Catalysis Today 153 (2010) 95–102

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Knowledge and know-how in improving the sulfur tolerance of deNO$_x$ catalysts

Zhiming Liu[a,*], Junhua Li[b,*], Abu S.M. Junaid[c]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[b] Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China
[c] Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2G6, Canada

ARTICLE INFO

Article history:
Available online 15 March 2010

Keywords:
Selective catalytic reduction
NO$_x$ storage and reduction
Sulfur tolerance
deNO$_x$ catalyst

ABSTRACT

Catalytic removal of NO$_x$ under lean-burn conditions is challenging to attain the future stringent NO$_x$ emission standards. Selective catalytic reduction (SCR) of NO$_x$ with different reducing agents and NO$_x$ storage-reduction (NSR) are viewed as the two most promising technologies for NO$_x$ removal. Although a variety of catalytic systems have been developed for these processes, their practical applications remain difficult due to catalyst deactivation caused by SO$_2$ in the exhaust gases. Therefore, improving catalyst tolerance against SO$_2$ is one of the most important targets in the deNO$_x$ catalyst development. This review focuses on the knowledge and know-how that have been developed in improving the sulfur tolerance of deNO$_x$ catalysts. Ag/Al$_2$O$_3$ is the most promising catalyst for the HC-SCR of NO$_x$. Support modification, H$_2$ co-feeding and some other strategies to improve the sulfur tolerance of Ag/Al$_2$O$_3$ are discussed. Some novel catalyst systems with high sulfur tolerance for NH$_3$-SCR, H$_2$-SCR and NSR are addressed, respectively. For NSR catalysts, developing novel sulfur resistant NO$_x$ storage systems and effective desulfation processes seem to be two avenues to improve their sulfur resistance.

1. Introduction

Catalytic removal of NO$_x$ under oxidizing conditions is one of the most important targets in environmental catalysis research. There are two major strategies to control the NO$_x$ emissions in the presence of oxygen: selective catalytic reduction (SCR) of NO$_x$ by different reducing agents (hydrocarbons, NH$_3$ or H$_2$) and NO$_x$ storage and reduction (NSR) [1]. SO$_2$, typically present in the exhaust, usually plays a detrimental role on the performance of deNO$_x$ catalysts [1,2]. The poisoning caused by SO$_2$ is assumed that under reaction conditions SO$_2$ reacted with O$_2$ on the catalyst surface to form thermodynamically stable sulfate phases, which then covered the catalyst surface and reduced the number of chemisorption sites for NO$_x$ [3]. When hydrocarbons are used as reducing agents, SO$_2$ can lead to additional formation of carbonaceous deposits, which also deactivate catalytic sites [4]. SO$_2$ resistance is therefore a crucial and desirable aspect for assessment of any potential deNO$_x$ catalysts [1].

To date, extensive studies have been conducted on the development of deNO$_x$ catalysts and many of these have been reviewed [1,5–7], where some aspects of either the overall reaction mechanism or material properties of different catalyst systems were reported, but only limited effort has been made to address the knowledge and advancements in improving the sulfur tolerance of deNO$_x$ catalysts [8]. The main focus of the paper is to address the knowledge and know-how that have been developed in improving the sulfur resistance of deNO$_x$ catalysts to shed light on designing more sulfur tolerant catalysts.

2. Selective catalytic reduction of NO$_x$

2.1. Selective catalytic reduction of NO$_x$ by hydrocarbons (HC-SCR)

Selective catalytic reduction of NO$_x$ by hydrocarbons (HC-SCR) has been extensively studied for NO$_x$ removal from diesel engine and lean-burn gasoline engine [1,6]. Composition of supports is one of the important factors for the SO$_2$ tolerance of deNO$_x$ catalysts undergoing HC-SCR reactions. As the most promising HC-SCR catalyst, Ag/Al$_2$O$_3$ has been studied by many researchers to improve its sulfur tolerance [1,9]. Li et al. suggested that Ag/TiO$_2$–Al$_2$O$_3$ catalyst was more sulfur resistant than Ag/Al$_2$O$_3$ [10]. Temperature programmed desorption (TPD) studies demonstrated that less amounts of SO$_2$ were adsorbed on composite amorphous TiO$_2$–Al$_2$O$_3$, and formed less alumina sulfate. Taking into consideration that TiO$_2$ and SiO$_2$ are weakly sulfating supports, and their sulfates decompose at lower temperatures than that of Al$_2$O$_3$ [11,12], Jagtap et al. [13] doped the support of Ag/Al$_2$O$_3$ with 1% TiO$_2$ or SiO$_2$ and found that the conversions of NO$_x$ remained

---

* Corresponding authors. Tel.: +86 10 64421077/10 62782030.
E-mail addresses: liuzm@mail.buct.edu.cn (Z. Liu), lijunhua@tsinghua.edu.cn (J. Li).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.01.061

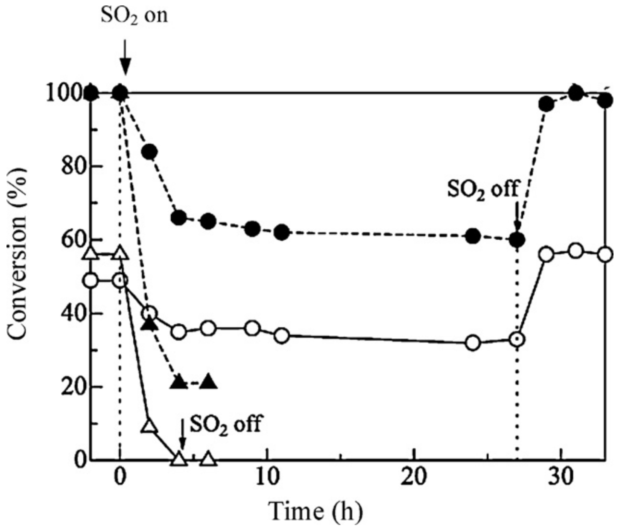

Fig. 1. Conversions of NO_x (unfilled symbols) and C_3H_8 (filled symbols) over 3% Ag/Al_2O_3 catalyst at 500 °C in the absence (△, ▲) or in the presence of 0.5% H_2 (○, ●). (Reproduced from the Ref. [16] with the permission from Elsevier).

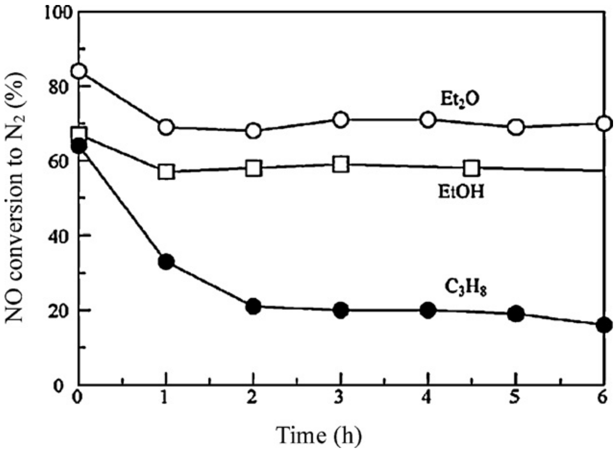

Fig. 2. Effect of reducing agents on the sulfur tolerance of 3% Ag/Al_2O_3 catalyst at 500 °C. Conditions: 0.1% NO; 6000 ppm oxygenates (based on C); 10% O_2; 3% H_2O; 50 ppm SO_2. (Reproduced from the Ref. [17] with the permission from Elsevier).

unchanged in the presence of SO_2 over both of these modified catalysts. FTIR spectra confirmed drastic reduction of both silver sulfate and aluminum sulfate formation on the surfaces, resulting in a remarkable enhancement in the sulfur tolerance of Ag/Al_2O_3 catalyst. Using $Ce_{0.16}Zr_{0.84}O_2$ instead of Al_2O_3 as the support of Ag, the catalyst can be facilely regenerated from SO_2 poisoning. This in a sense was an improvement in the sulfur tolerance property of the catalyst. $Ce_{0.16}Zr_{0.84}O_2$ support was suggested to act as a sink for sulfur-containing species accountable for the improved sulfur resistance of the catalyst [14].

Hydrogen co-feeding over Ag/Al_2O_3 can improve its sulfur tolerance, as illustrated in Fig. 1 [15,16]. In absence of H_2, conversions of both NO and C_3H_8 over 3% Ag/Al_2O_3 decreased significantly as 50 ppm SO_2 was added to the reaction gas mixture. And the catalyst was completely deactivated after operating for 4 h under the specified reaction conditions. When hydrogen was co-fed, the conversions, although decreasing after SO_2 addition, were relatively high compared to those without hydrogen and stable after 4 h. Moreover, the catalyst was fully recoverable following SO_2 removal from the gas stream [16]. Shimizu et al. [16] proposed that the improved sulfur tolerance was due to the reduction of sulfates to SO_2 by H_2 over silver sites and its subsequent desorption. Increasing Ag loading can result in a higher rate of sulfate reduction thus contribute to enhance the sulfur tolerance of the catalyst [16]. H_2 co-feeding was also found to be effective to improve the sulfur tolerance of Ag/Al_2O_3 catalyst with oxygenated hydrocarbons such as Et_2O, ETBE and EtOH as the reducing agents [17]. Park and Boyer [18] reported that the sulfur resistance of Ag/Al_2O_3 catalyst was dependent on Ag loading and that 8% Ag/Al_2O_3 exhibited high sulfur tolerance with C_3H_6 used as reducing agent. They attributed such resistance to the formation of Ag_2SO_4 in the presence of SO_2, which enhanced the NO_x reduction capability via producing more intermediate species (–NCO) that is known as a key intermediate species of lean-NO_x catalysis [19].

Sulfur tolerance of Ag/Al_2O_3 catalyst is also dependent on the type of reducing agents [17,20]. Fig. 2 demonstrates the effect of C_3H_8, Et_2O or EtOH on the sulfur tolerance of 3% Ag/Al_2O_3 catalyst at 500 °C. In the case of C_3H_8 as a reductant, the NO conversion significantly decreased from 64% to 20% within 3 h of SO_2 co-feeding. In contrast, the NO conversions were only slightly decreased when Et_2O or EtOH were used as reductant, respectively. To evaluate the degree of sulfur tolerance Shimizu et al. [17] introduced the sulfur tolerance factor, the ratio of steady-state NO conversion in the presence of SO_2 to that in the absence of SO_2. In this case the values showed the following order: EtOH (0.87) > Et_2O (0.85) ≫ C_3H_8 (0.31) [17]. Obviously, the deNO_x system in EtOH-SCR showed high degree of sulfur tolerance. Wu et al. [20] also found the high sulfur resistance in EtOH-SCR, which was very different from the serious SO_2 suppression occurring in the case of isopropyl alcohol (IPA)-SCR under the same experimental conditions. In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) analysis showed that no sulfate species was formed on the Ag/Al_2O_3 catalyst in presence of EtOH, which explains the effectiveness of EtOH as a reducing agent compared to IPA in the presence of SO_2 [20]. Zhu et al. [21], on the other hand, contributed the enhanced NO_x reduction by CH_3OH over Ag/Al_2O_3 between 300 and 400 °C in presence of SO_2 to the formation of active sulfate species. In the case of decane as a reducing agent, the presence of 1 ppm SO_2 contributed the NO_x reduction to proceed on Ag/Al_2O_3 catalyst and the promoting effect was more noticeable on $Rh/Ag/Al_2O_3$ catalyst. The presence of SO_2 inhibited decane combustion, making it more available for NO_x reduction, thus resulted in higher NO_x conversion [22].

Non-thermal plasma (NTP) can assist in improving the sulfur tolerance of Ag/Al_2O_3 catalyst. Fig. 3 compares the NO_x conversions in thermal SCR and NTP assisted SCR over sulfated Ag4N–Ag4S/Al_2O_3 (where N and S represent the catalyst was prepared from precursor $AgNO_3$ and Ag_2SO_4, respectively, and the number before N and S indicates the contents of Ag) catalysts relative to that over Ag5N/Al_2O_3 in presence of SO_2 [23]. It is evident that NO_x conversions below 400 °C were significantly increased with the assistance of NTP. Over 60% NO_x conversions were obtained within a wide temperature window of 300–550 °C. It was suggested that NTP simultaneously promotes the oxidation of NO and activation of propene, resulting in direct formation of N-containing organics which are important for NO_x reduction over a sulfated Ag/Al_2O_3 catalyst [23].

Selective catalytic reduction of NO_x by hydrocarbons on noble metal catalysts was also extensively studied and Pt catalyst is the most attractive one [3]. Corro et al. [24] found pre-sulfated Pt–Sn/Al_2O_3 catalyst showed higher sulfur tolerance than pre-sulfated Pt/Al_2O_3 catalyst. Addition of Sn to Pt phase over Al_2O_3 support modifies the electron density of Pt, which lowers the adsorption strength of SO_2 and weakens the interaction between SO_2 and O_2. This results in less sulfate formation on the catalyst surface, and an eventual increase in the number of sites available for NO_x reduction. On the other hand, addition of Sn also prevents Pt

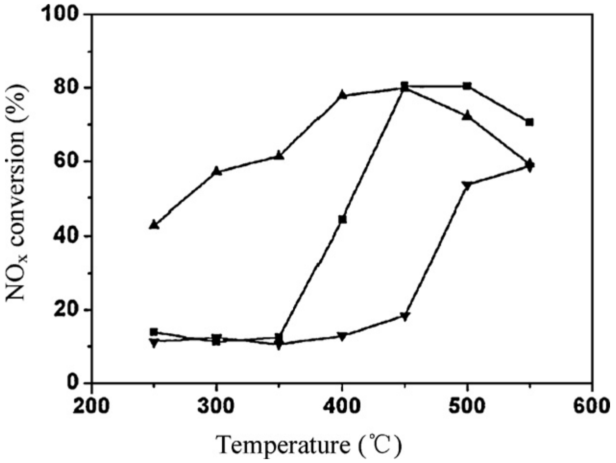

Fig. 3. NO_x conversions over Ag/Al_2O_3 catalysts in the following process: SCR over fresh $Ag5N/Al_2O_3$ catalyst (▼), SCR over sulfated $Ag4N–Ag4S/Al_2O_3$ (■), non-thermal plasma assisted SCR over sulfated $Ag4N–Ag4S/Al_2O_3$ (▲). Conditions: 1000 ppm NO; 1000 ppm C_3H_6; 8% O_2; 100 ppm SO_2; N_2 balance; GHSV = 14,000 h^{-1}. (Reproduced from the Ref. [23] with the permission from Elsevier).

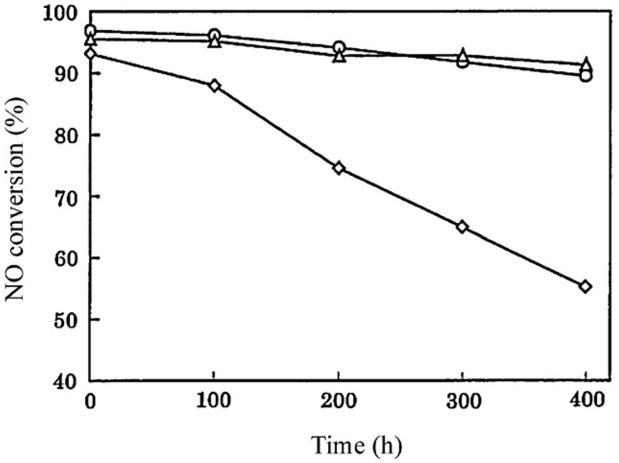

Fig. 4. Sulfur tolerance of 8 wt% V_2O_5/T7S10M (○), 8 wt% V_2O_5/T20S10M (△) and 8 wt% V_2O_5–10 wt% MoO_3/TiO_2 (◊) catalysts at 175 °C. Reaction conditions: 100 ppm NO, 80 ppm NH_3, 150 ppm SO_2, 10% O_2, 10% H_2O, N_2 balance. NO conversion was measured at NH_3/NO molar ratio of 1. (Reproduced from the Ref. [31] with the permission from Springer).

particles from sintering during sulfation at 500 °C, thus maintaining the Pt surface unaltered for the oxidation of NO to NO_2, which is regarded as an important process for NO_x reduction [24,25]. Salem et al. [26] also observed such higher sulfur tolerance of pre-sulfated $Pt–Sn/Al_2O_3$ catalyst as compared to pre-sulfated Pt/Al_2O_3 catalyst.

Arakawa et al. [27] proposed a new concept for a lean-NO_x catalyst with high sulfur resistance. Two-stage catalyst composed of Cu/ZSM-5 followed by $Au–Pt/TiO_2$ confirmed the possibility of recovering the activity of the lean-NO_x catalyst in the presence of SO_2. Over the front Cu/ZSM-5 catalyst, the presence of SO_2 would cause the formation of $CuSO_4$ on the surface, leading to the conversion of NO_x decreased. However, CO formed due to the incomplete combustion of C_3H_6 over the poisoned Cu/ZSM-5. The formed CO can be used to reduce NO_x over the rear $Au–Pt/TiO_2$ catalyst. Compared with a single Cu/ZSM-5, about a 50% recovery of the lost NO_x conversion was achieved by the two-stage catalyst.

2.2. Selective catalytic reduction of NO_x by NH_3 (NH_3-SCR)

Selective catalytic reduction of NO_x with NH_3 under lean conditions is a widely commercialized technology for NO_x removal from stationary sources [1]. V_2O_5/TiO_2, an active catalyst for this process, shows significant resistance against SO_2 within the temperature range of 300–400 °C. However, below 300 °C SO_2 poisoning becomes a serious issue as $(NH_4)_2SO_4$ and NH_4HSO_4 form on the catalyst surface and cover the active sites, reducing the activity to a great extent [28]. Composite active phases were investigated to enhance the sulfur tolerance of catalysts in NH_3-SCR. It was reported that 5–10% W addition to V_2O_5/TiO_2 catalyst improved its sulfur tolerance at low temperatures [29]. Considering the fact that the cost of W addition will increase the price of the catalyst significantly, Phil et al. [30] tried several alternative promoters (Se, Sb, Cu, B, Bi, etc.) on the catalyst and found that Sb was efficient to improve the sulfur tolerance of the catalyst. Addition of 2% Sb can result in higher sulfur tolerance than that resulting from 10% W addition. The research showcased $Sb–V_2O_5/TiO_2$ as a highly promising catalyst for NO_x reduction at low temperatures.

Sulfur tolerance of V_2O_5 catalysts can also be improved by using composite oxide supports. Kobayashi et al. [31] found $V_2O_5/TiO_2–SiO_2–MoO_3$ (TSM) catalyst exhibited excellent sulfur tolerance below 250 °C. As shown in Fig. 4, the activity of $V_2O_5–MoO_3/TiO_2$ significantly decreased after 400 h of operation in the presence of SO_2. In contrast, little decrease in activity was observed on both V_2O_5/T7S10 M (the number before S and M indicates the contents of SiO_2 and MoO_3, respectively) and V_2O_5/T20S10 M catalysts. It was suggested that due to higher acidity of the V_2O_5/TSM catalysts the SO_2 oxidation activity is lower, which causes remarkable improvement of sulfur tolerance of the catalyst. Hou et al. [32] replaced TiO_2 with activated carbon fiber (ACF) as the support of V_2O_5 and discovered good SO_2 tolerance and higher SCR activity for NO removal within the temperature range of 120–200 °C. Fig. 5 illustrates that the presence of SO_2 has a promoting effect on NO_x conversion over V_2O_5/ACF catalyst, as the NO conversion increased from 50% to 90% upon introducing 300 ppm SO_2 over 50 min. More importantly, transient response study revealed that removal of SO_2 did not lead to any decline in NO conversion but rather exhibited a slight increase. This indicates that the promoting effect is not from the gas phase SO_2 but from some sulfur-containing species formed and deposited on the catalyst surface (shown in Fig. 6). Formation of $SO_4{}^{2-}$ via SO_2 oxidation increased the acidity of the catalyst surface and contributed to ammonia adsorption on the surface [32,33].

Mn/TiO_2 catalyst was reported to be an active low-temperature catalyst for NH_3-SCR [34,35]. However, SO_2 exerts a serious poison-

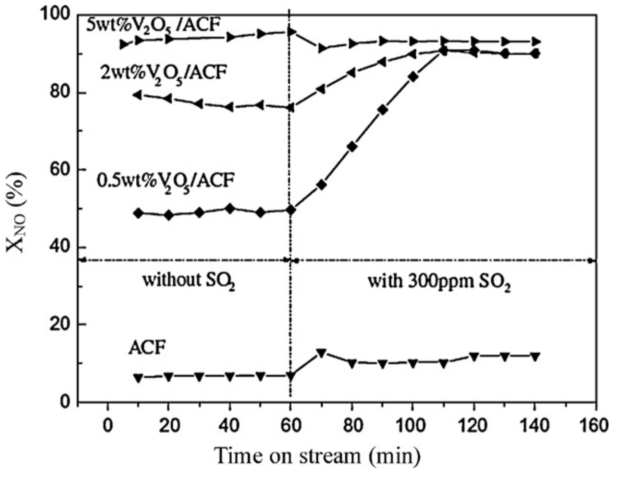

Fig. 5. Effect of SO_2 on the activity of V_2O_5/ACF and ACF catalysts at 180 °C. Reaction conditions: 600 ppm NO, 600 ppm NH_3, 5% O_2, 0 or 300 ppm SO_2, Ar balance. (Reproduced from the Ref. [32] with the permission from Elsevier).

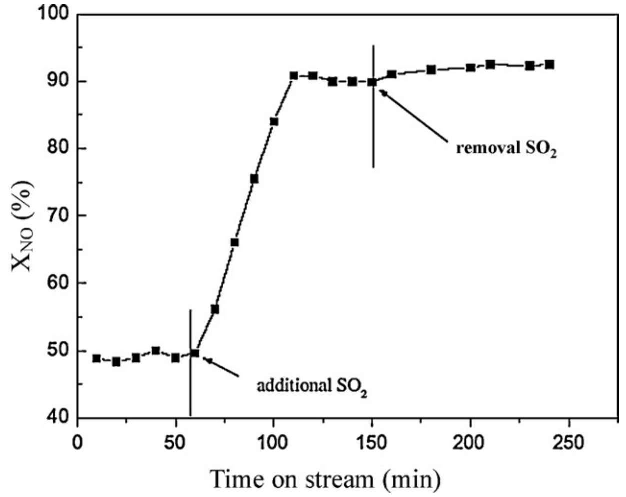

Fig. 6. Transient response of SO_2 in the SCR reaction over 0.5 wt% V_2O_5/ACF catalyst. Reaction conditions are the same as the case presented in Fig. 5. (Reproduced from the Ref. [32] with the permission from Elsevier).

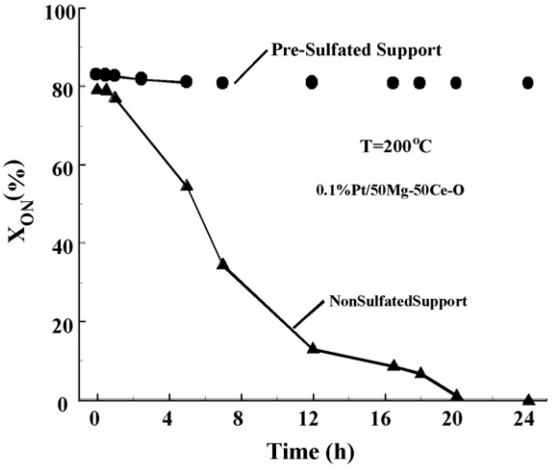

Fig. 7. Stability test performed at 200 °C on 0.1 wt% Pt catalysts over pre-sulfated (●) and non-sulfated (▲) 50Mg–50Ce–O supports. Conditions: 1.0% H_2, 0.25% NO, 5% O_2, 5% H_2O, 25 ppm SO_2, GHSV = 80,000 h^{-1}. (Reproduced from the Ref. [44] with the permission from Elsevier).

ing effect on its activity [36]. Wu et al. [36] found that the resistance against SO_2 can be greatly enhanced by adding Ce to Mn/TiO_2 catalyst, a strategy similar to the addition of W or Sb to V_2O_5. They claimed that such doping can prevent the formation of $Ti(SO_4)_2$ and $Mn(SO_4)_x$ and inhibit the deposition of $(NH_4)_2SO_4$ and NH_4HSO_4 on the catalyst surface, contributing to improve the sulfur tolerance.

Ag/Al_2O_3 catalyst was also highly active for NH_3-SCR in the copresence of H_2 [37]. More importantly, the catalyst exhibited NO_x conversion over 90% for 120 h at 200 °C with no indication of catalyst deactivation in the presence of 50 ppm SO_2, demonstrating that this catalyst was highly tolerant to SO_2 [38].

Metal-exchanged zeolite catalysts have received much attention because they can operate in a wider temperature window [39]. Considering the different channel size of mordenite and clinoptilolite zeolites, Moreno-Tost et al. [40] compare the sulfur tolerance of Cu-exchanged mordenite and clinoptilolite catalysts for NH_3-SCR. They found that Cu-exchanged clinoptilolite underwent a severe deactivation caused by SO_2. However, Cu-exchanged mordenite exhibited a high stability (100% of conversion) in the presence of SO_2 at 300 °C. The deactivation of Cu-exchanged clinoptilolite was suggested to be due to the formation of $(NH_4)_2SO_4$ on the surface, which could block the access of the reactant molecular to the pores thus prevent the SCR reaction to occur. However, in the case of Cu-exchanged mordenite, even though there were higher sulfate formed, the access was not impeded due to the larger size of the channels of this zeolite. Mn–Ce/ZSM-5, as a new superior catalyst, has been found to be highly resistant against SO_2 [41]. A barely detectable decrease in the NO_x conversion over Mn–Ce/ZSM-5 was observed upon switching to a feed containing water and SO_2, indicating that this catalyst is promising for industrial application.

2.3. *Selective catalytic reduction of NO_x by H_2 (H_2-SCR)*

H_2 was found to be a very efficient reducing agent for the catalytic reduction of NO_x at low temperatures (<200 °C) [42,43]. Pre-sulfation of the support can indirectly induce extreme SO_2 resistance on the catalysts in course of H_2-SCR. Costa et al. [44,45] found that pre-sulfation of the MgO–CeO_2 support of Pt/MgO–CeO_2 catalyst prior to H_2-SCR can significantly improve the sulfur tolerance of the catalyst. Before Pt deposition, the MgO–CeO_2 was initially impregnated with a proper amount of NH_4NO_3 aqueous solution to prevent sulfation of NO_x adsorption sites [46]. Following water evaporation and drying at 120 °C the residue was sieved, heated in air at 300 °C for 2 h, and then impregnated with an appropriate amount of $(NH_4)_2SO_4$ aqueous solution. After water evaporation and drying again at 120 °C, the resulting solid was ground and heated in air at 600 °C for 2 h prior to Pt deposition on the sulfated support [44]. Fig. 7 illustrates that while the activity of the non-sulfated MgO–CeO_2 supported catalyst gradually decreased and was completely lost in about 20 h in the presence of SO_2, the pre-sulfated MgO–CeO_2 supported catalyst remained its activity and was extremely stable during 24 h of continuous reaction [44]. Costa et al. [45] proposed a mechanistic scheme involving the role of sulfates present on the surface of the support to explain such extra-ordinary prohibition of deactivation, as shown in Fig. 8. According to this scheme, SO_2 is primarily chemisorbed on the basic sites (O^{n-}) of the support to form bidentate or unidentate sulfite species, while SO_3 is mainly chemisorbed on the acidic sites (Mg^{2+}/Ce^{4+}) to form bidentate sulfates [47]. Both basic and acidic sites of MgO and CeO_2 were proven to accommodate chemisorbed NO [48]. Considering that the chemisorptions of SO_2 and SO_3 were stronger than that of NO on the latter sites [49], the support surface was expected to be gradually covered by sulfite and sulfate species as shown in Fig. 8a, leading to the loss of active sites for NO adsorption and thus deactivation of the catalyst. However, when the support is pre-sulfated, the formed sulfates ($SO_4{}^{2-}$) adsorbed particularly on Mg^{2+} but not on two adjacent Mg^{2+} cations due to geometrical constrains (Fig. 8b–d). The available space between two adjacent surface adsorbed sulfate species is about 2.5 Å, whereas the required space for the adsorption of SO_3 and SO_2 is greater than 2.5 Å (Fig. 8b and c) [50]. Therefore, adsorption of any more gas phase SO_2 or SO_3 is inhibited. However, NO molecule, being substantially smaller than SO_2 or SO_3, can be chemisorbed on a free O–Mg^{2+}–O to form an active bidentate nitrate species (Fig. 8d) [51]. Thus, the pre-sulfated MgO–CeO_2 forms the support of an extremely SO_2-resistant NO_x control catalytic material, and to date, Pt/MgO–CeO_2 catalyst remains the most active and stable catalyst for H_2-SCR in the presence of SO_2.

3. NO_x storage and reduction (NSR)

NO_x storage and reduction (NSR) technology is one of the promising methods for the removal of NO_x from lean-burn engines [1,7]. The typical NSR catalyst consists of noble metals (mainly Pt), alkaline and alkaline earth metal oxides as the NO_x storage materials (usually Ba), and a metal oxide as the support. Under lean-burn

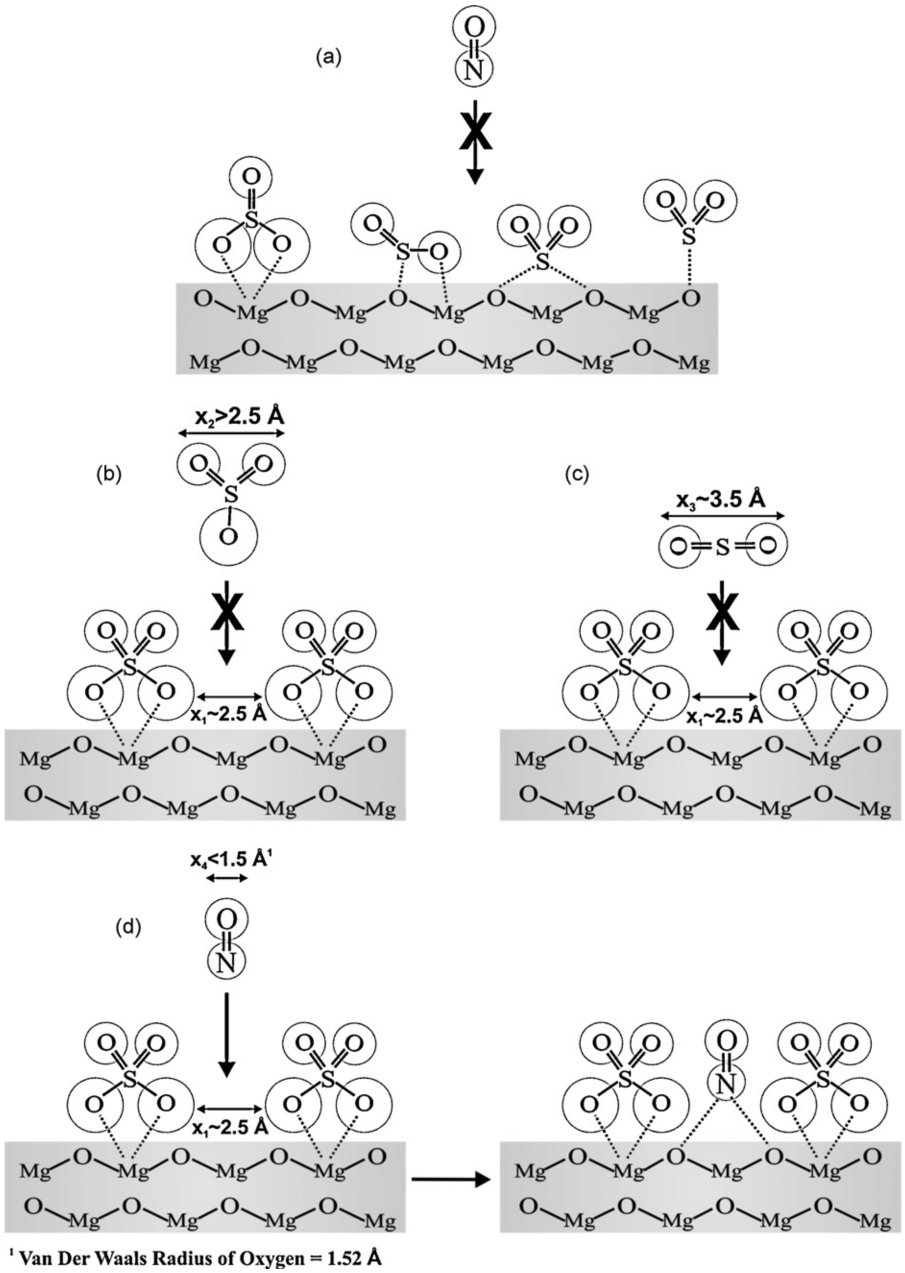

Fig. 8. Mechanistic scheme illustrating the role of sulfates present on the surface of MgO–CeO$_2$ support in prohibiting the deactivation of 0.1 wt% Pt/MgO–CeO$_2$ catalyst in the presence of SO$_2$ below 250 °C. (Reproduced from the Ref. [45] with the permission from Elsevier).

conditions NO was oxidized to NO$_2$ over Pt catalyst and then was stored in a form of nitrate on the surface of Ba-containing material. After changing periodically to short cycles of fuel-rich conditions the stored NO$_x$ was released and subsequently reduced to N$_2$ by HC, CO, and H$_2$ over noble metal catalyst. The major drawback of the NSR approach is that the catalysts are quite susceptible to sulfur poisoning [1]. Sulfur tolerance experiments established the loss of storage and reduction behavior primarily a result of surface sulfate formation. Surface sulfate is more stable than nitrate for such storage components, and hinders the reaction with NO$_x$ [52]. Competitive adsorption between NO$_x$ and SO$_2$ can be an additional cause. Therefore, in order to develop a practically effective NSR process, the catalyst needs to be modified to inhibit adsorption of SO$_2$ and promote desorption of sulfur species. SO$_2$ deactivation of NSR catalysts is a function of its concentration. Lower concentration of SO$_2$ deactivates NSR catalysts to a lesser extent, even if the total SO$_2$ exposure was higher [53].

The acidity of the support is an important factor regarding the sulfur tolerance of a NSR catalyst [54]. Recent studies showed that the TiO$_2$ component in the support provided high tolerance against sulfur poisoning because of its high acidity/low basicity [55,56]. For ZrO$_2$–TiO$_2$ support, there was an optimum amount of TiO$_2$, corresponding to the optimum ZrO$_2$/TiO$_2$ ratio of 7:3 with highest acidity, and thus highest sulfur tolerance [57]. A nano-composite of Al$_2$O$_3$ and a ZrO$_2$–TiO$_2$ solid solution (AZT) doped with Ti (Ti-AZT) exhibited high sulfur durability in NSR by facilitating sulfur desorption from the support [58]. Pt–Rh/TiO$_2$/Al$_2$O$_3$ also showed high sulfur resistance: in the presence of 100 ppm SO$_2$ and 2.3% H$_2$O, approximately 90% NO$_x$ conversion was obtained at 250 °C after 5 h of lean-rich cyclic runs [59].

Addition of transition metal promoters can provide significant improvements in sulfur tolerance of NSR catalysts. Hammache et al. [53] suggested that when Cu was added to Pt–BaO/Al$_2$O$_3$ catalyst, a Pt–Cu bimetallic phase formed because of the close proximity of the two metals, resulting in a reduced affinity for SO_2 adsorption relative to Pt, and a diminished activity for SO_2 oxidation. Cu addition also promoted SO_2 resistance in Mg/Al-hydrotalcite (HT)-based catalysts [60]. In this case the promoting effect was attributed to a possible surface modification by Cu, creating a Cu-containing surface mixed oxide which stabilized the catalyst against the formation of a $MgAl_2O_4$ spinel phase. Another possibility was the formation of Pt-Cu alloys, as evidenced by FTIR characterization upon reduction [61]. Another catalyst derived from HT, with a molar ratio of Co/Mg/Al = 15/60/25 and containing 1% V, also showed high sulfur resistance [62]. This is due to the low SO_3 capture rate of the Mg sites, which were less basic than the Ba sites, and also to the higher resistance against poisoning of V compared to Pt.

Fe was also reported to exhibit promoting effect for sulfur tolerance. When added to Pt–Ba/Al_2O_3 catalysts, Fe facilitates formation of bulk nitrate species, which is resistant to the effects of SO_2 [63]. In addition, Yamazaki et al. [64] claimed that Fe-compounds inhibited the growth of $BaSO_4$ particles under oxidizing conditions in the presence of SO_2, and promoted the decomposition of $BaSO_4$ and desorption of sulfur compounds under reducing conditions. Ba–Fe–O complex oxide catalyst prepared by sol–gel method was found to be active for NO_x storage and 45 ppm SO_2 feeding showed no inhibition on its activity [65]. Such high sulfur tolerance can be attributed to the formation of perovskite type $BaFeO_3$ and $BaFeO_{3-x}$ phases.

The role of Ce as a promoter to improve the sulfur resistance of Pt–Ba/Al_2O_3 catalyst has also been proposed [66]. The Ce additive was sulfated rather than the BaO phase, thus the active BaO phase near the Pt clusters was protected and remained available for NO_x storage even after SO_2 exposure, showing higher sulfur tolerance. Kwak et al. [67] investigated the variation in NO_x uptake (for a 30 min lean uptake) at 250 °C by sulfation/desulfation treatment for the Pt/Ba/Al_2O_3 and Pt/Ba/CeO_2 catalysts and the results are shown in Fig. 9. The NO_x uptake on Pt/Ba/CeO_2 (43%) was much higher than that on Pt/Ba/Al_2O_3 (23%) after SO_2 treatment. The former catalyst was still more active that the latter one even after reductive desulfation treatment at 600 °C. X-ray photoelectron spectroscopy (XPS) combined with transmission electron microscopy and energy dispersive X-ray spectroscopy (TEM-EDS) analysis revealed that the high sulfur tolerance of Pt/Ba/CeO_2 catalyst was due to the suppression of SO_2 oxidation to SO_3 over smaller Pt particles present on the catalyst.

Incorporation of alkali metal (Na, K, Cs) to Ba-based NSR catalyst results in significantly improved sulfur tolerance. For the Ba-based NSR catalyst, NO_x conversions decreased to about 30–40% after each sulfur poisoning and the conversion can be recovered to 65–70% after desulfation. In contrast, for the Ba-based NSR catalyst with alkali metal added, NO_x conversions were in the range of 70–75% after sulfur poisoning and 95–100% after desulfation [68].

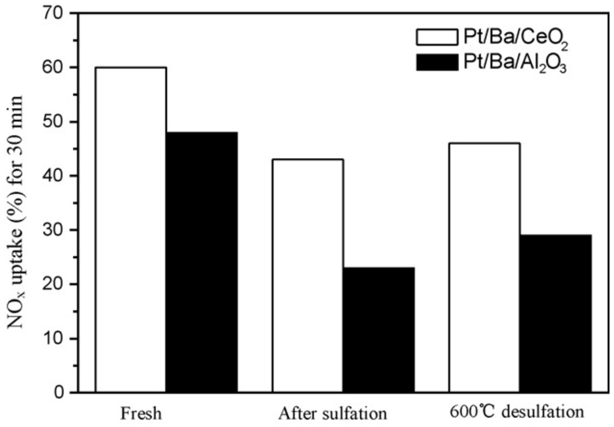

Fig. 9. The variation in NO_x uptake (for a 30 min lean uptake) at 250 °C by sulfation/desulfation treatment for the Pt/Ba/Al_2O_3 and Pt/Ba/CeO_2 catalysts. (Reproduced from the Ref. [67] with the permission from Elsevier).

Controlling the basicity of surfaces can contribute to develop successful deNO_x catalysts. Clacens et al. [69] reported one Pt-free NO_x traps based on a mixture of CuO/$ZrSO_4$ and KNO_3/Al_2O_3. The basicity of the surface in this case was controlled by changing the dispersion of CuO. It was found that the capacity for NO_x adsorption slightly increased instead of decreasing in presence of 25 ppm SO_2 on badly dispersed CuO. It should be noted that the study was conducted on mixed powder catalysts. For a potential commercial product, the coating process may lead to an interaction of the mixed components, which could impart negative effects on the sulfur tolerance.

To solve the sulfur problem, Toyota researchers have conducted a lot of research and the sulfur tolerance was improved by adding TiO_2 or Li_2O to the alumina support [54]. Addition of Rh/ZrO_2, a steam reforming catalyst, promoted in situ generation of hydrogen, which enhanced the reduction of barium sulfate and regenerated the catalyst from SO_2 poisoning [54]. Another interesting approach to increase sulfur resistance is to change the shape of the monolithic substrate from square cells to hexagonal cells [54]. For the same amount of wash-coat, the variation of wash-coat thickness is much less in the hexagonal cell substrate than in the square cell substrate (Fig. 10). The fraction of wash-coat less than 100 μm thick was about 90% on the hexagonal cell substrate, compared to about 66% on the square cell substrate. The uniform wash-coat of

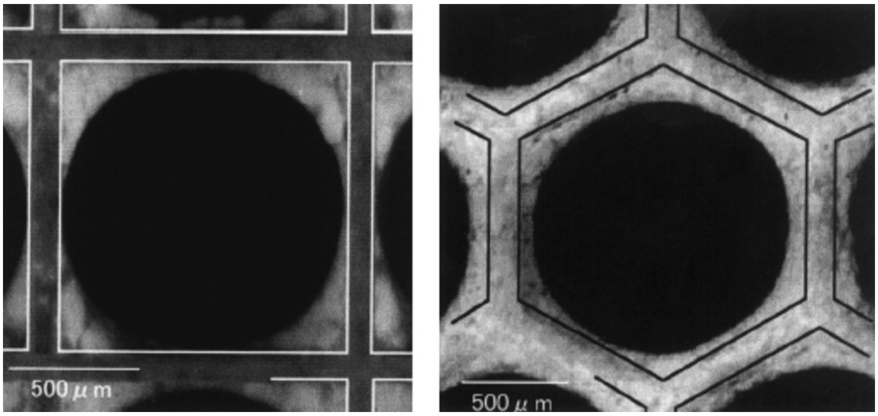

Fig. 10. Photographs of wash-coat layer on square cell (left) and hexagonal cell (right) monolithic substrate. (Reproduced from the Ref. [54] with the permission from Elsevier).

the hexagonal cell substrate distributes the catalytic components evenly, leading to high sulfur tolerance.

Parks II et al. [70] proposed a sorbate catalyst system that can reduce the effect of sulfur poisoning on a NO_x sorbate catalyst. The system places a sulfur sorbate catalyst ($SCOSO_x$^{TM}) upstream of a NO_x sorbate catalyst ($SCONO_x$^{TM}). The sulfur induced deactivation of the NO_x catalyst can be reduced by a factor greater than 10 with the protection provided by the sulfur sorbate catalyst, thus excellent NO_x conversion can be obtained. An effective desulfation process may also contribute to improve the sulfur tolerance of NSR catalysts, provided the process does not otherwise adversely affect the catalyst properties. Kim et al. [71] found that desulfation by hydrogen was significantly easier at lower Ba loadings in $Pt/Ba/Al_2O_3$ catalyst. Although NO_x conversion for $Pt/Ba/Al_2O_3$ was as high as that for $Pt/Sr/Al_2O_3$ [72], the regeneration of SO_2 poisoned $Pt/Sr/Al_2O_3$ was easier than that of $Pt/Ba/Al_2O_3$ [73]. This is due to the lower stability of $SrSO_4$ in the desulfation process compared to $BaSO_4$ [73,74]. The atmosphere was also found to be important for the desulfation process. For example, H_2 is more efficient than CO in removing the sulfur form the trap [75], and regeneration with H_2 in combination with CO_2 was more effective than with H_2 solely for both $Pt/Ba/Al_2O_3$ and $Pt/Sr/Al_2O_3$ catalysts [73].

4. Conclusions

The promoting effect of H_2 on the sulfur tolerance of Ag/Al_2O_3 catalyst makes it more promising for the practical application since there is some amount of H_2 in the exhaust. However, the exact mechanism of the "H_2 effect" has not been well understood yet. Further studies are necessary to elucidate the mechanism which will direct us towards making full use of the hydrogen in the SCR reaction. For NH_3-SCR, activated carbon could be a promising support for V_2O_5 catalyst. Greater understanding of activated carbon structure together with the chemistry of the interfaces of activated carbon and V_2O_5 is needed. Although investigations have been conducted on H_2-SCR, many of these were conducted in the absence of SO_2. Even the stability of some catalyst was tested in the presence of SO_2, the reaction time was relatively short. Therefore, the effect of sulfur on these catalysts should be studied extensively.

To date NSR is the most promising deNO_x technology, although there are still issues with the sulfur tolerance, particularly at high SO_2 concentration. In order to satisfy strengthening exhaust emission control and handle various type of fuel used in different countries, the tolerance to sulfur over NSR catalyst is still to be much improved. Complementary theoretical calculations can assist in the investigation of fundamental aspects which are difficult or impossible to access by experimental study. A combination of state-of-the-art experimental techniques and first principle calculations can help us fully comprehend the mechanisms of sulfur poisoning on NSR catalysts. Besides the conventional $Pt–Ba/Al_2O_3$ catalyst, novel NSR catalyst with high sulfur tolerance should be developed.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 20907003, 20677034), Beijing University of Chemical Technology Start-up Program for Attracting High-level Talents (2008) and State Key Laboratory of Chemical Resources Engineering Foundation (2009).

References

[1] Z. Liu, S.I. Woo, Catal. Rev. 48 (2006) 43.
[2] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu, N. Mizuno, Appl. Catal. 69 (1991) 15.
[3] F.C. Meunier, J.R.H. Ross, Appl. Catal. B 24 (2001) 23.
[4] Z. Liu, K.S. Oh, S.I. Woo, Catal. Surv. Asia 10 (2006) 8.
[5] S. Roy, A. Baiker, Chem. Rev. 109 (2009) 4054.
[6] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283.
[7] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks, Catal. Rev. 46 (2004) 163.
[8] G. Corro, React. Kinet. Catal. Lett. 75 (2002) 89.
[9] J.P. Breen, R. Burch, C. Hardacre, C.J. Hill, B. Krutzsch, B. Bandl-Konrad, E. Jobson, L. Cider, P.G. Blakeman, L.J. Peace, M.V. Twigg, M. Preis, M. Gottschling, Appl. Catal. B 70 (2007) 36.
[10] J. Li, Y. Zhu, R. Ke, J. Hao, Appl. Catal. B 80 (2008) 202.
[11] B.A. Morrow, R.A. Mcfarlane, M. Lion, J.C. Lavalley, J. Catal. 107 (1987) 232.
[12] O. Saur, M. Bensitel, A.B.M. Saad, J.-C. Lavally, C.P. Tripp, B.A. Morrow, J. Catal. 99 (1986) 104.
[13] N. Jagtap, S.B. Umbarkar, P. Miquel, P. Granger, M.K. Dongare, Appl. Catal. B 90 (2009) 416.
[14] N. Hickey, P. Fornasiero, J. Kăspar, M. Graziani, G. Martra, S. Coluccia, S. Biella, L. Prati, M. Rossi, J. Catal. 209 (2002) 271.
[15] S. Satokawa, J. Shibata, K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 42 (2003) 179.
[16] K. Shimizu, T. Higashimata, M. Tsuzuki, A. Satsuma, J. Catal. 239 (2006) 117.
[17] K. Shimizu, M. Tsuzuki, A. Satsuma, Appl. Catal. B 71 (2007) 80.
[18] P.W. Park, C.L. Boyer, Appl. Catal. B 59 (2005) 27.
[19] Z. Liu, S.I. Woo, W.S. Lee, J. Phys. Chem. B 110 (2006) 26019.
[20] Q. Wu, Q. Feng, H. He, Catal. Commun. 7 (2006) 657.
[21] T. Zhu, J. Hao, W. Li, Chem. Lett. (2000) 478.
[22] K. Sato, T. Yoshinari, Y. Kintaichi, M. Haneda, H. Hamada, Catal. Commun. 4 (2003) 315.
[23] R. Ke, Q. Chen, J. Li, Y. Zhu, J. Hao, Catal. Commun. 8 (2007) 589.
[24] G. Corro, J.L.G. Fierro, R. Montiel, S. Castillo, M. Moran, Appl. Catal. B 46 (2003) 307.
[25] G. Corro, R. Montiel, J. Mol. Catal. A 184 (2002) 443.
[26] I. Salem, X. Courtois, E.C. Corbos, P. Marecot, D. Duprez, Catal. Commun. 9 (2008) 664.
[27] K. Arakawa, S. Matsuda, H. Kinoshita, SAE paper 980930, 1998, pp. 377.
[28] P.G. Smirniotis, D.A. Peña, B.S. Uphade, Angew. Chem. Int. Ed. 40 (2001) 2479–2482.
[29] S.T. Choo, S.D. Yim, I.-S. Nam, S.-W. Ham, J.-B. Lee, Appl. Catal. B 44 (2003) 237–252.
[30] H.H. Phil, M.P. Reddy, P.A. Kumar, L.K. Ju, J.S. Hyo, Appl. Catal. B 78 (2008) 301.
[31] M. Kobayashi, R. Kuma, A. Morita, Catal. Lett. 112 (2006) 37.
[32] Y. Hou, Z. Huang, S. Guo, Catal. Commun. 10 (2009) 1538.
[33] Z. Zhu, Z. Liu, S. Liu, H. Niu, J. Catal. 197 (2001) 6.
[34] P.R. Ettireddy, N. Ettireddy, S. Mamedov, P. Boolchand, P.G. Smirniotis, Appl. Catal. B 76 (2007) 123.
[35] Z.B. Wu, B.Q. Jiang, Y. Liu, H.Q. Wang, R.B. Jin, Environ. Sci. Technol. 41 (2007) 5812.
[36] Z.B. Wu, R.B. Jin, H.Q. Wang, Y. Liu, Catal. Commun. 10 (2009) 935.
[37] E. Kondratenko, V.A. Kondratenko, M. Richter, R. Fricke, J. Catal. 239 (2006) 23.
[38] K. Shimizu, A. Satsuma, Appl. Catal. B 77 (2007) 202.
[39] R.Q. Long, R.T. Yang, J. Catal. 207 (2002) 274.
[40] R. Moreno-Tost, J. Santamaría-González, E. Rodriguez-Castellón, A. Jiménez-López, M.A. Autié, E. González, M.C. Glacial, C.D. Pozas, Appl. Catal. B 50 (2004) 279.
[41] G. Carja, Y. Kameshima, K. Okada, C.D. Madhusoodana, Appl. Catal. B 73 (2007) 60.
[42] J. Shibata, M. Hashimoto, K. Shimizu, H. Yoshida, T. Hattori, A. Satsuma, J. Phys. Chem. B 108 (2004) 18327.
[43] M. Machida, T. Watanabe, Appl. Catal. B 52 (2004) 281.
[44] C.N. Costa, A.M. Efstathiou, Appl. Catal. B 72 (2007) 240.
[45] C.N. Costa, P.G. Savva, J.L. Fierro, A.M. Efstathiou, Appl. Catal. B 75 (2007) 147.
[46] A.M. Efstathiou, C.N. Costa, J.L.G. Fierro, Spanish Patent ES 2 192 985 B1 (2005), US Patent 7,105,137 B2 (2006).
[47] J.A. Wang, C.-L. Li, Appl. Surf. Sci. 161 (2000) 406.
[48] X. Lu, X. Xu, N. Wang, Q. Zhang, Chem. Phys. Lett. 300 (1999) 109.
[49] E. Xue, K. Seshan, J.R.H. Ross, Appl. Catal. B 11 (1996) 65.
[50] G. Ahari, K. Sharp, W.E. Lee, J. Eur. Ceram. Soc. 22 (2002) 495.
[51] C.N. Costa, A.M. Efstathiou, J. Phys. Chem. C 111 (2007) 3010.
[52] D. Uy, K.A. Wiegand, A.E. O'Neill, M.A. Dearth, W.H. Weber, J. Phys. Chem. B 106 (2002) 387.
[53] S. Hammache, L.R. Evans, E.N. Coker, J.E. Miller, Appl. Catal. B 78 (2008) 315.
[54] S. Matsumoto, Y. Ikeda, H. Suzuki, M. Ogai, N. Miyoshi, Appl. Catal. B 25 (2000) 115.
[55] T. Kanazawa, Catal. Today 96 (2004) 171.
[56] K. Ito, S. Kakino, K. Ikeue, M. Machida, Appl. Catal. B 74 (2007) 137.
[57] N. Takahashi, A. Suda, I. Hachisuka, M. Sugiura, H. Sobukawa, H. Shinjoh, Appl. Catal. B 72 (2007) 187.
[58] H. Imagawa, T. Tanaka, N. Takahashi, S. Matsunaga, A. Suda, H. Shinjoh, Appl. Catal. B 86 (2009) 63.
[59] H.Y. Huang, R.Q. Long, R.T. Yang, Appl. Catal. B 33 (2001) 127.
[60] G. Centi, G. Fornasari, C. Gobbi, M. Lili, F. Trifirò, A. Vaccari, Catal. Today 73 (2002) 287.
[61] G. Fornasari, F. Trifirò, A. Vaccari, F. Prinetto, G. Ghiotti, G. Centi, Catal. Today 75 (2002) 421.
[62] A.E. Palomares, A. Uzcátegui, A. Corma, Catal. Today 137 (2008) 261.
[63] P.T. Fanson, M.R. Horton, W.N. Delgass, J. Lauterbach, Appl. Catal. B 46 (2003) 393.

[64] K. Yamazaki, T. Suzuki, N. Takahashi, K. Yokota, M. Sugiura, Appl. Catal. B 30 (2001) 459.
[65] X. Li, J. Chen, P. Lin, M. Meng, Y. Fu, J. Tu, Q. Li, Catal. Commun. 5 (2004) 25.
[66] M.A. Peralta, V.G. Milt, L.M. Cornaglia, C.A. Querini, J. Catal. 242 (2006) 118.
[67] J.H. Kwak, D.H. Kim, J. Szanyi, C.H.F. Peden, Appl. Catal. B 84 (2008) 545.
[68] D. Dou, J. Balland, SAE paper 2002-01-0734, 2002, pp. 301.
[69] J. Clacens, R. Montiel, H. Kochkar, F. Figueras, M. Guyon, J.C. Beziat, Appl. Catal. B 53 (2004) 21.
[70] J.E. Parks II, G.J. Wagner, W.E. Epling, M.W. Sanders, L.E. Campbell, SAE paper 1999-01-3557, 1999, pp. 1749.4
[71] D.H. Kim, J. Azanyi, J.H. Kwak, T. Szailer, J. Hanson, C.M. Wang, C.H.F. Peden, J. Phys. Chem. B 110 (2006) 10441.
[72] P.H. Han, Y.K. Lee, S.M. Han, H.K. Rhee, Top. Catal. 16–17 (2001) 165.
[73] J. Dawody, I. Tönnies, E. Fridell, M. Skoglundh, Top. Catal. 42–43 (2007) 183.
[74] J.P. Breen, M. Marella, C. Pistarino, J.R.H. Ross, Catal. Lett. 80 (2002) 123.
[75] S. Erkfeldt, M. Larsson, H. Hedblom, M. Skoglundh, SAE paper 1999-01-3504, 1999, pp. 1510.