

Promotional Effect of Titanium on the Catalytic Performance of Anodic Alumina Supported Silver Catalyst for the Selective Reduction of NO with Propene

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A series of anodic alumina supported silver/titanium catalysts (Ag/Ti/Al₂O₃) were synthesized to investigate the effect of Ti on the selective catalytic reduction of NO with propene.

In the low temperature region, the SCR activity was greatly enhanced on Ag/Ti/Al₂O₃ compared to Ag/Al₂O₃, and this promotion became more significant with increasing Ti loading. Adding Ti to an anodic alumina support did not cause obvious improvement of activity, indicating that the presence of Ti acted as a catalytic promoter of Ag, but did not directly participate in the SCR reaction. The result of NO_x-TPD in flowing He showed that no obvious difference in the desorption performance of ads-NO_x species was found between Ag/Al₂O₃ and Ag/Ti/Al₂O₃. However, in flowing O₂/C₃H₆/He the desorption peak of nitrate species was decreased by about 50°C when Ti was present. The promoted partial oxidation of the reducing agent was believed to be a main reason. The result of H₂-TPR suggested that besides Ag⁺ ion and metallic Ag another type of silver existed in Ag/Ti/Al₂O₃, possibly a moderately agglomerated Ag_n^{δ+} cluster.

Additionally, in comparison with the SO₂-aged Ag/Al₂O₃ catalyst, the SO₂-aged Ag/Ti/Al₂O₃ catalyst provided a favorable tolerance to SO₂ poisoning, and led to higher activity. A relatively lower SO₂ adsorption amount and a faster reduction rate of sulfate species by propene were considered to be a reasonable interpretation.

Introduction

Selective catalytic reduction of nitric oxide with hydrocarbons (SCR of NO with C₃H₆) (Iwamoto *et al.*, 1992) has received a great deal of attention as a possible means of controlling emissions from diesel engines operating under oxygen-rich conditions. In the last decade, Ag-based alumina catalyst was considered one of the most promising de-NO_x catalysts, and was extensively investigated using methane (Keshavaraja *et al.*, 2000), propene (Jen, 1998; Meunier *et al.*, 1999, 2001; Martínez-Arias *et al.*, 2000), propane (Angelidis and Kruse, 2001; Satokawa *et al.*, 2001, 2003), long paraffins (Shimizu *et al.*, 2000, 2001) and alcohols (Miyadera, 1993; Masuda *et al.*, 1996; Bion *et al.*, 2003) as reductants, due to its relatively high and durable de-NO_x activity even in the presence of SO₂ and water, moderate operating temperature window and inexpensive preparation cost.

In Ag/alumina, the activity and selectivity greatly depend on Ag loading, and different Ag loadings result in different catalytic phases, which are related to different reaction pathways (Burch *et al.*, 2002). When using low or moderate Ag loadings (from 1 to 3 wt%), silver oxide species and increased dispersion were observed, and higher conversions were also attained (Bethke and Kung, 1997; Hoost *et al.*, 1997; Kung *et al.*, 1997; Miyadera, 1997; Li and Flytzani-Stephanopoulos, 1999; Burch *et al.*, 2002). In contrast to this, increasing silver loading was related to the formation of metallic Ag on the catalytic surface, which favored oxidation of the reductant by oxygen, and led to limited de-NO_x activity (Satsuma *et al.*, 2003). Several authors focused on a reaction mechanism in which a hydrocarbon reducing agent was activated through partial oxidation. This activated hydrocarbon was proposed to react with nitrates on the catalyst surface to form organic nitrate intermediates, and finally lead to nitrogen and carbon oxides (Shimizu *et al.*, 2001; Furusawa *et al.*, 2003; He *et al.*, 2003; Sato *et al.*, 2003). In SCR of NO with propene, oxygenated hydrocarbons adsorbed on the

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catalyst surface (acetate) were detected by *in situ* Fourier-Transform infrared (FTIR) spectroscopy (Satokawa *et al.*, 2003). The isocyanate ($-\text{NCO}$) species from the reaction between oxygenated hydrocarbons and adsorbed NO_x species were detected by *situ* diffuse reflectance infrared Fourier-Transform (DRIFT) spectroscopy and presumed to be key reaction intermediates (Bion *et al.*, 2003). In addition, the absence of appreciable activity of Ag/alumina at low temperatures was ascribed to the inhibition of active sites due to adsorbed nitrates (Meunier *et al.*, 1999; Shimizu *et al.*, 2001; Furusawa *et al.*, 2003; Satokawa *et al.*, 2003).

Although Ag-based alumina catalysts offer favorable activity, they are known to have two major disadvantages: the poor low-temperature activity caused by adsorbed nitrates poisoning and the inhibition effect of sulfur oxides. The considerable promotional effect of a small amount of H_2 additive is a promising means to improve the low-temperature activity of Ag/Alumina in the present system (Satokawa *et al.*, 2003, 2007; Richter *et al.*, 2004; Shibata *et al.*, 2004). However, the hazard related to the presence of an H_2 tank on-board cannot be neglected. Therefore, the addition of a second metal element as catalyst promoter is considered to be another candidate. A promotional effect on the low-temperature activity by adding 0.05 wt% Rh to 4 wt% Ag/ Al_2O_3 was reported by Sato *et al.* (2003). The higher formation rate of isocyanate, which was a major reaction intermediate, was considered to be a main reason. The addition of 0.01 wt% Pd to 5 wt% Ag/ Al_2O_3 was also found to increase the de- NO_x activity in SCR with C_3H_6 at low temperatures, both in the absence and presence of SO_2 (He *et al.*, 2003; Wang *et al.*, 2004). The results of *in situ* DRIFTS spectra suggested that the presence of trace Pd catalyzed the formation of enolic species which were converted from C_3H_6 , whereas the presence of Pt and Au did not show this effect. The surface enolic species were very active towards NO_3^- , resulting in the formation of $-\text{NCO}$ species. Son *et al.* (2001) studied the effect of adding alkali metals (Li, Na, K, Cs) to Ag/ Al_2O_3 , and found that the activity was slightly improved by the addition of either 0.5 wt% Cs or 1 wt% Cs to 2 wt% Ag/ Al_2O_3 . However, the enhancement of activity was insufficient for practical applications.

TiO_2 , as a support for the commercial catalyst ($\text{V}_2\text{O}_5/\text{TiO}_2$) has been widely used for the selective catalytic reduction of NO with ammonia for stationary sources. The catalyst exhibits high catalytic activity and tolerance to SO_2 . Mixtures of Al_2O_3 with support oxides like TiO_2 for hydrodesulfurization catalysts have been studied to improve the sulfur-resistance (Ramirez *et al.*, 1989; Dhar *et al.*, 2003). Li *et al.* (2008) prepared a 5 wt% Ag/ $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalyst with a ratio of TiO_2 to Al_2O_3 of 1:1 to investigate its denitration activity in SCR with C_3H_6 . They found that the activity

was greatly enhanced on Ag/ $\text{TiO}_2/\text{Al}_2\text{O}_3$ compared with Ag/ Al_2O_3 , especially in the low temperature region, both in the absence and presence of SO_2 . The enhancement of Lewis acid sites was proposed to be responsible for this promotion effect. However, a relatively high TiO_2 content (about 50 wt%) is considered to limit its application. In this paper, a lower Ti loading was adopted to add to Ag/alumina to investigate its effect on the present reaction.

Many reviews on the present reaction discuss the conventional process, which is carried out on bead or powder catalysts in fixed bed reactors. However, this reactor suffers from several drawbacks, such as a poor heat transfer coefficient, diffusion limitations, great pressure drop and large volume. Consequently, constructed wall type reactors have become the focus of recent research, due to their excellent gas diffusion, heat transmission and compact size. For the preparation of a plate catalyst, though various methods have been reported, such as sol-gel coating and nano-particle-based coating, the thermal endurance of the catalysts was seldom mentioned. At high temperatures, it is difficult to prevent the coating layers peeling from the base materials due to the difference in their thermal expansions. To avoid such a problem, a novel metal-monolithic anodic alumina catalyst with high thermal endurance and conductivity was developed by Kameyama *et al.* (1995). Porous alumina film can be formed on the surface of Al plate by anodization. Hot water treatment and subsequent calcination greatly increase its surface area, making it comparable to even some types of commercial bead alumina (Guo *et al.*, 2003). Since the alumina layer is derived from the base material, a close uniformity throughout the alumina layers can effectively prevent the mismatch in thermal expansion. The thermal endurance test showed a high heat resistance, and the alumina layer was not observed to peel from the catalyst during a test of up to 40,000 heating cycles (Zhang *et al.*, 2005).

Our previous work showed that a metal monolithic anodic alumina supported Ag catalyst (Ag/ $\text{Al}_2\text{O}_3/\text{Al}$) provided a favorable de- NO_x activity (Guo *et al.*, 2008). In this paper, a relatively low Ti loading (about 1 wt%) was used to investigate the effect of Ti on the activity of the Ag/ $\text{Al}_2\text{O}_3/\text{Al}$ catalyst in NO-SCR with C_3H_6 , through the SCR activity measurements, NO_x - and SO_2 -TPD in He, NO_x - and SO_2 -TPSR in $\text{C}_3\text{H}_6/\text{O}_2/\text{He}$, XRD, FE-SEM and H_2 -TPR analyses.

1. Experimental

1.1 Catalyst preparation

A commercial aluminum plate (JIS A1050, thickness 0.3 mm) was pretreated in 20 wt% of sodium hydroxide for 3 min and 30 wt% of nitric acid for 1 min, and then rinsed with deionized water. The pretreated aluminum plate was anodized in 4.0 wt% of oxalic acid

for 16 h at an electric current density of 50 A/m² and a temperature of 20°C, to form porous alumina film (ca. 100 µm). The plate was then washed, dried naturally, and calcined at 350°C to remove residual oxalic acid. Subsequently, hot water treatment in deionized water at 80°C was conducted for 1 h. The resulting plate was calcined in air at 500°C for 3 h to obtain an anodic γ-alumina support (Guo *et al.*, 2003). Using the plate-type support, the anodic alumina supported Ag/Ti catalyst was prepared by the two-stage impregnation method using aqueous solutions of (NH₄)₂TiO(C₂O₄)₂ and AgNO₃, respectively, where Ti was supported in advance of Ag. The plate was then dried naturally for 4 h, and calcined in air at 500°C for 3 h.

1.2 Catalyst characterization

The thickness of resulting alumina film was measured by the eddy current probe method (T3.3B, ANOTECH Inc.). BET specific surface area and pore radius were measured by a nitrogen adsorption method (SA3100, Beckman Coulter, Inc.). Metal loading was analyzed by atomic absorption spectrometry (AA-680, Shimadzu Corp.), and reported here based on the quantity of the surface alumina layer. Unless otherwise stated, the quantity of the inner Al layer was excluded from the calculation of the quantity of the plate-type catalyst. Powder X-ray diffraction (XRD) analyses were performed on the XRD-6000 (Shimadzu Corp.) using Cu Kα radiation. Micrographs of the catalysts were taken using FE-SEM (S-4500, Hitachi Ltd.).

1.3 Catalytic activity measurement

The activities of synthesized catalysts were measured in a fixed bed quartz reactor (i.d. 6 mm). The plate-type catalyst was cut into small pieces (ca. 5 mm²) and packed in the reactor, using quartz sand for dilution with a loading density of 0.4 cm²_{catalyst}/(g_{quartzsand}). Both inlet and outlet stream mixtures were analyzed with gas chromatographs: C₃H₆ (FID), O₂, N₂, N₂O and CO₂ (TCD). NO_x (NO and NO₂) was measured with a PG-250 portable gas analyzer with NO_x, NO, CO, SO₂ and O₂ detectors (Horiba, Ltd.). The reactor temperature was controlled with a programmable temperature controller (818P4, Eurotherm Inc.). The reaction feed stream was prepared by mixing certified and analyzed model gases (supplied by Tohei Industrial Co. Ltd.), with helium as base gas. The total gas flow rate was set at 150 mL/min (i.e. F/W = 65000 mL/(g·h)), consisting of 1000 ppm NO, 1500 ppm C₃H₆, 15% O₂. All catalysts were pretreated in 15% O₂/He of 150 mL/min for 1 h prior to the activity test. In addition, a SO₂-aged catalyst was obtained through treating a fresh catalyst in 500 ppm SO₂/15% O₂/He at 500°C for 3 h. The results obtained were evaluated in terms of NO_x conversion and C₃H₆ conversion as follows:

$$\text{NO}_x \text{ conversion} = \frac{(\text{NO} + \text{NO}_2)_{\text{inlet}} - (\text{NO} + \text{NO}_2)_{\text{outlet}}}{(\text{NO} + \text{NO}_2)_{\text{inlet}}} \times 100\%$$

$$\text{C}_3\text{H}_6 \text{ conversion} = \frac{(\text{C}_3\text{H}_6)_{\text{inlet}} - (\text{C}_3\text{H}_6)_{\text{outlet}}}{(\text{C}_3\text{H}_6)_{\text{inlet}}} \times 100\%$$

1.4 TPD, TPSR and H₂-TPR studies

NO_x-TPD (temperature programmed desorption) and -TPSR (temperature programmed surface reaction) tests were carried out using the same catalytic reaction apparatus. The same fixed bed quartz reactor was used to load the powder catalyst (about 50 mg), which was prepared by scraping off surface alumina layers from the plate-type catalyst. The samples for NO_x-TPD/TPSR were pretreated in 15% O₂/He of 150 mL/min at 500°C for 1 h in advance of NO_x adsorption. Subsequently, the pretreated samples were exposed to 1000 ppm NO/15% O₂/He of 150 mL/min at 25°C for 3 h, and then purged with He of 150 mL/min at 25°C until the concentration of adsorption gas in He returned to zero level, which was monitored by the portable gas analyzer. On the other hand, the samples for SO₂-TPD/TPSR were pretreated in 500 ppm SO₂/15% O₂/He of 150 mL/min at 500°C for 3 h, and in He of 150 mL/min for the next 0.5 h, and then were cooled to 25°C in He. The TPD or TPSR run was started from 25 to 1000°C at a ramping rate of 10 °C/min in different gas mixtures with a flow of 150 mL/min (He, 1500 ppm C₃H₆/15% O₂/He). The portable gas analyzer was used to analyze NO_x, NO, NO₂ ([NO₂] = [NO_x] - [NO]), CO and SO₂.

Temperature programmed reduction with hydrogen (H₂-TPR) analyses were performed on a CHEMBET 3000 (Quantachrome Instruments Co.) coupled with a thermal conductivity detector (TCD). After loading the powder sample (about 50 mg) into a U-shaped quartz tube (i.d. 4 mm), the sample cell was pretreated in 40% O₂/He of 70 mL/min for 1 h at 500°C and then in Ar for 30 min. Subsequently, it was cooled to ambient temperature in Ar. Then, the inlet gas flow was switched to 70 mL/min of the 65% H₂/Ar reductant gas. When the system was stable, the sample was heated from ambient temperature to 1000°C at a ramping rate of 10°C/min, while the outlet dry gas was continuously monitored by the TCD detector.

2. Result and Discussion

2.1 Effect of Ti additive

Using the anodic alumina support, a series of anodic alumina supported Ag/Ti catalysts, designated *x* Ag/*y* Ti/Al₂O₃, were prepared to investigate the effect of Ti on the Ag catalyst. Here, *x* and *y* were the loadings of Ag (*x* wt%) and Ti (*y* wt%), respectively.

Figure 1 shows the effect of Ag loading in the Ag/Al₂O₃ catalyst on the de-NO_x activity. The comparison of C₃H₆ conversion with NO_x conversion shows that C₃H₆ oxidation is coincident with NO_x reduction. That is, NO_x reduction was promoted as C₃H₆ was

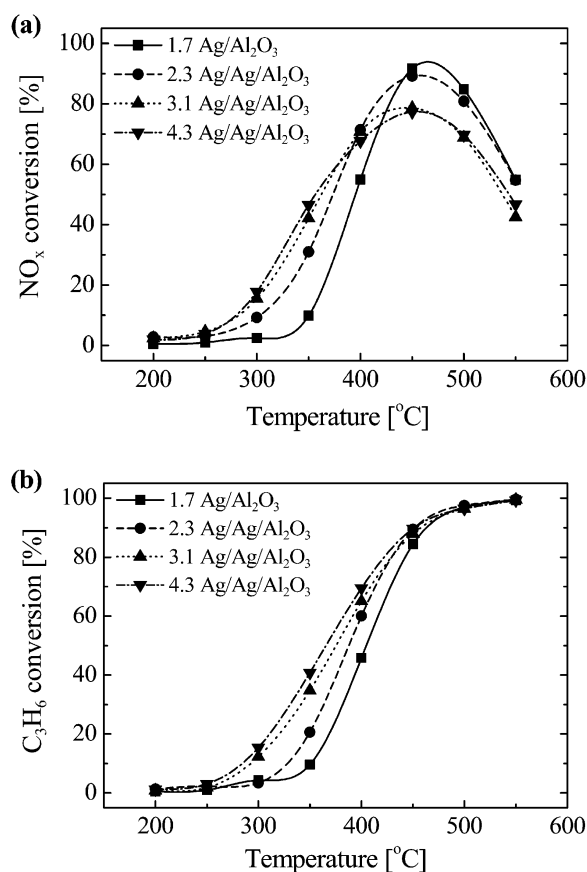


Fig. 1 The denitration activity of Ag/Al₂O₃ in SCR of NO with C₃H₆: (a) NO_x conversion; (b) C₃H₆ conversion. Reaction conditions: 1000 ppm NO, 1500 ppm C₃H₆, 15% O₂, F/W = 65000 mL/(g·h)

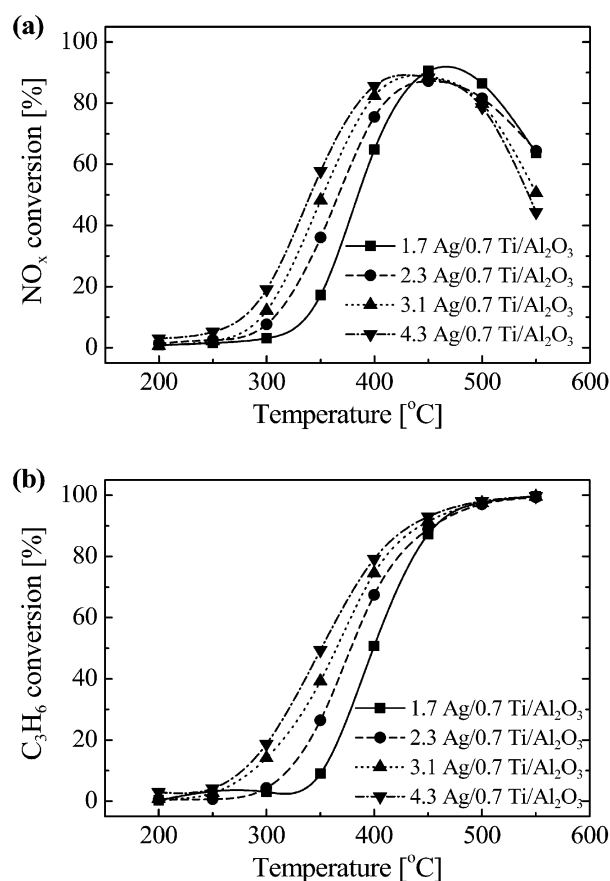


Fig. 2 The effect of Ag loading in Ag/0.7 Ti/Al₂O₃ on the denitration activity: (a) NO_x conversion; (b) C₃H₆ conversion. Reaction conditions: 1000 ppm NO, 1500 ppm C₃H₆, 15% O₂, F/W = 65000 mL/(g·h)

effectively oxidized. However, once C₃H₆ conversion approached 100%, NO_x reduction was depressed. Thus, the lack of C₃H₆ available for NO_x reduction is responsible for the loss of NO_x conversion at high temperatures (>450°C). In addition, the temperature where NO_x reduction was initiated was observed to closely depend on the “light-off” temperature for C₃H₆ oxidation (about 300°C). These results clearly reveal a critical role of propene in the present reaction.

Increasing Ag loading in Ag/Al₂O₃ significantly promoted NO_x reduction and C₃H₆ oxidation in the low temperature region (<400°C). However, the peak value of NO_x conversion at 450°C was gradually depressed though C₃H₆ oxidation still monotonously increased with an increase of Ag loading.

We know from earlier work on the SCR of NO by hydrocarbons over Ag/Al₂O₃ (Bethke and Kung, 1997; Hoost *et al.*, 1997; Kung *et al.*, 1997; Burch *et al.*, 2002; Satsuma *et al.*, 2003) and our own previous work (Guo *et al.*, 2008), that generally, in a Ag/Al₂O₃ catalyst with low or moderate Ag loadings (from 1 to 3 wt%), Ag⁺ ions are dominant and highly dispersed, which is related to higher NO conversions. In contrast to this, in-

creasing silver loading is related to the formation of metallic Ag on the catalytic surface, which favors oxidation of the reductant by oxygen, and leads to limited de-NO_x activity. However, light hydrocarbons such as CH₄, C₃H₆ and C₃H₈ oxidize less readily than higher alkanes and ethanol, and temperatures above 400°C are required for activation of reductants (Shibata *et al.*, 2004). Therefore, Ag⁺ ion does not act as an active species for SCR by light hydrocarbons at lower temperatures. An increased Ag loading produces more metallic Ag, which favors the nonselective oxidation of light hydrocarbons compared to Ag⁺ ion, resulting in an enhanced low-temperature activity. On the other hand, metallic Ag is inactive in the production of organic nitrate intermediates (–NCO), which are the key reaction intermediates, resulting in a limited de-NO_x activity especially at moderate and high temperatures.

Catalytic activities of Ag/0.7 Ti/Al₂O₃ with different Ag loadings as a function temperature are shown in **Figure 2**. In the low temperature region, comparison of Figure 2 with Figure 1 shows a similar result of increased Ag loading promoting NO_x reduction and C₃H₆ oxidation. In comparison with Figure 1, NO_x

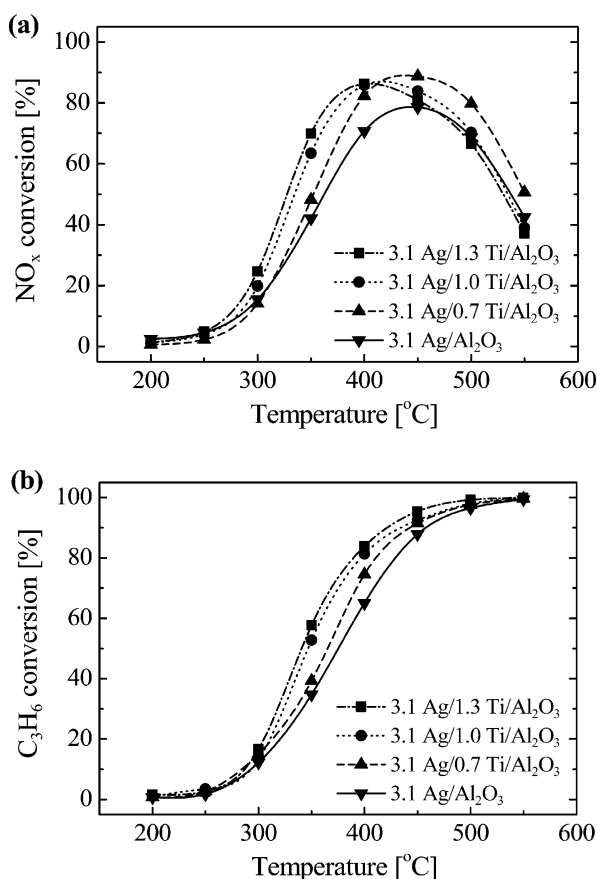


Fig. 3 The effect of Ti loading in 3.1 Ag/Ti/Al₂O₃ on the denitration activity: (a) NO_x conversion; (b) C₃H₆ conversion. Reaction conditions: 1000 ppm NO, 1500 ppm C₃H₆, 15% O₂, F/W = 65000 mL/(g·h)

conversion was enhanced by about 10% in temperatures ranging from 300 to 400°C, when 0.7 wt% was present. Especially at 450°C where the peak of NO_x reduction appeared, the limited NO_x conversion was not observed, and all NO conversions maintained about 90%. In **Figure 3**, the effect of Ti loading on the catalytic performance of Ag/Ti/Al₂O₃ with a constant Ag loading of 3.1 wt% is shown. It was clear that increasing Ti loading significantly promoted NO_x reduction and C₃H₆ oxidation, and shifted the plots of NO_x reduction and C₃H₆ oxidation to lower temperatures. Furthermore, when Ti loading exceeded 1.0 wt%, the maximum NO_x conversion of about 90% could be obtained at 400°C.

As shown in Figures 1–3, the promotional effect of Ti of above 1.0 wt% was very significant, in particular in the low and moderate temperature region (300–450°C). In **Figure 4**, the denitration activities of the Ti/Al₂O₃ catalysts without supported Ag are shown. The result obtained on an anodic alumina support and the result of a blank test without any catalyst are also shown in Figure 4. The presence of Ti slightly improved the catalytic activity by 1–3% compared to the anodic

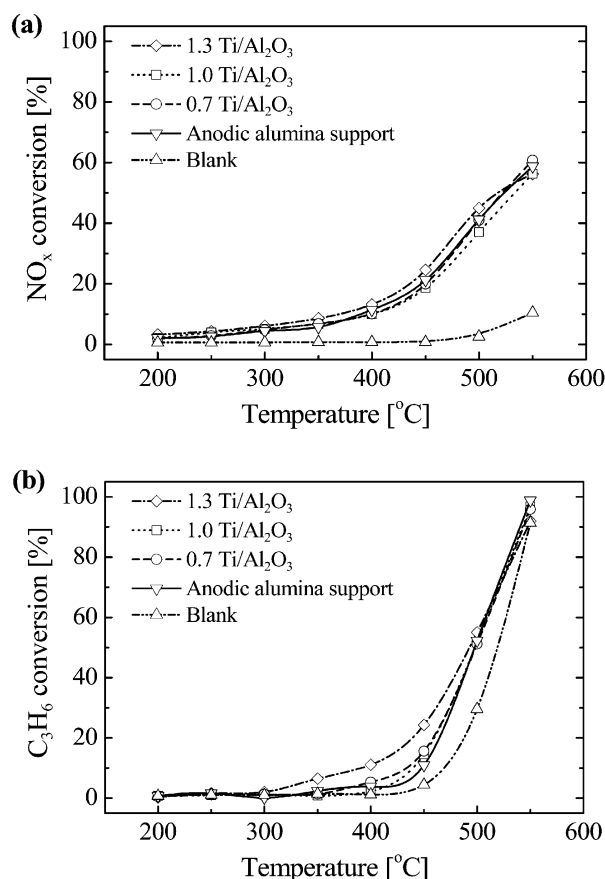
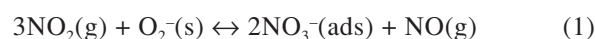


Fig. 4 The denitration activities of different catalysts in SCR of NO with C₃H₆: (a) NO_x conversion; (b) C₃H₆ conversion. Reaction conditions: 1000 ppm NO, 1500 ppm C₃H₆, 15% O₂, F/W = 65000 mL/(g·h)

alumina support. However, in comparison with the significant promotional effect of Ti in Figures 2 and 3, this slight increment is negligible, indicating that Ti in Ag/Ti/Al₂O₃ acts as a catalytic promoter of Ag, but does not directly in the present reaction.

2.2 NO_x-TPD and -TPSR studies

Our group reported a mechanism for SCR of NO with C₃H₆ over the anodic alumina supported Ag catalyst concluded from NO_x adsorption and desorption phenomena and surface reaction with reductant, shown as follows (Eqs. (1)–(4)) (Guo *et al.*, 2008).



In the case of NO₂ adsorption, at first the disproportion of adsorbed NO₂ results in the formation of nitrosyl and nitrate. NO+ rapidly undergoes reaction

with the surface oxide to form nitrite. Nitrite then reacts with the strong oxidant NO_2 , leading to the formation of NO_3^- as well as gaseous NO (Eq. (1)). In the case of adsorption of $\text{NO} + \text{O}_2$, the formation of nitrate species is considered to probably proceed via the route of NO_2 , originating from the oxidation of NO by O_2 . At the same time as the NO_x adsorption, reducing agent is oxidized (or activated) into oxygenated hydrocarbons $-\text{CHO}$ (Eq. (2)). Subsequently, $-\text{CHO}$ reacts with nitrate species, rather than inactive nitrite species, to form organic nitrate intermediates $-\text{NCO}$ (Eq. (3)), which is the key reaction intermediate, and finally lead to nitrogen and carbon oxides (Eq. (4)).

The inhibition of active sites due to adsorbed nitrates is considered responsible for the poor low temperature activity of Ag/alumina (Meunier *et al.*, 1999; Shimizu *et al.*, 2001; Furusawa *et al.*, 2003; Satokawa *et al.*, 2003). Therefore, improving the desorption of nitrate species in the low temperature region is one of effective means to promote the low temperature activity, because it can free catalytic sites to oxidize reducing agent to produce $-\text{CHO}$. Our recent work (not shown here) showed that a small amount of H_2 additive effectively decreased the desorption temperature of nitrate species and provided a favorable promotional effect on the low temperature activity.

Figure 5 shows the TPD profiles in flowing He after exposure of (a) the Ag/ Al_2O_3 catalyst and (b) the Ag/Ti/ Al_2O_3 catalyst to 1000 ppm $\text{NO}/15\% \text{O}_2/\text{He}$ for 3 h at 25°C . 3.1 Ag/ Al_2O_3 as well as 3.1 Ag/1.3 Ti/ Al_2O_3 provided a low temperature peak of NO_x desorption (LT peak) and a high temperature peak of NO_x desorption (HT peak). According to previous work (Guo *et al.*, 2008), the LT peak was assigned to nitrite species, whereas the HT peak was associated with nitrate species. Due to the inactivity of nitrite species with $-\text{CHO}$, though, the HT peak, rather than the LT peak, should be responsible for the “nitrate poisoning” in the low temperature region. However, in comparison of 3.1 Ag/ Al_2O_3 with 3.1 Ag/1.3 Ti/ Al_2O_3 , the difference in the HT peaks was not obvious and both peak temperatures of the HT peaks were approximately the same, though the initial temperature of the HT peak was decreased by about 25°C (from 226 to 201°C) when Ti was present.

To investigate the difference of the reactivity of ads- NO_x species with C_3H_6 between Ag/ Al_2O_3 and Ag/Ti/ Al_2O_3 , TPSR tests were performed by flowing 1500 ppm $\text{C}_3\text{H}_6/15\% \text{O}_2/\text{He}$ on 3.1 Ag/ $\text{Al}_2\text{O}_3/\text{Al}$ and 3.1 Ag/1.3 Ti/ $\text{Al}_2\text{O}_3/\text{Al}$ after exposure to 1000 ppm $\text{NO}/15\% \text{O}_2/\text{He}$ for 3 h at 25°C , and the results are shown in **Figure 6**. The NO_x desorption profile displayed a LT peak and a HT peak, similar to Figure 5. The LT peaks for NO_x were nearly the same as those in the TPD test in both cases of Ag/ Al_2O_3 and Ag/Ti/ Al_2O_3 , considering peak shape, temperature, and peak area, which demonstrated that no reaction took place be-

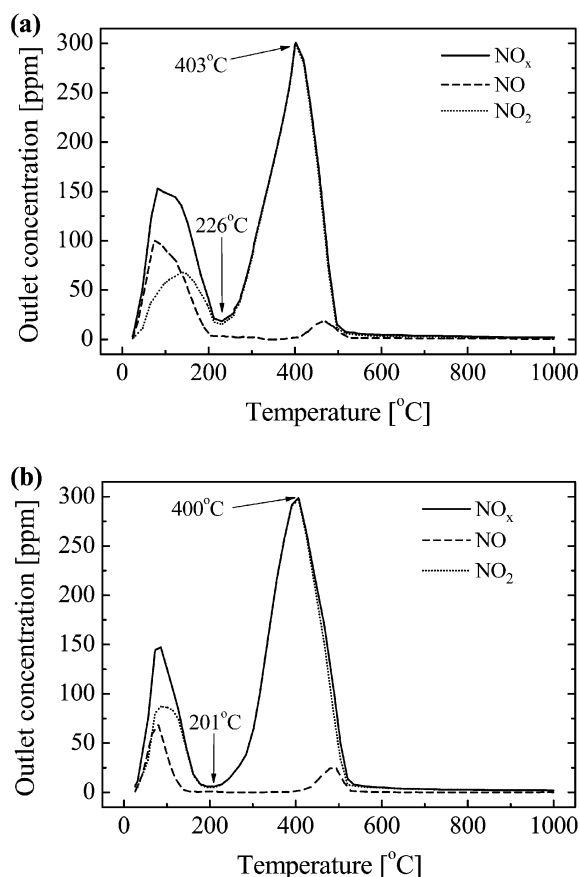


Fig. 5 TPD profiles of NO_x , NO and NO_2 in flowing He after exposure of (a) 3.1 Ag/ Al_2O_3 and (b) 3.1 Ag/1.3 Ti/ Al_2O_3 to 1000 ppm $\text{NO}/15\% \text{O}_2/\text{He}$ for 3 h at 25°C

tween the surface nitrite species and propene. However, in the high temperature region, the $\text{C}_3\text{H}_6/\text{O}_2$ stream obviously shifted the peak temperature of nitrate species desorption from 403 to 352°C in the case of 3.1 Ag/ $\text{Al}_2\text{O}_3/\text{Al}$, and from 400 to 299°C in the case of 3.1 Ag/1.3 Ti/ $\text{Al}_2\text{O}_3/\text{Al}$. Our previous work showed that in NO_x -TPSR in flowing $\text{C}_3\text{H}_6/\text{O}_2/\text{He}$, nitrate species would react with reductant and oxygen into N_2 , accompanied by the formation of CO_x originating from the oxidation of reductant (Guo *et al.*, 2008). The peak temperature of nitrate species desorption determines the terminal temperature of “nitrate poisoning”. That is, in SCR of NO with C_3H_6 , when reaction temperature is lower than the HT peak temperature, the reducing agent can not be effectively activated into $-\text{CHO}$, and results in limited NO_x reduction. In Figure 6, it was apparent that the presence of 1.3 wt% Ti effectively decreased the peak temperature of nitrate species desorption from 352 to 299°C . Considering the result shown in Figure 5 that no obvious difference existed in the desorption performance of nitrate species between Ag/ Al_2O_3 and Ag/Ti/ Al_2O_3 in NO_x -TPD, the result of Figure 6 suggests that the presence of

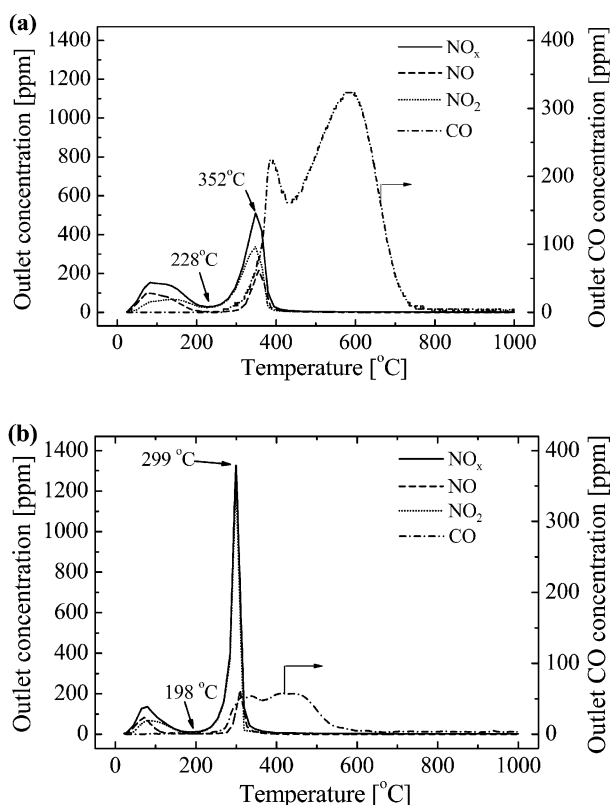


Fig. 6 TPSR profiles of NO_x , NO , NO_2 and CO in flowing 1500 ppm C_3H_6 /15% O_2 /He after exposure of (a) 3.1 Ag/ Al_2O_3 and (b) 3.1 Ag/1.3 Ti/ Al_2O_3 to 1000 ppm NO /15% O_2 /He for 3 h at 25°C

1.3 wt% Ti enhances the low temperature activity of NO_x reduction through the promotion of partial oxidation of C_3H_6 .

2.3 The reason for the effect of Ti

The effect of Ti on propene oxidation in the absence and presence of NO was also investigated, and the result is shown in **Figure 7**. In the case of 3.1 Ag/ Al_2O_3 , the effect of NO can be divided into two regions below and above 350°C, which is coincident with the peak temperature of nitrate species desorption in **Figure 6(a)**. In the region above 350°C, the presence of NO improved propene oxidation. This promotional effect of NO is associated with the higher reaction rate of the reaction of propene with nitrate species rather than the direct oxidation with oxygen (Guo *et al.*, 2008). In the region below 350°C, however, it inhibited propene oxidation and acted as a catalyst poison. In the low temperature region, the surface nitrate species occupy active sites, and decomposition does not occur, which inhibits propene oxidation. A similar result was also observed in the case of 3.1 Ag/1.3 Ti/ Al_2O_3 , though the difference between reactions with and without NO was not very obvious. Furthermore, 3.1 Ag/1.3 Ti/ Al_2O_3 exhibited a stronger oxidation ability for the propene oxidation than 3.1 Ag/ Al_2O_3 regardless of

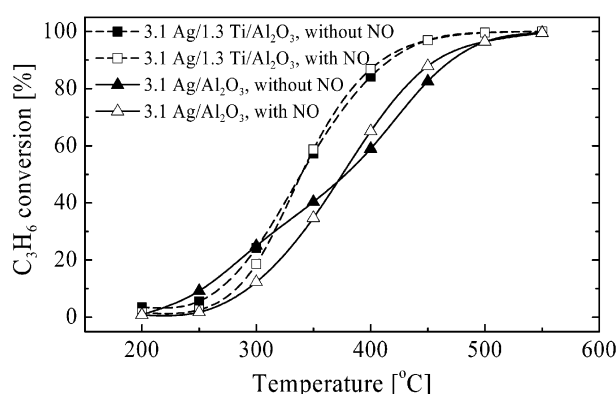


Fig. 7 Effect of Ti on propene oxidation in the absence and presence of NO . Reaction conditions: 0 or 1000 ppm NO , 1500 ppm C_3H_6 , 15% O_2 ; $F/W = 65000 \text{ mL}/(\text{g}\cdot\text{h})$

the presence and absence of NO .

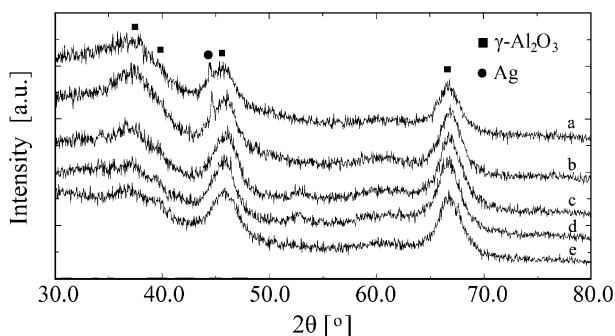
Because of the result that Ti/ Al_2O_3 did not provide a remarkable oxidation ability for propene oxidation (see **Figure 4**), the stronger oxidation ability of 3.1 Ag/1.3 Ti/ Al_2O_3 shown in **Figure 7** should be attributed to some changes to the supported Ag caused by the presence of Ti. Considering their same Ag loading between 3.1 Ag/ Al_2O_3 and 3.1 Ag/1.3 Ti/ Al_2O_3 , the change of the state of Ag is suggested to be a plausible interpretation. Generally, the state of the supported Ag in the Ag/alumina catalyst mainly includes Ag^+ ions and metallic Ag. Ag^+ ions and metallic Ag can be transformed into each other, closely depending on Ag loading, reaction conditions and so on. However, a presumption that an increased ratio of metallic Ag to the supported Ag is the primary reason for the promoted oxidation ability is considered to be in contradiction with the fact that the formation of metallic Ag brings not only enhanced oxidation ability but also limited de- NO_x activity, as discussed above. In **Figure 2**, when increasing Ag loading with a constant Ti loading, the limited NO_x reduction has not been observed, though the oxidation of the reducing agent was undoubtedly promoted. In particular, as Ti loading increased with a constant Ag loading (see **Figure 3**), not only the low-temperature denitration activity but also the maximum NO_x conversion was considerably enhanced, indicating that the increased ratio of metallic Ag is not a reasonable explanation.

To search the primary reason for the effect of Ti, the Ag/Ti/ Al_2O_3 catalyst was further analyzed by XRD, BET, FE-SEM and H_2 -TPR.

Figure 8 shows the XRD pattern of the various catalysts. The diffraction pattern of 1.7 Ag/ Al_2O_3 was attributed to $\gamma\text{-Al}_2\text{O}_3$, and no Ag^+ or metallic Ag was detected. With increasing Ag loading, the diffraction line of metallic Ag could be seen on 3.1 Ag/ Al_2O_3 , which agrees with the previous discussion that increasing silver loading promotes the formation of metallic Ag

Table 1 BET Surface area, pore diameter and pore volume

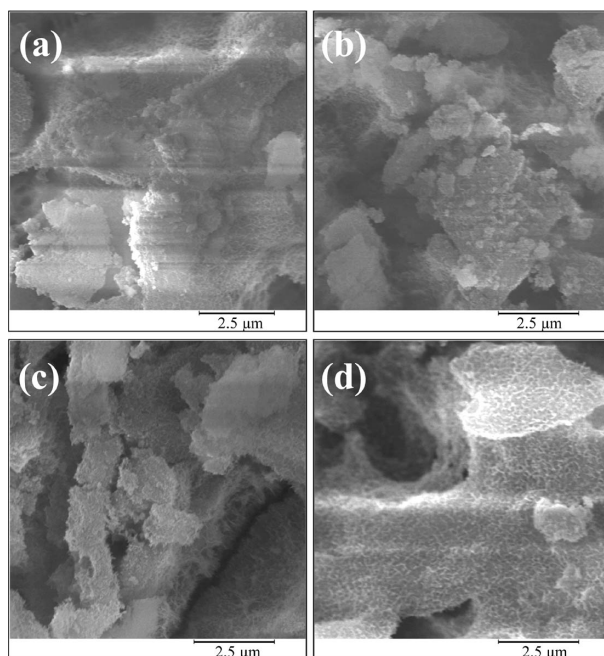
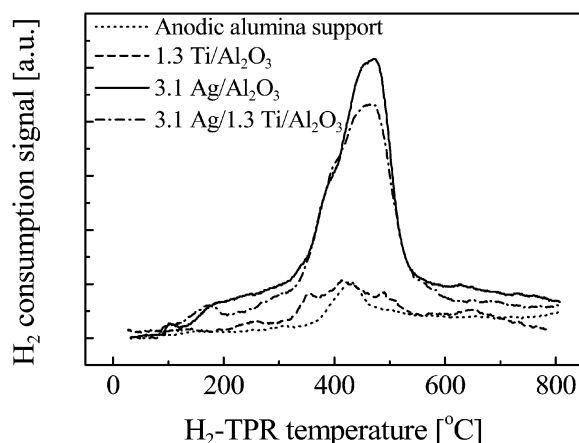
	Support	1.3 Ti/Al ₂ O ₃	3.1 Ag/Al ₂ O ₃	3.1 Ag/1.3 Ti/Al ₂ O ₃
Specific area [m ² /g]	145.3	145.4	135.9	129.7
Pore diameter [Å]	39.5	39.6	39.6	39.4
Pore volume [cm ³ /g]	0.22	0.25	0.24	0.23

**Fig. 8** XRD spectras of different catalysts: (a) 3.1 Ag/1.3 Ti/Al₂O₃; (b) 3.1 Ag/Al₂O₃; (c) 1.7 Ag/Al₂O₃; (d) 1.3 Ti/Al₂O₃; (e) Anodic alumina support

on the catalytic surface. No Ag⁺ peak was detected, which indicated that silver oxide particles were well dispersed. The result obtained on 1.3 Ti/Al₂O₃ was associated with γ-Al₂O₃. Similar to 3.1 Ag/Al₂O₃, metallic Ag was also observed on 3.1 Ag/1.3 Ti/Al₂O₃, though the relative intensity of diffraction line was weaker than that of the 3.1 Ag/Al₂O₃.

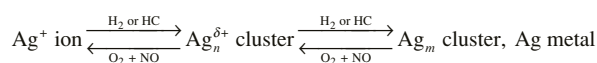
BET surface area, pore diameter and pore volume of the various catalysts are summarized in **Table 1**. No noticeable difference was observed among the anodic alumina support, 1.3 Ti/Al₂O₃, 3.1 Ag/Al₂O₃ and 3.1 Ag/1.3 Ti/Al₂O₃. FE-SEM photographs related to four samples (**Figure 9**) were also analogous in their micro-pore structure. These results demonstrate that the micro-pore structure is not the primary reason for the effect of Ti on the catalytic performance of Ag/Ti/Al₂O₃.

Figure 10 shows H₂-TPR results of the various catalysts. Adding 1.3 wt% Ti to the anodic alumina support resulted in a barely detectable increase in the H₂ consumption amount, whereas a remarkable consumption peak of H₂ occurred at 465°C when adding Ag to the anodic alumina support or to Ti/Al₂O₃. It was clear that the amount of H₂ consumption related to 3.1 Ag/1.7 Ti/Al₂O₃ was less than that of 3.1 Ag/Al₂O₃. From this result, and considering the poor amount of H₂ consumption of 1.7 Ti/Al₂O₃, it seems reasonable that the presence of Ti increases the ratio of metallic Ag to the supported Ag in 3.1 Ag/1.7 Ti/Al₂O₃ compared with 3.1 Ag/Al₂O₃. However, as discussed above, this conclusion is in contradiction with the unlimited and even promoted maximum NO_x conversion shown in Figures 2 and 3. According to the results discussed

**Fig. 9** FE-SEM surface photographs of different catalysts: (a) anodic alumina support; (b) 1.3 Ti/Al₂O₃; (c) 3.1 Ag/Al₂O₃; (d) 3.1 Ag/1.3 Ti/Al₂O₃**Fig. 10** H₂-TPR profiles of different anodic alumina catalysts

above, in particular the result of Figure 10, it is speculated that besides Ag⁺ and metallic Ag a new type of Ag probably exists in 3.1 Ag/1.7 Ti/Al₂O₃, caused by the presence of Ti.

The Satokawa group studied the promotional effect of H₂ additive on the SCR of NO by C₃H₈ by using Ag/Al₂O₃ and Ag-MFI (Satokawa *et al.*, 2003, 2007; Shibata *et al.*, 2004). On the basis of UV-vis spectroscopic analysis, they proposed that Ag⁺ ions were mainly in existence during C₃H₈-SCR in the absence of H₂, while the addition of hydrogen in the reaction feed reduced Ag⁺ ions to produce moderately agglomerated Ag_n^{δ+} clusters (2 ≤ n ≤ 4). It was concluded that the excellent Ag_n^{δ+} cluster activity was attributed to the higher ability of C₃H₈ to promote partial oxidation compared with Ag⁺ ions and its higher selectivity than metallic Ag_m clusters (3 ≤ m ≤ 5) and Ag metal. In addition, the type of Ag species was reversibly changed among Ag⁺ ions, Ag_n^{δ+} clusters, and metallic Ag_m clusters together with Ag metal, depending on the reaction atmosphere—not only H₂ but also NO and C₃H₈, shown as follows:



In addition, Sato *et al.* (2003) investigated the effect of noble metal additives (Rh, Ir, Ru, Pd, Pt) on the catalytic activity of 4 wt% Ag/Al₂O₃, and reported that Ag/Al₂O₃ with small amounts of Rh (0.05 wt%) showed excellent activity for NO reduction by decane at low temperatures. FT-IR measurements revealed that the formation rate of isocyanate species was higher on Rh-promoted Ag/Al₂O₃. On the basis of catalyst characterization by UV-vis spectroscopy, they reported the areas of the observed absorption bands for Ag/Al₂O₃, Ag/Ir/Al₂O₃, Ag/Ru/Al₂O₃ and Ag/Rh/Al₂O₃, as shown in **Table 2**. For Ag/Al₂O₃, Ag⁺ and Ag_{n2} clusters were the major Ag species. On Ag/Ir/Al₂O₃ and Ag/Ru/Al₂O₃, metallic Ag clusters (Ag_{n1} and Ag_{n2}) were the main species. For Ag/Rh/Al₂O₃, which had a promotional effect on NO reduction, the presence of Ag_n^{δ+} species was observed, which was considered responsible for the high activity.

The aforementioned literature overview demonstrates that the presence of Ag_n^{δ+} clusters promotes the partial oxidation of the reducing agent (Eq. (2)) and the formation of -NCO (Eq. (3)), and eventually enhances the low-temperature activity, due to increased reductant partial oxidation compared with Ag⁺ ions and higher selectivity than metallic Ag. Referring to the statements about the effect of Ag_n^{δ+} clusters, our experimental results shown above can be explained well. The presence of Ti in the Ag/Ti/Al₂O₃ catalyst promoted the formation of Ag_n^{δ+} clusters, and led to the enhanced NO_x reduction in the low and moderate temperature regions, as shown in Figures 1–3. Though the reactivity among Ag⁺ ions, Ag_n^{δ+} clusters and metallic Ag are different, all types of Ag could be oxidized into nitrate species by the relatively strong oxidant of NO₂, resulting in the disappearance of the difference in NO_x-TPD

Table 2 Relative intensities of UV-Vis absorption bands (Sato *et al.*, 2003)

	Integrated area of absorption band [a.u.]			
	Ag ⁺	Ag _n ^{δ+}	Ag _{n1}	Ag _{n2}
4 wt% Ag/Al ₂ O ₃	0.16	0	0	0.37
4 wt% Ag/0.05 wt% Ir/Al ₂ O ₃	0.08	0	0.23	0.58
4 wt% Ag/0.05 wt% Ru/Al ₂ O ₃	0.05	0	0.21	0.34
4 wt% Ag/0.05 wt% Rh/Al ₂ O ₃	0.01	0.30	0	0.31

performance (see Figure 5). Zemlyanov *et al.* (1998) reported a complicated sandwich structure consisting of superimposed AgNO₃ and Ag₂O layers at the surface of metallic Ag after exposure of a piece of Ag foil to a mixture of NO/O₂ at 300 K. However, when using C₃H₈/O₂/He as desorption gas (Figure 6), a considerable difference appeared between Ag/Ti/Al₂O₃ and Ag/Al₂O₃, due to the promotional effect of Ag_n^{δ+} clusters on the formation of -CHO and -NCO. Because of the higher ability of Ag_n^{δ+} clusters for reductant oxidation as compared to Ag⁺ ions, Ag/Ti/Al₂O₃ exhibited stronger oxidation of propene by oxygen, as shown in Figure 7. In particular, the moderate agglomeration of Ag⁺ ions into Ag_n^{δ+} clusters resulted in decreased H₂ consumption in the H₂-TPR test, as shown in Figure 10. Additionally, Li *et al.* (2008) reported a similar promotion effect of Ti by using 5 wt% Ag/TiO₂/Al₂O₃ catalyst with a ratio of TiO₂ to Al₂O₃ of 1:1 in the SCR of NO with C₃H₆. The enhancement of Lewis acid sites caused by the presence of Ti was proposed to be responsible for the promotion effect. However, this interpretation is considered to be insufficient because it is difficult to explain the result of H₂-TPR shown in Figure 10.

2.4 The effect of Ti in the presence of SO₂

In this paper, the effect of SO₂ was also investigated, by comparing the denitration activities achieved with a fresh catalyst versus a SO₂-aged catalyst. The Ag/Al₂O₃ and Ag/Ti/Al₂O₃ catalysts were pretreated in 500 ppm SO₂/15% O₂/He (150 mL/min) at 500°C for 3 h. Subsequently, the SCR activities of the fresh catalysts and the SO₂-aged catalysts were tested in the absence of SO₂, and the result is shown in **Figure 11**. In comparison with the fresh catalysts, NO_x reduction and propene oxidation of the SO₂-aged catalysts were greatly depressed over both Ag/Al₂O₃ and Ag/Ti/Al₂O₃. The formation of sulfate species caused by the SO₂ pretreatment is considered to be responsible for this drop. Nevertheless, the presence of Ti still effectively enhanced the tolerance of Ag/Ti/Al₂O₃ to SO₂ poisoning. For example, at 400°C, the SO₂ pretreatment slightly decreased NO_x conversion of 3.1 Ag/1.3 Ti/Al₂O₃ from 86 to 78%, while it substantially depressed NO_x conversion of 3.1 Ag/Al₂O₃ from 70 to 43% at the same temperature. The SO₂-aged 3.1 Ag/1.3 Ti/Al₂O₃

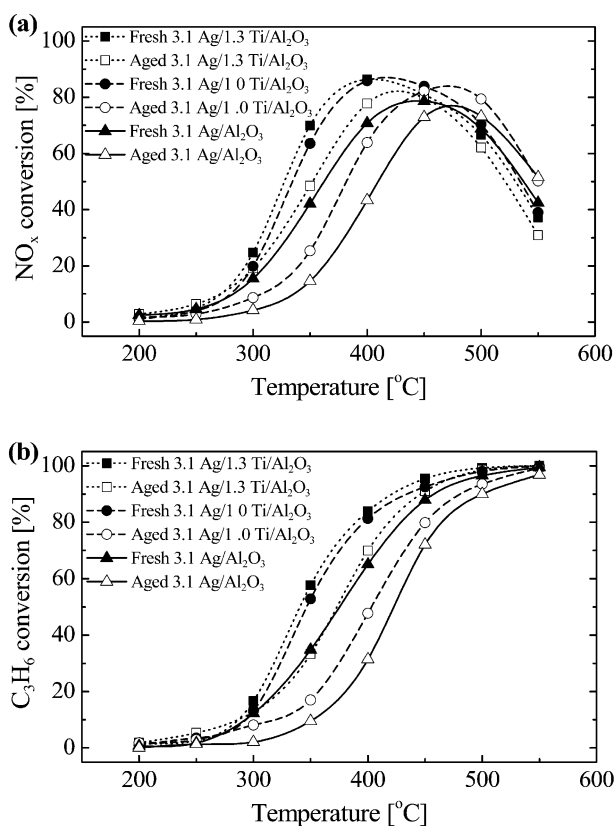


Fig. 11 The denitration activities of the fresh catalysts and the SO₂-aged catalysts in SCR with C₃H₆: (a) NO_x conversion; (b) C₃H₆ conversion. Reaction Conditions: 1000 ppm NO/1500 ppm C₃H₆/15% O₂/He; F/W = 65000 mL/(g·h). Aging conditions: 500 ppm SO₂/15% O₂/He; 150 mL/min; 500°C, 3 h

catalyst provided a favorable NO_x reduction, even before exposure to the fresh Ag/Al₂O₃ catalyst. In addition, the tolerance of Ag/Ti/Al₂O₃ to SO₂ poisoning was found to be gradually strengthened with an increasing Ti loading. In Figure 11(b), compared with the SO₂-aged Ag/Al₂O₃, the SO₂-aged Ag/Ti/Al₂O₃ catalyst provided higher propene oxidation, which is probably an explanation for the higher NO_x conversion associated the SO₂-aged Ag/Ti/Al₂O₃ catalyst.

To further investigate the effect of SO₂, using the 3.1 Ag/Al₂O₃ and 3.1 Ag/1.3 Ti/Al₂O₃ catalysts with different pretreatments, SO₂-TPD/TPSR measurements were carried out, and results are shown in **Figure 12**. After exposure to 500 ppm SO₂/15% O₂/He at 500°C for 3 h, SO₂-TPD measurement was started in flowing He. Both catalysts exhibited the obvious desorption peaks of SO₂ from 700 to 1000°C (peaked at 880°C). Due to the favorable tolerance of TiO₂ to SO₂ poisoning (Yamamoto *et al.*, 2006; Ito *et al.*, 2007), the peak of 880°C is assigned to the decomposition peak of sulfate species on the surface of catalyst, i.e. Ag₂SO₄ and Al₂(SO₄)₃ (Satokawa *et al.*, 2001). The desorption curve of SO₂ was integrated to volumetrically deter-

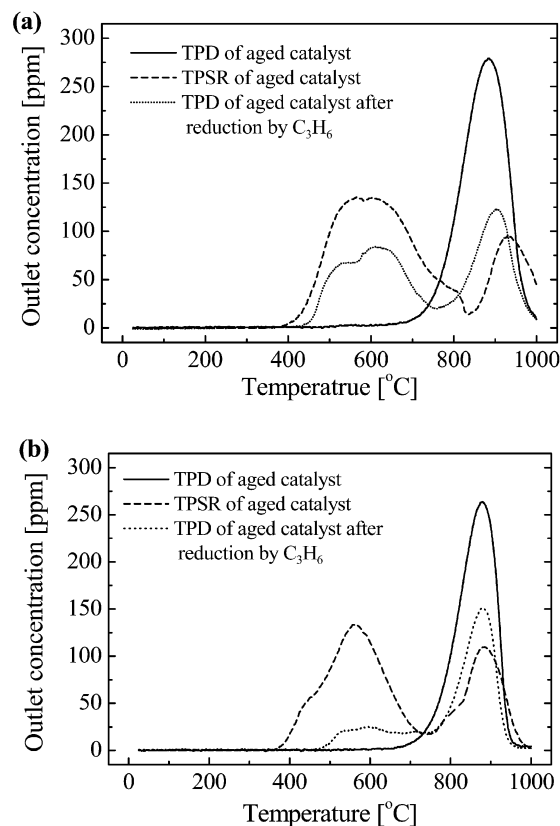


Fig. 12 SO₂-TPD/TPSR analyses over (a) 3.1 Ag/Al₂O₃ and (b) 3.1 Ag/1.3 Ti/Al₂O₃ with different pretreatments. SO₂-Aging: 500 ppm SO₂/15% O₂/He, 500°C, 3 h. Reduction: 1500 ppm C₃H₆/15% O₂/He, 500°C, 1 h. TPD: in He. TPSR: in 1500 ppm C₃H₆/15% O₂/He. All flows were set at 150 mL/min

mine the desorption amount of SO₂. The determination result showed that the presence of Ti decreased the desorption amount of SO₂ from 514.2 μmol/g of 3.1 Ag/Al₂O₃ to 420.1 μmol/g of 3.1 Ag/1.3 Ti/Al₂O₃, which undoubtedly demonstrates that the presence of Ti effectively strengthens the tolerance of the catalyst to SO₂ poisoning. Subsequently, the samples with the same SO₂ pretreatment were tested in 1500 ppm C₃H₆/15% O₂/He of 150 mL/min from ambient temperature to 1000°C (SO₂-TPSR). On both the SO₂-aged Ag/Al₂O₃ catalyst and the SO₂-aged Ag/Ti/Al₂O₃ catalyst, a new desorption peak of SO₂ was observed from 400 to 800°C, down from the peak of 880°C. The decomposition of sulfite species seems to be a plausible explanation for the new peak of 400–800°C, though we can not yet provide any direct evidence to support it. In the absence of a reducing agent, the sulfate species directly decomposed, accompanied with gaseous SO₂ and O₂ release. In the presence of propene, however, it is supposed that at first propene reduced sulfate species into sulfite species because of the relatively weak reduction ability of propene, and then sulfite species thermally decomposed into SO₂. A further SO₂-TPSR

study coupled with a mass spectrometer is now in progress. The results of our experiment indicated that the overall desorption amount of SO₂ was slightly decreased in comparison of that in SO₂-TPD on either the SO₂-aged Ag/Al₂O₃ catalyst or the SO₂-aged Ag/Ti/Al₂O₃ catalyst. However, after reduction of the SO₂-aged catalysts by 1500 ppm C₃H₆/15% O₂/He at 500°C for 1 h ahead of the SO₂-TPD run in He, a substantial difference in the desorption amount of SO₂ appeared between the SO₂-aged Ag/Al₂O₃ (426.6 μmol/g) and the SO₂-aged Ag/Ti/Al₂O₃ (251.8 μmol/g). These results indicate that the presence of Ti (1) decreased the amount of SO₂ adsorption on the catalyst surface; (2) promoted the decomposition of the sulfate species via the reduction by propene, and (3) eventually enhanced the tolerance to SO₂ poisoning.

So far, there is no conclusive consensus regarding the influence of SO₂ on Ag-based catalysts due to the different experimental conditions and conflicting results reported in the literature. For instance, some researchers found a promotional effect on the catalyst activity in the presence of SO₂ (Angelidis and Kruse, 2001). Park and Boyer (2005) studied the effect of SO₂ on the activity of Ag/Al₂O₃ with various Ag loadings on the SCR of NO with C₃H₆. The authors concluded that the improvement of NO_x conversion might be due to the formation of Ag₂SO₄ phase. They claimed that Ag₂SO₄ could produce more -NCO species and better suppress propene oxidation than Ag₂O. The decrease of catalytic performance in the presence of SO₂ was mainly due to the poisoning of alumina active sites which were responsible for NO reduction to N₂. In this study, the promotional effect of Ti is probably due to the improvement on the tolerance of the anodic alumina support to SO₂ poisoning. Because the effect of SO₂ on the present reaction is an extremely complicated process, a further study is now in progress.

In this paper, the effect of Ti on the de-NO_x performance of the anodic alumina supported Ag/Ti/Al₂O₃ catalyst was investigated. The favorable de-NO_x activity shows that the application of the anodic alumina catalyst in controlling NO_x exhaust is a promising area, especially for the NO_x exhaust from diesel vehicles in which a more compact reactor, smaller pressure drop and more favorable thermal conductivity are required. Though in this paper some interpretations and hypotheses were made to explain the promotional effect of Ti, the discussion is still insufficient because we still do not have direct evidence to prove the actual existence of Ag_n^{δ+} clusters. Study of the effect of Ti on the formation of the organic nitrate intermediates is considered to be required. In addition, some qualitative analyses about the desorption peak of SO₂ of 400–800°C in Figure 12 should be carried out. Further study of these influences is now in progress and will be discussed elsewhere later.

Conclusions

In this paper, a relatively low loading of Ti was used to investigate the effect of Ti on the denitration activity of the Ag/Ti/Al₂O₃/Al catalyst, which was prepared by anodization of aluminum, hot water treatment and active metal impregnation, through the SCR activity measurements, NO_x- and SO₂-TPD in He, NO_x- and SO₂-TPSR in C₃H₆/O₂/He, XRD, FE-SEM, H₂-TPR analyses.

The presence of Ti greatly enhanced the low temperature denitration activity of Ag/Al₂O₃, and this was observed to be further intensified with an increase of Ti loading. It was suggested that Ti acted as a catalytic promoter of Ag sites. The result of NO_x-TPD showed that no obvious difference in the desorption performance of ads-NO_x species was observed between Ag/Al₂O₃ and Ag/Ti/Al₂O₃. However, in flowing O₂/C₃H₆/He, the desorption peak of nitrate species was decreased from 352 to 299°C when Ti was present. The promoted partial-oxidation of propene was believed to be a main reason. The H₂-TPR result suggested that a third kind of silver state existed in Ag/Ti/Al₂O₃ besides Ag⁺ and metallic Ag, possibly a moderately agglomerated Ag_n^{δ+} cluster.

Additionally, in comparison with the SO₂-aged Ag/Al₂O₃ catalyst, the SO₂-aged Ag/Ti/Al₂O₃ provided a favorable tolerance to SO₂ poisoning, and led to higher activity, which was attributed to a relatively lower adsorption amount of SO₂ and a faster reduction rate of sulfate species by propene, caused by the presence of Ti.

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