CeO₂-WO₃ 复合氧化物催化剂的 NH₃-SCR 反应机理

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摘要: 采用共沉淀法制备了新型 CeO₂-WO₃ 复合氧化物催化剂, 并用于氨选择性催化还原 (NH₃-SCR) NO_x 反应中. 活性测试表明, 在 200~450 °C NO_x 转化率接近 100%. 采用程序升温脱附和原位漫反射红外光谱研究了该催化剂上的 NH₃-SCR 反应机理. 结果表明, 该催化剂的主要活性位是 CeO₂, 而 WO₃ 的加入大大提高了其表面 Brönsted 酸位的数量与强度及其氧化 NO 的能力. 另外还发现, 除了催化剂表面 Lewis 酸与 Brönsted 酸参与反应外, 表面的桥式与单齿硝酸盐也是活性很高的物种. 整个 SCR 反应可通过以上两种途径进行.

关键词: 氮氧化物去除; 选择性催化还原; 活性; 一氧化氮氧化能力; 机理

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Mechanism of Selective Catalytic Reduction of NO_x with NH₃ over CeO₂-WO₃ Catalysts

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Abstract: The mechanism of NH₃-selective catalytic reduction (SCR) over a CeO₂-WO₃ catalyst was investigated by temperature-programmed desorption (TPD) analysis and in situ diffuse reflectance infrared Fourier transform spectroscopy. The active sites were on CeO₂, while WO₃ greatly enhanced the amount and strength of the surface Brönsted acid sites and the NO oxidation ability. Both NH₄⁺ and coordinated NH₃ contributed to the SCR reaction. Bridging nitrate and monodentate nitrate were confirmed as the reactive nitrate species. Under SCR reaction conditions, surface NH₄NO₃ was formed, which played the role of an important intermediate species. Two different pathways for the SCR reaction were suggested for the CeO₂-WO₃ catalyst.

Key words: nitrogen oxide removal; selective catalytic reduction; activity; nitrogen oxide oxidation ability; mechanism

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The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia is one of the state-of-the-art technologies for abating NO_x in flue gas from stationary sources and mobile sources. The most widely used commercial catalyst system is V₂O₅-WO₃(MoO₃)/TiO₂ [1]. However, this catalyst system has these problems: poor N₂ selectivity in the high temperature range because of N₂O formation and NH₃ over-oxidation, toxicity of vanadium pentoxide in the environment, high conversion of SO₂ to SO₃, and transformation from the anatase to rutile phase of TiO₂ at high temperature (above 500 °C) that can result in catalyst deactivation [2]. Therefore, many researchers have sought to develop a novel SCR catalyst with high efficiency and non-toxicity to the environment, such as Fe_xTiO_y [3], CeO₂/TiO₂ [4,5], CeO₂/Al₂O₃ [6], CuO_x-WO_x/ZrO₂ [7], and other oxides.

In the literature, cerium is a potential candidate under investigation [4–6,8–11]. Recently, we developed a cerium-tungsten catalyst (CeO₂-WO₃) that showed high SCR activity, N₂ selectivity, and SO₂ durability in a wide temperature range (175–450 °C) [12]. In this paper, the effect of CeO₂ and WO₃ on the CeO₂-WO₃ mixed oxide catalyst was studied. A possible mechanism for SCR was proposed using in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) data.

1 Experimental

1.1 Catalyst preparation

CeO₂-WO₃ catalysts were prepared by a standard co-precipitation method. Weighed amounts of cerium nitrate and ammonium paratungstate were dissolved in oxalic acid solution, and excess solution of ammonium bicarbonate was added slowly with stirring to the solution as precipitator. The precipitate cake was filtrated and washed with distilled water, followed by desiccation at 110 °C in air for 12 h and calcination at 500 °C for 4 h in air. Finally, the samples were crushed and sieved to 40–60 mesh. Pure CeO₂ and WO₃ were prepared by direct decomposition of cerium nitrate and ammonium paratungstate, respectively, and were calcined at 600 °C for 5 h.

1.2 Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor (i.d. 9 mm) using 0.5 g catalyst of 40–60 mesh. The feed gas mixture contained 0.05% NO, 0.05% NH₃, 3% O₂, and N₂ as the balance gas. The total flow rate of the feed gas was 300 ml/min, corresponding to a space velocity of 47000 h⁻¹. The concentrations of NO_x, N₂O, and NH₃ in the inlet and outlet gas were measured by an FT-IR

(Fourier transform infrared) gas analyzer Gasmet Dx-4000. The activity data were collected when the catalytic reaction reached steady state after 0.5 h at each temperature.

1.3 Mechanism study

NH₃-TPD and NO_x-TPD (temperature-programmed desorption) were performed in a fixed-bed quartz reactor using an FT-IR gas analyzer Gasmet Dx-4000. A sample mass of 0.5 g and a gas flow rate of 300 ml/min were used during the experiment. The experiment consisted of four stages: (1) degasification of the sample in N₂ at 500 °C for 1 h, (2) adsorption by 0.05% NO/N₂ + 3% O₂/N₂ or 0.05% NH₃/N₂ at room temperature for 1 h, (3) isothermal desorption in N₂ at the temperature of the final step until no NO_x or NH₃ was detected, and (4) temperature-programmed desorption in N₂ (TPD stage) at 10 °C/min up to 600 °C.

In situ DRIFTS spectra were recorded by a Nicolet NEXUS 870-FTIR spectrometer equipped with a SMART collector and an MCT detector cooled by liquid N₂. The diffuse reflectance FT-IR measurements were carried out in situ in a high temperature cell fitted with ZnSe windows. The catalyst was finely ground and placed in a ceramic crucible and manually pressed. Mass flow controllers and a sample temperature controller were used to simulate reaction conditions. Prior to each experiment, the catalyst was heated to 350 °C in N₂ at a total flow rate of 100 ml/min for 60 min. The background spectrum was collected in flowing N₂ atmosphere and was subtracted from the sample spectra. All IR spectra were recorded by accumulating 100 scans at a resolution of 4 cm⁻¹. The reaction conditions were 0.05% NO, 0.05% NH₃, 3% O₂, and N₂ balance.

2 Results and discussion

2.1 Catalytic activity

Figure 1 shows NO_x conversions in the SCR reaction over the CeO₂, WO₃, and CeO₂-WO₃ catalysts as a function of temperature from 150 to 500 °C. Pure CeO₂ and WO₃ showed very narrow operation temperature windows, and their maximum NO_x conversions did not reach 100%. With the CeO₂-WO₃ catalyst, the operation window was greatly enhanced and NO_x was completely reduced from 200–450 °C with high N₂ selectivity [12]. In our previous work [12], a CeO₂-WO₃ catalyst with a Ce/W molar ratio of 3/2 showed the best NO_x conversion, which was attributed to the strong interaction between Ce and W.

2.2 NH₃-TPD and NO_x-TPD

Figure 2 shows the NH₃-TPD results over the CeO₂,

Fig. 1. NH_3 -SCR activity of CeO_2 , WO_3 , and CeO_2 - WO_3 catalysts as a function of temperature. Reaction conditions: 0.05% NO , 0.05% NH_3 , 3% O_2 , N_2 as balance gas, GHSV = 47000 h^{-1} .

WO_3 , and CeO_2 - WO_3 catalysts. One broad desorption peak appeared in the temperature range of 100–400 $^{\circ}\text{C}$ for CeO_2 , while one weak peak centered at 340 $^{\circ}\text{C}$ appeared over WO_3 . This implied that the acid sites over CeO_2 and WO_3 were different in strength. For the CeO_2 - WO_3 catalyst, a strong desorption peak appeared at 300 $^{\circ}\text{C}$. Therefore, there was a significant increase in the adsorption capacity of NH_3 over the CeO_2 - WO_3 catalyst, which, to some extent, favored the SCR reaction [8,24]. The detailed relationship between surface adsorbed NH_3 species and SCR activity will be discussed in the following section.

Fig. 2. TPD profiles of NH_3 over CeO_2 , WO_3 , and CeO_2 - WO_3 catalysts.

The NO_x -TPD results are shown in Fig. 3. No NO_x could be desorbed from WO_3 (not shown). Similar phenomena were also observed in other catalysts, such as $\text{V}_2\text{O}_5/\text{TiO}_2$ [13] and MnCeO_x [14]. The CeO_2 catalyst showed two obvious NO_x desorption bands centered at 130 and 440 $^{\circ}\text{C}$. The CeO_2 - WO_3 catalyst gave two peaks at 110 and 280 $^{\circ}\text{C}$. On comparing the two figures, it was seen that more NO_2 than NO could be desorbed from the CeO_2 - WO_3 catalyst, while for the CeO_2 catalyst, the amounts of NO and NO_2

Fig. 3. TPD profiles of $\text{NO}+\text{O}_2$ over CeO_2 (a) and CeO_2 - WO_3 (b) catalysts.

were nearly the same. This indicated that the NO_x adsorbed species over CeO_2 - WO_3 was mainly NO_3^- , which was beneficial for the NH_3 -SCR. Furthermore, both NO_x desorption peaks were shifted to the low temperature range for CeO_2 - WO_3 , which indicated that unstable nitrate species appeared at low temperature. According to the analysis of Shimizu et al. [15], stable nitrates that occupy the active sites over $\text{Ag}/\text{Al}_2\text{O}_3$ were bad for the SCR reactions at low temperatures. Hence, the unstable nitrates over the CeO_2 - WO_3 catalyst would result in more effective SCR catalysis, especially in the temperature range of 150–300 $^{\circ}\text{C}$, which was confirmed by the activity of CeO_2 and the CeO_2 - WO_3 catalyst.

2.3 DRIFTS

2.3.1 In situ DRIFTS of NH_3 adsorption

Since the DRIFTS spectra of NH_3 and NO_x adsorbed on WO_3 were very weak, we do not give the DRIFTS data for WO_3 in this work. Prior to NH_3 adsorption, the samples were treated at 350 $^{\circ}\text{C}$ in N_2 for 1 h to remove adsorbed species. After the sample was cooled to room temperature, 0.05% NH_3 was introduced into the IR cell and IR spectra were recorded with increasing temperature. Figure 4(a) shows the DRIFTS spectra of NH_3 adsorption on the CeO_2 catalyst under different reaction temperatures. Several bands at 1600, 1551, 1527, 1420, and 1300 cm^{-1} and one broad band in the range of 1000–1200 cm^{-1} were detected. The

Fig. 4. DRIFTS spectra of CeO_2 (a) and $\text{CeO}_2\text{-WO}_3$ (b) treated in flowing 0.05% NH_3 at room temperature for 1 h and then purged by N_2 at 30, 100, 150, 200, 250, 300, and 350 °C.

bands centered at 1600 and 1100 cm^{-1} were attributed to the asymmetric and symmetric deformation of coordinated ammonia on Lewis sites, respectively [16,17]. The band at 1300 cm^{-1} can be assigned to the symmetric deformation of ammonia coordinatively bonded to one type of Lewis acid sites [18]. The weak band at 1420 cm^{-1} was due to the asymmetric deformation of ammonium ions adsorbed on Brönsted sites [18]. Furthermore, two different bands appeared at 1527 and 1551 cm^{-1} , which were not due to adsorption on Lewis or Brönsted acid sites. According to the literature [19–22], the band at 1520 cm^{-1} can be attributed to amide ($-\text{NH}_2$) species and that at 1560 cm^{-1} can be assigned to the intermediate of the oxidation of ammonia. These results also clearly indicated that the number of Lewis acid sites were much higher than that of Brönsted acid sites on the CeO_2 catalyst, which was in agreement with Qi's work [26].

Figure 4(b) shows the DRIFTS spectra of NH_3 adsorption on $\text{CeO}_2\text{-WO}_3$ catalyst, which was different from that of pure CeO_2 . Bands at 1153, 1440, 1590, and 1660 cm^{-1} and a broad band in the range of 1700–2000 cm^{-1} were detected. The bands centered at 1800 and 1660 cm^{-1} were due to the symmetric bending vibrations of NH_4^+ , that at 1440 cm^{-1} were due to asymmetric bending vibrations of NH_4^+ chemi-

sorbed on Brönsted acid sites [23]. The bands at 1153 and 1590 cm^{-1} were attributed to coordinated NH_3 linked to Lewis acid sites. Clearly, $\text{CeO}_2\text{-WO}_3$ possessed both strong Lewis acid sites and Brönsted acid sites. WO_3 was reported as the main additive that increases the amount and strength of Brönsted acid sites for a $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst [24,25]. Therefore, on comparing with the $\text{NH}_3\text{-TPD}$ results in Fig. 2, we can assign the different peaks of the TPD curves as follows: the peak between 100–250 °C as caused by the desorption of coordinated NH_3 bound to Lewis acid sites, and the broad peaks centered at 300–400 °C were due to NH_4^+ strongly bonded to Brönsted acid sites. From the above results, we concluded that CeO_2 provided most of the Lewis acid sites and Brönsted acid sites, while WO_3 promoted the increase of the amount and strength of the Brönsted acid sites. The $\text{CeO}_2\text{-WO}_3$ mixed oxide catalyst possessed both strong acid sites, and adsorbed much more NH_3 , which were effective for the SCR reaction.

2.3.2 Co-adsorption of NO and O_2

NO_x adsorbed species on CeO_2 and $\text{CeO}_2\text{-WO}_3$ at various temperatures were also investigated by FT-IR spectroscopy. Figure 5(a) presents the in situ DRIFTS results of NO_x adsorption on pure CeO_2 at different temperatures. Several bands at 1013, 1030, 1235, 1284, 1440, 1530, 1590, and 1611 cm^{-1} were observed. According to the literature [26–29], the band at 1013 cm^{-1} can be assigned to *cis*- $\text{N}_2\text{O}_2^{2-}$. In the case of *cis*- $\text{N}_2\text{O}_2^{2-}$ another band should appear in the 1300–1400 cm^{-1} region. In our work, in the 1300–1400 cm^{-1} regions, there was a weak peak around 1350 cm^{-1} , which can also be assigned to *cis*- $\text{N}_2\text{O}_2^{2-}$. The band at 1440 cm^{-1} was due to *trans*- $\text{N}_2\text{O}_2^{2-}$ because the N-stretching modes of *trans*- $\text{N}_2\text{O}_2^{2-}$ were at 1419 cm^{-1} . With increasing temperature, bands at 1235 and 1611 cm^{-1} due to bridging nitrate species moved gradually to lower wavenumbers, while the bands at 1030 and 1590 cm^{-1} attributed to bidentate nitrate species became stronger. Bands at 1284 and 1530 cm^{-1} were assigned to monodentate nitrate (ν_3 high at 1543 or 1518 cm^{-1} and ν_3 low at 1286 or 1296 cm^{-1}).

Figure 5(b) shows the DRIFTS spectra of NO_x adsorption on $\text{CeO}_2\text{-WO}_3$, which were quite different from that of CeO_2 . All bands showed less thermal stability than those of CeO_2 , which was consistent with $\text{NO}_x\text{-TPD}$ results. New bands at 1785 and 1745 cm^{-1} were assigned to *cis*-(NO)₂ and *trans*-(NO)₂, respectively, while the weak bands at 1450 and 1013 cm^{-1} were attributed to *trans*- $\text{N}_2\text{O}_2^{2-}$ and *cis*- $\text{N}_2\text{O}_2^{2-}$ [27]. Broad bands centered at 1260 cm^{-1} can be divided into two peaks assigned to monodentate nitrate and bridging nitrate species, respectively. Only a weak band at 1570 cm^{-1} due to bidentate nitrate existed. On comparing

Fig. 5. DRIFTS spectra of CeO_2 (a) and $\text{CeO}_2\text{-WO}_3$ (b) treated in flowing 0.05% $\text{NO} + 3\% \text{O}_2$ at room temperature for 1 h and then purged by N_2 at 30, 100, 150, 200, 250, 300, and 350 °C.

with the NO_x -TPD results, on the $\text{CeO}_2\text{-WO}_3$ mixed oxides, more NO ad-species were oxidized to NO_2 ad-species, unfamiliar species such as bidentate nitrate were transformed into other active species, and all the nitrite and nitrate species showed less thermal stability than on pure CeO_2 . This was a possible reason why the $\text{CeO}_2\text{-WO}_3$ mixed oxide showed much better SCR activity than pure CeO_2 .

2.3.3 Reaction between nitrogen oxides and ammonia adspecies on the $\text{CeO}_2\text{-WO}_3$ catalyst

In this experiment, the $\text{CeO}_2\text{-WO}_3$ catalyst was first purged with NH_3 for 1 h, followed by N_2 purging. $\text{NO} + \text{O}_2/\text{N}_2$ was then introduced into the IR cell at 200 °C, and spectra were recorded as a function of time. As noted already, coordinated NH_3 species (1190 and 1590 cm^{-1}) and NH_4^+ species (1440, 1660, and the range of 1700–2000 cm^{-1}) were formed on the $\text{CeO}_2\text{-WO}_3$ catalyst upon treatment with NH_3 (Fig. 6). Subsequently, $\text{NO} + \text{O}_2/\text{N}_2$ was passed over the NH_3 -adsorbed catalyst and all ammonia adspecies decreased rapidly. After about 2 min, many new bands due to NO_x species appeared. From these results, it can be seen that both NH_3 and NH_4^+ were involved in this reaction.

Fig. 6. DRIFTS spectra taken at 200 °C upon passing 0.05% $\text{NO} + 3\% \text{O}_2$ over the NH_3 presorbed on $\text{CeO}_2\text{-WO}_3$ for 0, 1, 2, 5, 10, 20, and 30 min.

2.3.4 Reaction between ammonia and adsorbed nitrogen oxides species on the $\text{CeO}_2\text{-WO}_3$ catalyst

In this experiment, the reactants were introduced to $\text{CeO}_2\text{-WO}_3$ catalysts in the reversed order. The samples were first treated with $\text{NO} + \text{O}_2/\text{N}_2$ for 1 h and then purged with N_2 for 30 min. After NH_3 was introduced at 200 °C, the spectra were recorded as a function of time (Fig. 7). As we know, after the pre-adsorption of $\text{NO} + \text{O}_2$ and N_2 purge, the catalyst surface was mainly covered by three kinds of nitrate species. The subsequent introduction of NH_3 resulted in the rapid disappearance of bridging nitrate (1608 and 1240 cm^{-1}) and monodentate nitrate (1290 cm^{-1}), implying that both these kinds of nitrate species were reducible or reactive in the SCR reaction. In contrast, the bidentate nitrate species

Fig. 7. DRIFTS spectra taken at 200 °C upon passing 0.05% NH_3 over the $\text{NO} + \text{O}_2$ presorbed on $\text{CeO}_2\text{-WO}_3$ for 0, 1, 2, 5, 10, 20, and 30 min.

(1560 cm⁻¹) and N₂O₂⁻ species (1440 and 1013 cm⁻¹) still existed on the catalyst surface even after 30 min, showing that these species were inactive in the SCR reaction. Simultaneously, adsorbed NH₃ species rapidly formed on the catalyst surface, such as coordinated NH₃ at 1603 and 1180 cm⁻¹ and ionic NH₄⁺ at 1660, 1440, and the range of 1800–2000 cm⁻¹. During this process, additional bands at 1254 cm⁻¹ appeared, that were neither due to NH₃ nor NO_x species separately. According to Liu's work [30], this additional band could be surface ammonium nitrate (NH₄NO₃). All the results showed that bridging nitrate and monodentate nitrate can also react with NH₃ in the SCR reaction. This second reaction pathway could give some contribution to the improvement of catalytic activity.

Based on these TPD and DRIFTS studies, we suggest that over the CeO₂-WO₃ catalyst, CeO₂ mainly provided adsorption sites on the surface, while WO₃ increased the amount and strength of the Brönsted acid sites, and enhanced the NO oxidation ability. Brönsted acid sites and Lewis acid sites were both active in the SCR reaction. The mechanism of surface transformation of NO_x on mixed-oxide catalysts has been studied extensively [1]. Different hypotheses have been proposed for the mechanism of this reaction [1,31–33], including the reaction between ammonium ion and adsorbed NO₂, reaction between an amide and gaseous NO, and reaction between coordinated ammonia and a species generated by the spillover of NO on the support. In our work, the SCR reaction takes place through two pathways. In the first pathway, gaseous NH₃ molecules were adsorbed on the CeO₂-WO₃ catalysts to form coordinated NH₃ and ionic NH₄⁺, and simultaneously gaseous NO was oxidized into NO₂ in the presence of O₂. Then the reaction between the adsorbed NH₃ species and gaseous NO₂ occurred to form an intermediate species that easily decomposed into N₂ and H₂O. In the second pathway, the NO₂ produced was strongly adsorbed on the catalyst surface, and some active NO₂ adsorbed species, such as bridging nitrate and monodentate nitrate, reacted with NH₃ and NH₄⁺ species, and the NH₄NO₃ formed react with NO₂, producing N₂ and H₂O.

3 Conclusions

CeO₂-WO₃ mixed oxides were highly active in a wide temperature range for the SCR reaction of NO_x with NH₃. Nearly 100% NO_x conversion was obtained from 200–450 °C with high N₂ selectivity. In the CeO₂-WO₃ mixed oxide, CeO₂ provided adsorption sites, while WO₃ helped increase the amount and strength of Brönsted acid sites, and enhanced NO oxidation ability. Both ionic NH₄⁺ and coordinated NH₃ contributed to the SCR reaction. Bridging nitrate and monodentate nitrate were confirmed as the reactive

nitrate species. The reaction over the CeO₂-WO₃ catalyst takes place through two different pathways, which contributed to the higher catalytic activity.

References

- 1 Bosch H, Janssen F J. *Catal Today*, 1988, **2**: 369
- 2 Dunn J P, Koppula P R, Stenger H G, Wachs I E. *Appl Catal B*, 1998, **19**: 103
- 3 Liu F D, He H, Zhang C B. *Chem Commun*, 2008: 2043
- 4 Xu W Q, Yu Y B, Zhang C B, He H. *Catal Commun*, 2008, **9**: 1453
- 5 Gao X, Jiang Y, Zhong Y, Luo Z Y, Cen K F. *J Hazard Mater*, 2010, **174**: 734
- 6 Shen Y S, Zhu S M, Qiu T, Shen S B. *Catal Commun*, 2009, **11**: 20
- 7 Si Z C, Weng D, Wu X D, Li J, Li G. *J Catal*, 2010, **271**: 43
- 8 Gu T T, Liu Y, Weng X L, Wang H Q, Wu Z B. *Catal Commun*, 2010, **12**: 310
- 9 Chen L, Li J H, Ge M F, Zhu R H. *Catal Today*, 2010, **153**: 77
- 10 Chen L, Li J H, Ge M F. *J Phys Chem C*, 2009, **113**: 21177
- 11 Chen L, Li J H, Ge M F. *Environ Sci Technol*, 2010, **44**: 9590
- 12 Chen L, Li J H, Ge M F. *ACS Catal*, submitted
- 13 Tronconi E, Lietti L, Forzatti P, Malloggi S. *Chem Eng Sci*, 1996, **51**: 2965
- 14 Eigenmann F, Maciejewski M, Baiker A. *Appl Catal B*, 2006, **62**: 311
- 15 Shimizu K, Satsuma A, Hattori T. *Appl Catal B*, 1998, **16**: 319
- 16 Ramis G, Busca G, Bregani F, Forzatti P. *Appl Catal*, 1990, **64**: 259
- 17 Ramis G, Yi L, Busca G. *Catal Today*, 1996, **28**: 373
- 18 Matralis H K, Ciardelli M, Ruwet M, Grange P. *J Catal*, 1995, **157**: 368
- 19 Kijlstra W S, Brands D S, Smit H I, Poels E K, Blik A. *J Catal*, 1997, **171**: 219
- 20 Ramis G, Larrubia M A. *J Mol Catal A*, 2004, **215**: 161
- 21 Larrubia M A, Ramis G, Busca G. *Appl Catal B*, 2001, **30**: 101
- 22 Larrubia M A, Ramis G, Busca G. *Appl Catal B*, 2000, **27**: L145
- 23 Lin S D, Gluhoi A C, Nieuwenhuys B E. *Catal Today*, 2004, **90**: 3
- 24 Chen J P, Yang R T. *Appl Catal A*, 1992, **80**: 135
- 25 Choi E Y, Nam I S, Kim Y G. *J Catal*, 1996, **161**: 597
- 26 Qi G S, Yang R T, Chang R. *Appl Catal B*, 2004, **51**: 93
- 27 Mart'inez-Arias A, Soria J, Conesa J C, Seoane X L, Arcoya A, Cataluña R. *J Chem Soc, Faraday Trans*, 1995, **91**: 1679
- 28 Hadjiivanov K I. *Catal Rev-Sci Eng*, 2000, **42**: 71
- 29 Underwood G M, Miller T M, Grassian V H. *J Phys Chem A*, 1999, **103**: 6184
- 30 Liu F D, He H. *Catal Today*, 2010, **153**: 70
- 31 Komatsu T, Ogawa T, Yashima T. *J Phys Chem*, 1995, **99**: 13053
- 32 Salker A V, Weiweiler W. *Appl Catal A*, 2000, **203**: 221
- 33 Centi G, Perathoner S. *J Catal*, 1995, **152**: 93