低温等离子体协助 $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ 选择催化还原 NO

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摘要: 研究了低温等离子体协助催化条件下甲烷选择性催化还原 NO 反应 (SCR). 反应气体经等离子体活化后, 生成 NO_2 , HCHO , CH_3NO 和 CH_3NO_2 等活性更高的中间产物. 程序升温表面反应表明, 这些中间产物可在等离子体后置催化装置上进一步反应, 从而使 NO_x 还原为 N_2 . 在考察的一系列催化剂 (包括 $\gamma\text{-Al}_2\text{O}_3$, $\text{Ag}/\gamma\text{-Al}_2\text{O}_3$, $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{Ga}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{In}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ 等) 中, $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ 表现出最好的催化活性. 当反应温度为 $300\text{ }^\circ\text{C}$ 时, NO_x 转化率达到最高. 与 $\gamma\text{-Al}_2\text{O}_3$ 催化剂相比, 在 10 wt% $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ 催化剂上, $300\text{ }^\circ\text{C}$ 时, NO_x 转化为 N_2 的转化率从 33.4% 提高至 51.0%. 催化剂的酸性对于经等离子体活化后的反应气体在催化剂上的 SCR 反应起到重要作用. 同时, 催化剂上吸附态 NO_x 对于 NO_x 的转化也起到一定作用.

关键词: 氮氧化物; 选择性催化还原; 氧化硼; 氧化铝; 低温等离子体; 程序升温表面反应

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Cold Plasma-Assisted Selective Catalytic Reduction of NO over $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

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Abstract: A plasma-assisted catalytic system for the selective catalytic reduction of NO with methane was investigated. NO_2 , HCHO , CH_3NO , and CH_3NO_2 were the reactive intermediates generated by the plasma. The further reactions of these intermediates on the catalyst during the thermal catalytic stage resulted in the conversion of NO_x to N_2 , which was verified by temperature-programmed surface reaction characterization. $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ was the best catalyst with the maximum conversion of NO_x to N_2 increasing from 33.4% on $\gamma\text{-Al}_2\text{O}_3$ to 51.0% on 10 wt% $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ at $300\text{ }^\circ\text{C}$. NH_3 -TPD characterization showed that the acidity of the catalyst is important for the reduction of NO_x by the intermediates generated by the plasma. NO_x -TPD showed that the adsorbed NO_x species on the catalysts also played a role in the conversion of NO_x .

Key words: nitrogen oxide; selective catalytic reduction; boric oxide; alumina; cold plasma; temperature-programmed surface reduction

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Nitrogen oxides (NO_x) emitted from mobile and stationary sources are among the worst air pollutants for the atmosphere, ecosystem, and human health. Selective catalytic reduction (SCR) of NO_x by methane is an attractive technology for diminishing NO_x emissions from stationary sources as methane is the main component of natural gas.

However, the use of methane is limited by that its C-H activation requires a much higher reaction temperature than that of other reduction gases [1,2].

An alternative method for activating and dissociating reactant molecules is by using a non-thermal plasma (NTP) at ambient temperature [3,4]. Recently, the coupling of a NTP

with a catalyst for better NO_x removal has received more attention. The combination modes of the plasma and catalyst include in-plasma catalysis (IPC) and post-plasma catalysis (PPC). Hueso et al. [5] investigated the IPC removal of NO and CH_4 on a perovskite catalyst, and confirmed the active participation of the catalyst in the reaction. Chen and Mathur [6] investigated a PPC system using $\gamma\text{-Al}_2\text{O}_3$ as the catalyst for SCR of NO with CH_4 or C_2H_4 , and found that this combination mode is effective for NO_x removal. Niu et al. [7,8] investigated plasma assisted SCR of NO in the IPC mode, and found a synergism between the plasma and the catalyst for NO_x removal. Yoon et al. [9,10] investigated the reduction of NO_x with propene over NaY and Al_2O_3 catalysts in the PPC mode, and confirmed the chemical reduction of NO_x to N_2 on the catalyst. They proposed that aldehydes generated by the plasma were important for NO_x reduction on the catalyst. For both combination modes, the active role of the catalyst was established in these studies. However, the detailed roles played by the plasma and the catalyst are still needed for a better understanding of the mechanism to further increase the removal efficiency of NO_x .

We have investigated the SCR of NO_x with CH_4 in the IPC mode, confirmed the synergism between the plasma and the catalyst, and found that $\gamma\text{-Al}_2\text{O}_3$ is a good catalyst for the reaction [11]. In the present work, the PPC mode was investigated for the SCR of NO. The emphasis was on the investigation of the reactions on the catalyst of the reactive gaseous intermediates generated by plasma and how to improve the conversion of NO_x in the catalytic stage. $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ was found to be the best catalyst in the present system.

1 Experimental

1.1 Catalyst preparation

Ag, B_2O_3 , Ga_2O_3 , and In_2O_3 supported on $\gamma\text{-Al}_2\text{O}_3$ were prepared by wet impregnation, respectively, with aqueous solutions of AgNO_3 , H_3BO_3 , $\text{Ga}(\text{NO}_3)_3$, and $\text{In}(\text{NO}_3)_3$. Before use, $\gamma\text{-Al}_2\text{O}_3$ was calcined at $500\text{ }^\circ\text{C}$ for 4 h. After impregnation, the catalysts were dried at $110\text{ }^\circ\text{C}$ for 12 h and calcined at $500\text{ }^\circ\text{C}$ for 4 h. All catalysts used for the plasma-assisted reaction were 20–40 mesh size pellets.

1.2 Plasma-assisted SCR of NO_x

The reaction was performed in a PPC system. NTP was generated in a cylindrical dielectric barrier discharge (DBD) reactor. A quartz tube with inner diameter of 8.5 mm and wall thickness of 1.7 mm was used as the dielectric barrier for the discharge. A stainless steel rod with an outer diame-

ter of 3.5 mm was used as the high voltage electrode. The outer surface of the quartz tube was wrapped by a stainless steel net working as the ground electrode. The discharge length of the DBD reactor was 19.5 cm. An AC high voltage power supply was used to drive the discharge in the reactor. The discharge power was calculated according to the V-Q Lissajous method:

$$P_{\text{dis}}(\text{W}) = f \int_0^T U \text{d}Q = fC \int_0^T U \text{d}u$$

The charge Q was calculated by measuring the voltage on the capacitor ($0.47\text{ }\mu\text{F}$), which was connected to the low voltage end of the electrode. The discharge voltage (U), voltage on the capacitor (u), and frequency (f) were monitored and recorded by a digital oscilloscope (Tektronix, TDS1002B-SC). The discharge frequency was in the range of 9.2–10 kHz. A parallelogram Lissajous figure was obtained for all plasma conditions, indicating that the reactions were performed in a stable dielectric barrier discharge plasma. Figure 1 shows the typical waveforms of discharge voltage and current (Fig. 1(a)) and typical Lissajous figure (Fig. 1(b)). The plasma reaction was carried out at atmospheric pressure without external heating. For the plasma energy density used in the present work ($198\text{--}330\text{ J/L}$), the temperature of the DBD reactor was lower than $50\text{ }^\circ\text{C}$ during the discharge.

The catalyst was placed in a quartz tube reactor downstream of the plasma reactor. The feed gas was 0.4% NO, 0.8% CH_4 , 3% O_2 , and He as the balance gas. Its flow rate was 100 ml/min. The space velocity was 12000 h^{-1} . The gas concentrations in the effluent were analyzed by a gas chromatograph (GC-9750, FULI Analytical Instrument Co. Ltd., China) equipped with a TCD detector. Nitrogen was measured to show the chemical reduction of NO_x to N_2 . The conversion of NO_x was defined as

Fig. 1. Typical waveforms of discharge voltage and current (a) and typical Lissajous figure (b).

$$\text{Conv.}_{NO_x \rightarrow N_2} = \frac{2 \times [N_2]_{\text{out}}}{[NO_x]_{\text{in}}} \times 100\%$$

$$\text{Conv.}_{NO_x \rightarrow N_2O} = \frac{2 \times [N_2O]_{\text{out}}}{[NO_x]_{\text{in}}} \times 100\%$$

$[NO_x]_{\text{in}}$, $[N_2]_{\text{out}}$, and $[N_2O]_{\text{out}}$ are, respectively, the concentrations of NO_x in the inlet gas, and N_2 and N_2O in the outlet gas.

1.3 Catalyst characterization

BET surface area, pore size, and pore volume of the catalysts were determined by N_2 adsorption-desorption using a Micromeritics ASAP 2020M. Temperature programmed desorption (TPD) of NH_3 was performed using 100 mg catalyst. The catalyst was pretreated at 400 °C for 1 h in N_2 (50 ml/min), and then 20% NH_3 -80% N_2 (50 ml/min) was introduced at 100 °C until the catalyst was saturated with NH_3 . After purging with N_2 to remove gas phase NH_3 , the catalyst was heated from 100 to 700 °C at a heating rate of 10 °C/min. Desorbed NH_3 was detected by TCD. For NO_x -TPD, after pretreatment of the catalyst (100 mg) at 400 °C for 1 h, the adsorption of NO_x was performed by passing a flow of 0.05% NO , 0.05% NO_2 , and 10% O_2 diluted in N_2 (100 ml/min) at room temperature for 2 h. Then the catalyst was purged with N_2 to remove gas phase NO_x , and TPD was performed from room temperature to 600 °C at a heating rate of 10 °C/min. Desorbed NO_x was measured by a chemluminescent NO_x analyzer (Eco Physics).

Temperature-programmed surface reaction (TPSR) was performed with the same apparatus used for NO_x -TPD. The catalyst was pretreated in He and after it reached 60 °C, the effluent from the plasma was sent to the catalyst. TPSR was performed at a heating rate of 10 °C/min. The reaction product was analyzed by a NO_x analyzer and a Pfeiffer Omnistar mass spectrometer (CH_4 ($m/z = 15$), O_2 ($m/z = 32$), H_2O ($m/z = 18$), N_2/CO ($m/z = 28$), N_2O/CO_2 ($m/z = 44$), $HCHO$ ($m/z = 29$), HCN ($m/z = 27$), CH_3NO ($m/z = 45$), CH_3NO_2 ($m/z = 61$)).

2 Results and discussion

2.1 Activity measurements

2.1.1 Catalytic activity of the $\gamma-Al_2O_3$ -supported catalysts

In the plasma-induced gas phase reaction at an energy density of 264 J/L, the conversion of NO_x to N_2 and N_2O was 10.0% and 3.9%, respectively. When this was combined with the post-plasma catalytic stage, the conversion of NO_x

was further improved. Figure 2 shows the conversion of NO_x in the plasma-assisted SCR reaction on the catalysts. All the catalysts showed catalytic activities for the conversion of NO_x to N_2 (Fig. 2(a)). For comparison, quartz powder was used as a “blank” in the post-plasma reactor, and with it, with increasing temperature from 150 to 400 °C, the conversion of NO_x to N_2 and N_2O showed no change, indicating that the improvement of the conversion of NO_x in the plasma-assisted catalytic reaction was due to the catalysts. 1.0 wt% $Ag/\gamma-Al_2O_3$ showed an inferior activity for the conversion of NO_x to N_2 than $\gamma-Al_2O_3$. With B_2O_3 , Ga_2O_3 , or In_2O_3 on $\gamma-Al_2O_3$, the conversion of NO_x was further increased. Among the catalysts investigated, $B_2O_3/\gamma-Al_2O_3$ showed the best performance. The maximum conversion of NO_x to N_2 on 3.1 wt% $B_2O_3/\gamma-Al_2O_3$ was 40.5% at 300 °C.

The conversion of NO_x to N_2O showed an overall decreasing trend with increasing temperature. The reason may be that a higher reaction temperature favored the conversion of NO_x to N_2 rather than to N_2O .

Fig. 2. Plasma-assisted SCR of NO_x on different catalysts. (a) Conversion of NO_x to N_2 ; (b) Conversion of NO_x to N_2O . Conditions: 0.4% NO -0.8% CH_4 -3% O_2 , He as the balance gas, the energy density of the plasma was 264 J/L.

2.1.2 Effect of B_2O_3 loading amount on the catalytic activity

As $B_2O_3/\gamma-Al_2O_3$ showed the best catalytic effect, the emphasis was focused on this catalyst in subsequent investigations. Figure 3 shows the effect of B_2O_3 loading amount from 3.1 to 20 wt%. Compared with $\gamma-Al_2O_3$ (Fig. 2), the maximum conversion of NO_x to N_2 increased from 33.4% to

Fig. 3. Effect of B₂O₃ loading on the activity of B₂O₃/γ-Al₂O₃. (a) Conversion of NO_x to N₂; (b) Conversion of NO_x to N₂O. Conditions: 0.4% NO-0.8% CH₄-3% O₂, He as the balance gas, the energy density of plasma was 264 J/L.

51.0% at 300 °C with increasing B₂O₃ amount from 0 to 10 wt%. Further increase in the B₂O₃ amount led to a decrease of the activity. Thus, the optimal B₂O₃ loading of the catalyst was 10 wt%. The conversion of NO_x to N₂O attained a maximum at 200 °C, and then decreased with further increase in reaction temperature on all catalysts.

B₂O₃/γ-Al₂O₃ does not show any catalytic activity for thermal SCR of NO by methane in the temperature range used here. Thus the synergism of the plasma and the catalyst was due to the reactions on the catalyst of the reactive intermediates produced by the plasma.

2.1.3 Effect of plasma energy density on the conversion of NO_x

Figure 4 shows the effect of plasma energy density with 10 wt% B₂O₃/γ-Al₂O₃. The conversions of NO_x showed similar trends versus temperature at different energy densities. The maximum conversion of NO_x to N₂ was at an energy density of 264 J/L. The maximum conversion of NO_x to N₂O was also the highest when the energy density was 264 J/L. It can be proposed that when the energy density of the plasma was low, the amount of chemical intermediates produced by the plasma was limited, which limited the reduction of NO_x on the catalysts. When the energy density was high, the higher amount of intermediates gave a higher conversion in the subsequent catalytic SCR process, but also there was a decrease in the amounts of some intermediates

Fig. 4. Effect of energy density on the conversion of NO_x over 10 wt% B₂O₃/γ-Al₂O₃. (a) Conversion of NO_x to N₂; (b) Conversion of NO_x to N₂O. Conditions: 0.4% NO-0.8% CH₄-3% O₂, He as the balance gas.

due to their direct conversion in the plasma. Thus, there was an optimum energy density for the reaction.

2.2 Reaction mechanism

During the passage of reactant gas through the plasma, N₂, N₂O, CO, CO₂, H₂O, NO₂, HCHO, CH₃NO, and CH₃NO₂ were detected as products. In the present oxygen-rich reaction system, CO showed no SCR activity for the reduction of NO_x on all the catalysts investigated. Thus it is proposed that NO₂, HCHO, CH₃NO, and CH₃NO₂ were the reactive intermediates that gave the improvement of the conversion of NO_x on the post-plasma catalysts. TPSR was performed to confirm the function of the intermediates generated by the plasma. The composition of the reactant gas mixture was the same as that in the isothermal reaction. Figure 5 shows the TPSR profiles from 10 wt% B₂O₃/γ-Al₂O₃ of the gaseous chemical intermediates generated by the plasma. When the mixture containing NO_x and organic intermediates contacted the catalyst, the intermediates adsorb in the low temperature range, and then desorbed and reacted at increasing temperature. In Fig. 5(a), the decrease of the concentration of NO with increasing temperature from 60 to 140 °C was due to the oxidation of NO to NO₂ on the catalyst. The concentration of NO increased with further increase in the temperature. NO_x-TPD showed that the desorbed NO_x from the catalysts was mainly NO₂, as discussed in section 2.3.2. Since the thermodynamic con-

Fig. 5. TPRS profiles of intermediates generated by the plasma with the 10 wt% B₂O₃/γ-Al₂O₃ catalyst. (a) Concentration of NO_x versus temperature; (b) MS signal intensities of N₂/CO, CO₂/N₂O, HCHO, CH₃NO₂, CH₃NO, and HCN versus temperature.

version of NO₂ to NO needs a much higher temperature [12], the increase of the NO concentration above 140 °C was proposed to be caused by the decomposition of CH₃NO_x. The concentration of NO₂ showed a decreasing trend with increasing reaction temperature from 158 °C, indicating its reduction to N₂, N₂O, or NO on the catalyst. The concentrations of N₂/CO and CO₂/N₂O showed clear increasing trends from 120 °C, suggesting that the SCR reactions between the intermediates were taking place (Fig. 5(b)). GC analysis of the isothermal reaction has identified the simultaneous production of N₂ and CO on the catalyst. The concentration of N₂/CO reached the maximum at 300 °C, then decreased with further increasing temperature, which was consistent with the isothermal results. HCN was detected in the temperature range 200–350 °C, which suggested that HCN was an intermediate from the reactions on the catalyst.

In the plasma, CH₃ radical is formed by H-abstraction from CH₄. The reaction of CH₃ with O₂ formed CH₃O₂. CH₃O₂ can oxidize NO to NO₂. The CH₃O radicals also formed formaldehyde and HO₂ radicals through reactions with O₂. Moreover, CH₃ can also react with NO and NO₂ to form CH₃NO and CH₃NO₂, respectively. The reactions are

In the catalytic stage, HCHO reacted with NO₂ to form N₂ and CO, or reacted with O₂ to form CO_x and H₂O [13,14]. For the conversion of nitrogen-containing compounds, in the presence of NO_x or O₂, CH₃NO₂ and CH₃NO can decompose to N₂ and CO_x via several pathways [15,16]. HCN was observed during the reaction, probably produced by the decomposition of organic nitro-compounds [15,16].

2.3 Catalyst characterization results

2.3.1 Pore structure

The physical properties of the catalysts are summarized in Table 1. With increasing loading amount of B₂O₃ on γ-Al₂O₃, the BET surface area and pore volume gradually decreased. Supporting Ga₂O₃ or In₂O₃ on γ-Al₂O₃ also led to a decrease of the surface area and pore volume. Correlating these data with the reaction results, it is seen that the BET surface area did not play an important role in determining the catalytic activity.

Table 1 Physical properties of the catalysts

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
γ-Al ₂ O ₃	166	0.80	16.9
1 wt% Ag/γ-Al ₂ O ₃	168	0.81	16.6
3.1 wt% B ₂ O ₃ /γ-Al ₂ O ₃	158	0.76	16.6
7 wt% B ₂ O ₃ /γ-Al ₂ O ₃	155	0.73	16.6
10 wt% B ₂ O ₃ /γ-Al ₂ O ₃	151	0.70	16.5
15 wt% B ₂ O ₃ /γ-Al ₂ O ₃	141	0.62	15.8
20 wt% B ₂ O ₃ /γ-Al ₂ O ₃	138	0.58	14.8
4.5 atm% Ga ₂ O ₃ /γ-Al ₂ O ₃	142	0.69	16.2
4.5 atm% In ₂ O ₃ /γ-Al ₂ O ₃	144	0.67	16.0

2.3.2 NH₃-TPD and NO_x-TPD characterization

Figure 6 displays the TPD profiles of NH₃ and NO_x on B₂O₃/γ-Al₂O₃ catalysts. Figure 6(a) shows that the total desorbed ammonia increased with increasing B₂O₃ loading amount on γ-Al₂O₃ until the amount attained 10 wt%. There was an increase of desorbed ammonia in the high temperature range for increasing B₂O₃ loading from 7 to 10 wt%, and the NH₃ desorption profile did not show much variation with B₂O₃ amount on further increase to 15 wt%. On further

Fig. 6. NH₃-TPD (a) and NO_x-TPD (b) profiles of the catalysts. (1) γ -Al₂O₃; (2) 3.1 wt% B₂O₃/ γ -Al₂O₃; (3) 7 wt% B₂O₃/ γ -Al₂O₃; (4) 10 wt% B₂O₃/ γ -Al₂O₃; (5) 15 wt% B₂O₃/ γ -Al₂O₃; (6) 20 wt% B₂O₃/ γ -Al₂O₃.

increasing of the loading amount to 20 wt%, the total amount of desorbed NH₃ decreased due to the decrease of NH₃ desorption amount in the high temperature range. It is seen from NH₃-TPD that the number and strength of acid sites reached the maximum when the loading amounts of B₂O₃ on γ -Al₂O₃ were 10–15 wt%, and further increase in the B₂O₃ amount led to a decrease of the acidity of the catalyst.

NO_x-TPD (Fig. 6(b)) showed that the amount of adsorbed NO_x decreased with increasing loading of B₂O₃ on γ -Al₂O₃. The desorption temperature of NO_x in the high temperature range also showed a decreasing trend with increasing B₂O₃ amount. The reason is that the addition of B₂O₃ to γ -Al₂O₃ decreased the number and strength of basic sites on γ -Al₂O₃. Consequently, the amount of acidic NO_x adsorbed and their adsorption strength decreased with increasing loading of B₂O₃ on γ -Al₂O₃. Notably, the desorbed NO_x was mainly NO₂, and NO in the desorbed NO_x was lower than 2.5% on all the catalysts.

The B₂O₃/ γ -Al₂O₃ catalysts have no redox properties. It has been reported that Brønsted acid sites are created on the alumina surface by supported boron species [17,18]. Correlating this with the results of the isothermal reaction, it can be proposed that Brønsted acidity of the catalysts is impor-

tant in the reduction of NO_x by the reactive intermediates generated by the plasma. The important role of Brønsted acid sites for NO_x reduction to N₂ in CH₄ SCR has been reported in many reports [19–21]. It is thus suggested that the mechanism of the plasma-assisted reaction has some similar reaction pathways to the thermal catalytic mechanism for the conversion of NO_x to N₂. Furthermore, NO_x species formed on the catalyst is known to be an important factor in NO_x reduction [22,23]. Thus, despite the similar acidic properties, the inferior catalytic activity of 15 wt% B₂O₃/ γ -Al₂O₃ to 10 wt% B₂O₃/ γ -Al₂O₃ was attributed to the decreased amount of adsorbed NO_x on the catalyst, as the lack of nitrate species on the catalyst also suppressed the reduction process. The Brønsted acidity of the catalyst was the most important factor in the conversion of NO_x, as the NO_x adsorption capacity of the catalyst decreased monotonically with increasing the loading amount of B₂O₃ on γ -Al₂O₃, that is, the catalytic activity of the catalyst reached the maximum when the acidity of the B₂O₃/ γ -Al₂O₃ catalyst was the highest.

3 Conclusions

B₂O₃/ γ -Al₂O₃ was an efficient catalyst in the plasma-assisted SCR of NO with methane. NO₂, HCHO, CH₃NO, and CH₃NO₂ were generated as reactive intermediates by the plasma processing of NO, CH₄, and O₂. TPSR characterization showed that the synergism between the plasma and the catalyst was due to the further reaction on the catalyst of the plasma generated intermediates. TPD characterization showed that the acidity of the catalysts is the most important factor in the reduction of NO_x, and adsorbed NO_x species on the catalyst also plays a role in the reaction.

References

- Chen J P, Yang R T. *J Catal*, 1990, **125**: 411
- Georgiadou I, Papadopoulou Ch, Matralis H K, Voyiatzis G A, Lycourghiotis A, Kordulis Ch. *J Phys Chem B*, 1998, **102**: 8459
- Liu C J, Mallinson R, Lobban L. *Appl Catal A*, 1999, **178**: 17
- Kim H H, Lee Y H, Ogata A, Futamura S. *Catal Commun*, 2003, **4**: 347
- Hueso J L, Cotrino J, Caballero A, Espinos J P, Gonzakez-Eliphe A R. *J Catal*, 2007, **247**: 288
- Chen Z, Mathur V K. *Ind Eng Chem Res*, 2003, **42**: 6682
- 牛金海, 朱爱民, 石川, 史玲玲, 宋志民, 徐勇. 催化学报 (Niu J H, Zhu A M, Shi C, Shi L L, Song Z M, Xu Y. *Chin J Catal*), 2005, **26**: 803
- Niu J H, Yang X F, Zhu A M, Shi L L, Sun Q, Xu Y, Shi Ch. *Catal Commun*, 2006, **7**: 297

- 9 Yoon S, Panov A G, Tonkyn R G, Ebeling A C, Barlow S E, Balmer M L. *Catal Today*, 2002, **72**: 243
- 10 Yoon S, Panov A G, Tonkyn R G, Ebeling A C, Barlow S E, Balmer M L. *Catal Today*, 2002, **72**: 251
- 11 刘彤, 于琴琴, 王卉, 蒋晓原, 郑小明. 催化学报 (Liu T, Yu Q Q, Wang H, Jiang X Y, Zheng X M. *Chin J Catal*), 2011, **32**: 1502
- 12 Lukyanov D B, Sill G, d'Itri J L, Hall W K. *J Catal*, 1995, **153**: 265
- 13 Spencer N D. *J Catal*, 1988, **109**: 187
- 14 Miro E E, Imoberdorf G, Vassallo J, Petunchi J O. *Appl Catal B*, 1999, **22**: 305
- 15 Yokoyama C, Misono M. *J Catal*, 1994, **150**: 9
- 16 Gorce O, Baudin F, Thomas C, Costa P D, Djéga-Mariadassou G. *Appl Catal B*, 2004, **54**: 69
- 17 Sato S, Kuroki M, Sodesawa T, Nozaki F, Maciel G E. *J Mol Catal A*, 1995, **104**: 171
- 18 Bautista F M, Campelo J M, Garcia A, Luna D, Marinas J M, Moreno M C, Romero A A. *Appl Catal A*, 1998, **170**: 159
- 19 Yan J Y, Kung H H, Sachter W M H, Kung M C. *J Catal*, 1998, **175**: 294
- 20 Regalbuto J R, Zheng T, Miller J T. *Catal Today*, 1999, **54**: 495
- 21 Berndt H, Schütze F W, Richter M, Sowade T, Grünert W. *Appl Catal B*, 2003, **40**: 51
- 22 Burch R, Breen J P, Meunier F C. *Appl Catal B*, 2002, **39**: 283
- 23 Kwak J H, Szanyi J, Peden C H F. *J Catal*, 2003, **220**: 291