temperature of 80 °C which accorded well with previous report^[16], while pure FeO_x with negligible activity(5.4%). Under relatively high gas hourly space velocity (GHSV=30000

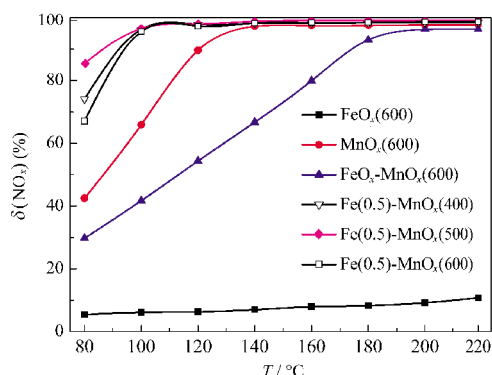


Fig.1 Catalytic reduction conversion of NO_x on FeO_x, MnO_x, FeO_x-MnO_x, and Fe(0.5)-MnO_x catalysts calcined at various temperatures

reaction conditions: $\varphi(\text{NO})=\varphi(\text{NH}_3)=0.1\%$, $\varphi(\text{O}_2)=3\%$, GHSV=30000 h⁻¹

h⁻¹), Fe(0.5)-MnO_x(600) catalyst showed very high NO_x conversion, i.e. 67.1% conversion of NO_x with 100% selectivity of N₂ at 80 °C, which implied that the mixed oxides prepared by sol-gel technique were able to improve the activity of low temperature SCR significantly. Fig.2 shows the XRD patterns of the above catalysts. FeO_x and MnO_x samples give sharp XRD peaks representing Fe₂O₃ (ICDD PDF #72-0469 2 θ =33.1°, 35.6°, and 54.0°) and Mn₂O₃ (ICDD PDF #89-4837 2 θ =36.1°, 59.9°, and 32.3°), respectively. The activity of FeO_x-MnO_x mixture at low temperature SCR was lower than that of MnO_x at the same reaction conditions. XRD pattern of FeO_x-MnO_x is attributed to the mixture of Fe₂O₃ and Mn₂O₃ (ICDD PDF #89-4836 2 θ = 32.9°, 55.1°, and 65.8°), no new crystalline phase generated. For Fe(0.5)-MnO_x(600) catalyst (Fig.2f), a brand new phase, Fe₃Mn₃O₈ (ICDD PDF #75-0034 2 θ =35.0°, 56.2°, and 61.7°) become the dominated

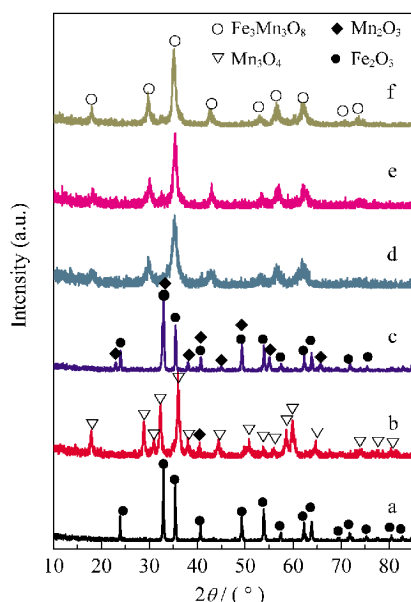


Fig.2 XRD patterns of FeO_x, MnO_x, FeO_x-MnO_x and Fe(0.5)-MnO_x catalysts calcined at various temperatures

(a) FeO_x(600), (b) MnO_x(600), (c) FeO_x-MnO_x(600), (d) Fe(0.5)-MnO_x(400), (e) Fe(0.5)-MnO_x(500), (f) Fe(0.5)-MnO_x(600)

phase. Above results showed that the mixed oxides have generated new Fe₃Mn₃O₈ phase after the addition of iron and Fe₃Mn₃O₈ might be the main active center in the mixed-oxide catalysts.

For the mixed oxides, the calcination temperature was an important factor to affect the formation of crystalline phase^[17]. Fig.2 (d-f) shows the XRD patterns of Fe(0.5)-MnO_x with equal molar ratio of Fe to Mn that accords with the stoichiometry of Fe₃Mn₃O₈ calcined at different temperatures. It was clear that the XRD peaks of all catalysts calcined at different temperature could be attributed to Fe₃Mn₃O₈. With the increasing of calcination temperature, the strength of the XRD peaks of Fe₃Mn₃O₈ became evident and sharp, which was explicit that the crystalline of mixed oxides was improved. Fig.1 (▽, ◆, □) shows the effect of calcination temperature on the activities of Fe(0.5)-MnO_x catalysts. NO_x conversions reached nearly 100% on every catalyst above 140 °C. Catalyst calcined at 500 °C had the optimum activity at declined temperature (85.4% NO_x conversion at 80 °C), and catalyst calcined at 600 °C with much more perfect lattice displayed relatively low activity. According to the above discussion, Fe₃Mn₃O₈ was the active center of mixed oxide catalysts at low temperature SCR reaction. Hence, it was thought that the possible existence of some lattice defects that could not be detected by XRD might play an important role in this low temperature SCR process.

2.2 Effect of the molar ratio of Fe to Mn on catalytic activities

The molar ratio of Fe to Mn was 1 for the above Fe(0.5)-MnO_x catalyst, which was accorded with the stoichiometry of Fe₃Mn₃O₈ mixed oxide. Thus, a series of Fe-MnO_x catalysts with different molar ratios of $n(\text{Fe})/n(\text{Fe})+n(\text{Mn})$ were prepared, calcined at 500 °C. Their catalytic performances were investigated (Fig.3). Experiments showed that NO_x conversion reached nearly 100% above 120 °C for each Fe-MnO_x catalyst except for Fe(0.1)-MnO_x. But, there were evident differences of activities between these catalysts under 100 °C, their catalytic activities enhanced with the increasing of Fe molar ratio and the optimum catalytic activity emerged while the molar ratio of Fe to Mn reached 2:3 for Fe(0.4)-MnO_x. 90.6% and 99.3% conversions of NO_x were

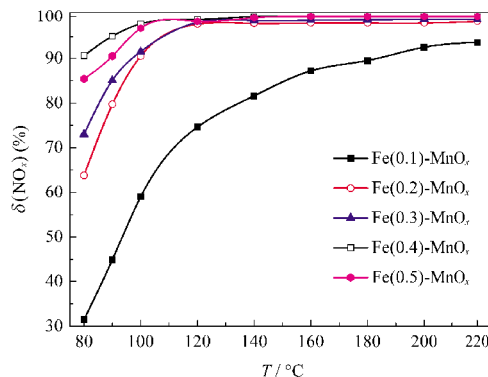


Fig.3 Effects of Fe content in Fe-MnO_x catalysts on NO_x conversion

All catalysts were calcined at 500 °C in air. reaction conditions: $\varphi(\text{NO})=\varphi(\text{NH}_3)=0.1\%$, $\varphi(\text{O}_2)=3\%$, and GHSV=30000 h⁻¹

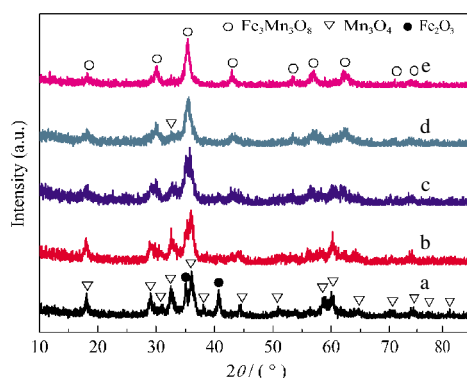


Fig.4 XRD patterns of various Fe-MnO_x catalysts calcined at 500 °C with different Fe contents

(a) Fe(0.1)-MnO_x, (b) Fe(0.2)-MnO_x, (c) Fe(0.3)-MnO_x, (d) Fe(0.4)-MnO_x, (e) Fe(0.5)-MnO_x

achieved at 80 and 100 °C, respectively, with 100% N₂ selectivity under the space velocity of 30000 h⁻¹ on the Fe(0.4)-MnO_x catalyst. Then, further increasing the Fe content resulted in the decline of the activities.

Fig.4 shows the XRD patterns of the above Fe-MnO_x catalysts calcined at 500 °C. Fe(0.1)-MnO_x could be considered as mixed oxides of Mn₃O₄ (majority) and Fe₂O₃ (minority). With increasing the Fe content, the XRD peak of Fe₃Mn₃O₈ phase enhanced regularly and the peak of Mn₃O₄ and Fe₂O₃ weakened gradually. For Fe(0.4)-MnO_x, the Fe₃Mn₃O₈ phase is dominant except one very weak diffraction peak of the Mn₃O₄. Fe(0.5)-MnO_x catalyst in which molar ratio of Fe to Mn accord with the stoichiometry of Fe₃Mn₃O₈ gave sharp XRD peaks contributing to Fe₃Mn₃O₈ phase and the manganese oxides had been transferred to Fe₃Mn₃O₈ by and large. But the low temperature SCR activity of Fe(0.5)-MnO_x was lower than Fe(0.4)-MnO_x obviously (Fig.5). This was similar to the activity result of Fe-MnO_x mixed oxides calcined at different temperatures (Fig.1) in which the activity of Fe(0.5)-MnO_x(600) with good crystallinity was lower than that of Fe(0.5)-MnO_x(400) with poor crystallinity. So it is implied that the special structure of Fe—O—Mn or Fe₃Mn₃O₈ phase with lattice defects in mixed oxides might be the catalytic reduction active center, and the existence of Fe could make mixed oxides better catalytic properties by modulating the electronic structure of Mn in Fe₃Mn₃O₈.

2.3 Oxidation activity of NO to NO₂

The oxidation activities of NO to NO₂ on catalysts doped with various ratio of $n(\text{Fe})/(n(\text{Fe})+n(\text{Mn}))$ from 80 to 160 °C are shown in Fig.5. With the increasing of iron content doped in Fe-MnO_x catalysts, the NO oxidation activity improved significantly and peaked on Fe(0.4)-MnO_x catalyst. It is concluded that the oxidation activity of NO to NO₂ at low temperature could be improved on Fe(0.4)-MnO_x catalyst dominated by Fe₃Mn₃O₈ phase. It is well known that ammonium nitrite decomposes quickly into N₂ (majority) and NO (minority) below 100 °C^[18], the formation of NH₄NO₂ from NO, O₂, and NH₃ requires the oxidation of NO to NO₂ by O₂. Thus, the ability of NO conversion to NO₂ on catalysts is the key of increasing activity of low-temperature SCR.

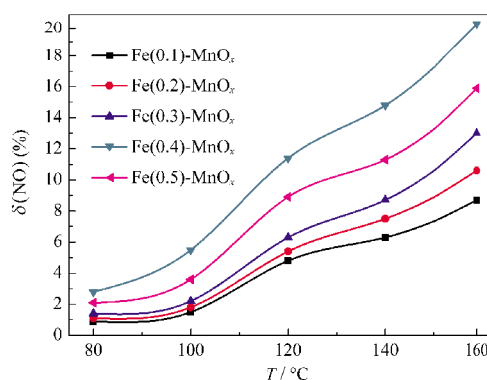


Fig.5 Oxidation activity of NO to NO₂ on Fe-MnO_x catalysts calcined at 500 °C

reaction conditions: $\varphi(\text{NO})=0.1\%$, $\varphi(\text{O}_2)=3\%$, and GHSV=30000 h⁻¹

Koebel^[19] and Long^[20] *et al.* had reported that a high activity for NO oxidation to NO₂ at low temperature should lead to enhance SCR activities. Hence, it is thought that the formation of Fe₃Mn₃O₈ could have the oxidation activity of NO to NO₂ improved, thereby enhanced the SCR activity.

The catalyst is usually deactivated mainly by SO₂ and water vapor in the combustion gases, so we will study the effects of SO₂ and H₂O on the SCR activities of the Fe(0.4)-MnO_x catalyst at 100 °C later.

3 Conclusions

In conclusion, a series of Fe-Mn mixed-oxide catalysts prepared by sol-gel method and the effects of Fe and Mn molar ratios and their calcination temperatures on catalytic reduction activities were investigated. The results showed that about 90.6% of NO_x conversion and 100% of N₂ selectivity at 80 °C under the condition of GHSV=30000 h⁻¹ were obtained on the Fe(0.4)-MnO_x(500) catalyst. According to the results of XRD, the formation of Fe₃Mn₃O₈ phase which contained the Fe—O—Mn bond was determined to be the active center for low temperature catalytic reduction process. Simultaneously, the oxidation activity of NO to NO₂ by O₂ on Fe-MnO_x catalysts suggested that the existence of Fe₃Mn₃O₈ was beneficial to increase the rate of the oxidation of NO to NO₂. Further characterization and catalytic reaction mechanism of these novel Fe-Mn mixed-oxide catalysts would be reported systematically later.

References

- Tomita, A.; Yoshii, T.; Teranishi, S.; Nagao, M.; Hibino, T. *J. Catal.*, **2007**, *247*(2): 137
- Li, X.; Zhu, P.; Wang, F.; Wang, L.; Tsang, S. C. *J. Phys. Chem. C*, **2008**, *112*(9): 3376
- Wu, P.; Liu, Y. X.; Zhang, F. X.; Li, L. D.; Yang, Y. L.; Guan, N. J. *Acta Phys. -Chim. Sin.*, **2008**, *24*(3): 369 [武鹏, 刘运霞, 章福祥, 李兰冬, 杨雅莉, 关乃佳. 物理化学学报, **2008**, *24*(3): 369]
- Ma, J. R.; Liu, Z. Y.; Huang, Z. G.; Liu, Q. Y. *Chin. J. Catal.*, **2006**, *27*(1): 91 [马建蓉, 刘振宇, 黄张根, 刘清雅. 催化学报,

- 2006, **27**(1): 91]
- 5 Busca, G.; Lietti, L.; Ramis, G.; Berti, F. *Appl. Catal. B*, **1998**, **18** (1–2): 1
- 6 Busca, G.; Larrubia, M. A.; Arrighi, L.; Ramis, G. *Catal. Today*, **2005**, **107**: 139
- 7 Lietti, L.; Nova, I.; Ramis, G.; Dall'Acqua, L.; Busca, G.; Giamello, E.; Forzatti, P.; Bregani, F. *J. Catal.*, **1999**, **187**(2): 353
- 8 Koebel, M.; Elsener, M.; Kleemann, M. *Catal. Today*, **2000**, **59**: 335
- 9 Tang, X.; Hao, J.; Xu, W.; Li, J. *Catal. Commun.*, **2007**, **8**(3): 329
- 10 Li, J.; Chen, J.; Ke, R.; Luo, C.; Hao, J. *Catal. Commun.*, **2007**, **8** (12): 1896
- 11 Qi, G.; Yang, R. T. *Appl. Catal. B*, **2003**, **44**(3): 217
- 12 Lin, T.; Zhang, Q. L.; Li, W.; Gong, M. C.; Xing, Y. X.; Chen, Y. Q. *Acta Phys. -Chim. Sin.*, **2008**, **24**(7): 1127 [林 涛, 张秋林, 李 伟, 龚茂初, 幸怡汛, 陈耀强. 物理化学学报, **2008**, **24**(7): 1127]
- 13 Kang, M.; Park, E. D.; Kim, J. M.; Yie, J. E. *Catal. Today*, **2006**, **111**: 236
- 14 Qi, G. S.; Yang, R. T. *Chem. Commun.*, **2003**, (7): 848
- 15 Long, R. Q.; Yang, R. T.; Chang, R. *Chem. Commun.*, **2002**, (5): 452
- 16 Tang, X. L.; Hao, J. M.; Xu, W. G.; Li, J. H. *Chin. J. Catal.*, **2006**, **27**(10): 843 [唐晓龙, 郝吉明, 徐文国, 李俊华. 催化学报, **2006**, **27**(10): 843]
- 17 Peña, D. A.; Uphade, B. S.; Smirniotis, P. G. *J. Catal.*, **2004**, **221** (2): 421
- 18 Notoya, F.; Su, C.; Sasako, E.; Nojima, S. *Ind. Eng. Chem. Res.*, **2001**, **40**(17): 3732
- 19 Koebel, M.; Elsener, M.; Madia, G. *Ind. Eng. Chem. Res.*, **2001**, **40**(1): 52
- 20 Long, R. Q.; Yang, R. T. *J. Catal.*, **2001**, **198**(1): 20