Selective catalytic reduction of NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst: from reaction mechanism to diesel engine test

Hong He*, Yunbo Yu

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P.R. China

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Abstract

Our recent research works on the selective catalytic reduction (SCR) of diesel engine NO_x by hydrocarbons over alumina-supported silver ($\text{Ag}/\text{Al}_2\text{O}_3$) were reviewed. The reaction mechanism of the SCR of NO_x by $\text{C}_2\text{H}_5\text{OH}$ over $\text{Ag}/\text{Al}_2\text{O}_3$ was studied using in situ DRIFTS and DFT calculations. A novel enolic species originating from the partial oxidation of $\text{C}_2\text{H}_5\text{OH}$ and C_3H_6 , was found on the surface of $\text{Ag}/\text{Al}_2\text{O}_3$ during the SCR of NO_x by in situ DRIFTS, which was also supported by DFT calculations. Based on this, a mechanism of the NO_x reduction was proposed, which can successfully explain the high efficiency of the NO_x reduction by $\text{C}_2\text{H}_5\text{OH}$ over $\text{Ag}/\text{Al}_2\text{O}_3$. A palladium promoted $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst (denoted $\text{Ag-Pd}/\text{Al}_2\text{O}_3$) was developed for the SCR of NO_x by C_3H_6 . The $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ showed a higher NO_x conversion than $\text{Ag}/\text{Al}_2\text{O}_3$, especially at temperatures ranging from 300 to 450 °C. The engine bench tests showed that the average NO_x conversion was greater than 80% in the diesel engine exhaust temperature range of 300–400 °C using our catalytic converter with $\text{C}_2\text{H}_5\text{OH}$ as reductant, which represents a leap from the Euro II standard to the Euro III standard for NO_x emission control in diesel engines.

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Keywords: Selective catalytic reduction (SCR) of NO_x ; Alumina supported silver ($\text{Ag}/\text{Al}_2\text{O}_3$); Ethanol ($\text{C}_2\text{H}_5\text{OH}$); Diesel engine; Enolic species

1. Introduction

Due to shortages of petroleum resources, lean-burn engines have become the main option for the vehicles. The diesel engine, which is a typical lean-burn engine, has the advantage of lower consumption of fuel and lower emission of CO_2 , CO and HC than stoichiometric gasoline engine. However, the exhaust from diesel engines contains a large amount of NO_x compared to stoichiometric gasoline engines equipped with three-way catalysts (TWCs). For a stoichiometric gasoline engine, a TWC provides a very high level of emission control for the removal of CO, NO_x , and unburnt hydrocarbons. However, diesel engines produce exhaust containing a large excess of oxygen. The platinum group metals based TWCs are completely ineffective for NO_x reduction under the oxygen-rich conditions. Removal of NO_x in the oxygen-rich exhausts demands a novel catalyst for a selective catalytic reduction (SCR) of NO_x . The SCR of NO_x by ammonia, or in some cases, urea, has become a fairly mature technology for stationary applications [1–4]. For

mobile applications such as diesel trucks and some lean-burn gasoline cars, however, commercialization still lies somewhere in the future. Up to now, multifarious catalysts such as zeolitic oxide, base oxide/metal and noble metal catalysts have been found to be effective for NO_x reduction in the presence of excess oxygen [3,5–8]. Among them $\text{Ag}/\text{Al}_2\text{O}_3$ is known as one of the most effective catalysts for the SCR of NO_x by hydrocarbons [9–45]. In particular, $\text{C}_2\text{H}_5\text{OH}$ is extremely effective for NO_x reduction over $\text{Ag}/\text{Al}_2\text{O}_3$ [10,11,17,36,38,41,46–51].

In this review, our recent research on the HC-SCR of NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$ was summarized systematically on a laboratory scale and an actual diesel engine bench scale. Also, our results provided new insight into the mechanism of this NO_x reduction process.

2. Characterization and fundamental performance of $\text{Ag}/\text{Al}_2\text{O}_3$ in the SCR of NO_x

The supported catalysts, $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{Al}_2\text{O}_3$, were prepared by an impregnation method with an aqueous solution of silver and copper nitrate, followed by evapora-

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62849123.
E-mail address: honghe@mail.rcees.ac.cn (H. He).

Table 1

BET surface area, pore volume and pore diameter of Ag/Al₂O₃ catalysts with different Ag loadings

Catalyst	BET surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore diameter (Å)
2 wt.% Ag/Al ₂ O ₃	239.8	0.7235	122.9
4 wt.% Ag/Al ₂ O ₃	222.4	0.7107	124.9
6 wt.% Ag/Al ₂ O ₃	211.8	0.6950	126.2
8 wt.% Ag/Al ₂ O ₃	209.9	0.6493	130.3

tion to dryness in a rotary evaporator under pressure reduction at 60 °C. The wet sample was dried at 120 °C for 12 h, and then calcined in air at 600 °C for 3 h [39].

BET results of the catalysts are shown in Table 1. The surface area of the Ag/Al₂O₃ catalysts gradually decreased with increasing silver loading. XRD patterns of a series of Ag/Al₂O₃ catalysts are shown in Fig. 1. Only the γ -Al₂O₃ phase was detected as the silver loading increased from 2 to 6 wt.%, but the Ag and Ag₂O phases were observed at 2 θ of 33.76°, 38.12°, 44.36° and 64.46° with 8 wt.% Ag loading [52,53]. TEM images of 4% Ag/Al₂O₃ catalyst are shown in Fig. 2. The Ag containing particles could be distributed evenly on the surface of Al₂O₃ with an optimum Ag loading of 4–6% and an average size of 15 nm.

Fig. 3 shows the NO_x conversions for the SCR of NO_x by C₃H₆ over Ag/Al₂O₃ catalysts with different silver loadings at various temperatures. The maximum of NO_x conversion increased significantly with an increase in silver loading from 2 to 4 wt.%, and the temperature at which the maximum NO_x conversion could be obtained (i.e. $T_{\max}$) shifted towards a lower temperature. Further increase of the silver loading from 4 to 8 wt.% did not show any promotion of low-temperature NO_x conversion but inhibited the high temperature conversion.

Fig. 1. XRD patterns of Ag/Al₂O₃ catalysts with different Ag loadings [39].

Fig. 2. TEM image of 4% Ag/Al₂O₃.

The NO_x conversions for the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃ catalysts with different silver loadings are shown in Fig. 4. As same as in Fig. 3, the maximum of NO_x conversion increased significantly with an increase in silver loading from 2 to 4 wt.%, and the temperature at which the

Fig. 3. NO_x conversion for the SCR of NO_x by C₃H₆ over Ag/Al₂O₃: (■) 2 wt.%, (▲) 4 wt.%, (▼) 6 wt.% and (◆) 8 wt.% at various temperatures. Conditions: 800 ppm NO, 1714 ppm C₃H₆, 10 vol.% O₂/N₂, catalyst weight = 1.2 g, W/F = 0.018 g s cm⁻³ [39].

Fig. 4. NO_x conversion over Ag/Al₂O₃ with different Ag loading: (□) 2 wt.% Ag and C₂H₅OH as reductant, (◇) 4 wt.% Ag and C₂H₅OH as reductant, (Δ) 6 wt.% Ag and C₂H₅OH as reductant, (×) 8 wt.% Ag and C₂H₅OH as reductant, and (○) 4 wt.% Ag and C₃H₆ as reductant. Conditions: 800 ppm NO, 1565 ppm C₂H₅OH, 10 vol.% O₂/N₂, 10 vol.% H₂O, catalyst weight = 1.2 g, W/F = 0.018 g s cm⁻³.

maximum NO_x conversion was obtained shifted towards a lower temperature. Further increase of the silver loading from 4 to 8 wt.% still enhanced the NO_x conversion at low temperatures but decreased the NO_x conversion at high temperatures. Since the 4 wt.% Ag/Al₂O₃ catalyst showed high activity for NO_x reduction in both cases using C₃H₆ or C₂H₅OH as a reductant, all of the Ag/Al₂O₃ catalysts that appeared below had a silver loading of 4 wt.%.

Fig. 5 shows a comparison of the performance of Ag/Al₂O₃ under different reaction conditions. When C₃H₆ was used as a reductant, the maximal conversion of NO_x reached 94.5% in the absence of water vapor (○ curve). The addition of 10% water vapor to the gas stream resulted in a drastic decrease of the average NO_x conversion, especially at the temperature range of 300–500 °C (● curve). However, the effect of water vapor was temporary and reversible. That is, when the addition of water vapor was stopped, the NO_x conversion recovered to its initial level in the absence of water vapor, and C₃H₆ conversion and CO₂ formation also showed the same level of recovery (data not shown). A similar temporal effect of water vapor was also observed when other hydrocarbons were used as reductants. In the case of C₂H₅OH, however, the presence of water vapor did not decrease the NO_x conversion, but enhanced the activity of Ag/Al₂O₃. In the diesel exhaust temperature region of 320–520 °C, the NO_x reduction was greater than 90% (■ curve). It is worth noting that, even in the presence of SO₂, the NO_x reduction by C₂H₅OH over Ag/Al₂O₃ hardly changed, which provided an opportunity for practical usage in a SO₂ containing exhaust. On the basis of these results, we selected Ag/Al₂O₃–C₂H₅OH as a promising

Fig. 5. Activity of Ag/Al₂O₃ for the SCR of NO_x by: C₃H₆ (○), C₃H₆ + H₂O (●), C₂H₅OH (□), and C₂H₅OH + H₂O (■). Conditions (C₃H₆): 800 ppm NO, 1714 ppm C₃H₆, 10 vol.% O₂/N₂, 0 or 10 vol.% H₂O, catalyst weight = 1.2 g, W/F = 0.018 g s cm⁻³. Conditions (C₂H₅OH): 800 ppm NO, 1565 ppm C₂H₅OH, 10 vol.% O₂/N₂, 0 or 10 vol.% H₂O, catalyst weight = 1.2 g, W/F = 0.018 g s cm⁻³.

combination of catalyst and reductant for NO_x reduction in diesel engine exhaust.

3. Mechanism of the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃

3.1. Formation of enolic species

Many researchers have intensively studied the reaction mechanism of the SCR of NO_x [11,13,16–19,24–28,31–34,47–50]. Our earlier work was focused on the formation and reactivity of isocyanate (NCO) species on Ag/Al₂O₃ [16]. A possible mechanism for NO_x reduction by C₂H₅OH over Ag/Al₂O₃ was judged to be similar to that of C₃H₆: approximately, NO + O₂ + C₂H₅OH → NO_x (nitrate in particular) + C_xH_yO_z (acetate in particular) → R–NO₂ + R–ONO → –NCO + –CN + NO + O₂ → N₂ [7,28]. However, this mechanism does not sufficiently explain why C₂H₅OH has a higher efficiency for the SCR of NO_x over Ag/Al₂O₃ than hydrocarbons such as C₃H₆.

In our recent papers [36–41], the formation and dynamic performance of partial oxidation products of C₂H₅OH and C₃H₆ over Ag/Al₂O₃ were studied by an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) method, and we found a novel enolic species originating from the partial oxidation of C₂H₅OH. As shown in Fig. 6, peaks at 1579 and 1466 cm⁻¹ were due to acetate. Peaks at 1633, 1416 and 1336 cm⁻¹ were assigned to the enolic species absorbed on the surface of Ag/Al₂O₃. This assignment was confirmed by using 2,3-dihydrofuran as an enolic model compound in our DRIFTS study, which has C=C bonded with an oxygen structure. A similar feature

Fig. 6. In situ DRIFTS spectra of adsorbed species in steady states on Ag/Al₂O₃ in a flow of C₂H₅OH + O₂ at (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C and (f) 600 °C. Conditions: 1565 ppm C₂H₅OH, 10 vol.% O₂/N₂ [38].

strongly supported our assignment: the surface enolic species was observed on Ag/Al₂O₃. From a comparison of the intensity of each peak in Fig. 6, we deduced that the enolic species is predominant during the oxidation of C₂H₅OH on the Ag/Al₂O₃ surface at low temperatures (within the range of 200–400 °C). However, at high temperatures ranging from 500 to 600 °C, the surface acetate species becomes dominant. In addition, our TPD experiments show the evidences for C₄ surface enolic species [41]. This indicates that a condensation reaction occurs synchronously during the partial oxidation of C₂H₅OH over Ag/Al₂O₃, which leads to chain growth of desorption products. The condensation reactions of aldehydes, as well as of ketones, are widely used in organic synthesis and are commonly catalyzed by zeolites, Al₂O₃, and TiO₂ [54–58].

Density functional theory (DFT) calculations were also used to confirm the structure of adsorbed enolic species on Ag/Al₂O₃ using the Gaussian 98 suite of programs. The simulation molecular structure model and FTIR spectrum of the surface enolic species on Ag/Al₂O₃ are shown in Fig. 7. In model A, the enolic species (CH₂=CH–O[–]) bonded with a silver atom, and the optimized distance between the oxygen and silver atom was 2.072 Å. Apparently, the calculated FTIR spectrum was reasonably similar to the corresponding experimental result. The asymmetric stretching vibration mode of the enolic species was calculated at

1645 cm^{–1} with a relatively high infrared intensity of 61 km mol^{–1}, which is 12 cm^{–1} higher than the experimental harmonic frequency (1633 cm^{–1}). Compared to the experimental value, the calculated symmetric stretching vibrational mode of this species varied within less than 13 cm^{–1} (1429 cm^{–1} against 1416 cm^{–1}). The calculated C–H deformation vibration mode (1328 cm^{–1}) was 8 cm^{–1} lower than the experimental one (1336 cm^{–1}). For model B (CH₂=CH₂–CH=CH–O–Al–Ag), the calculated FTIR spectrum was also reasonably similar to the corresponding experimental one (see Figs. 6 and 7D).

Thirty-two models of adsorbed species were calculated. Different kinds of adsorbed species and the interaction of the surface with the adsorbed species were considered. However, only the enolic species' DFT calculations were in good agreement with the experimental value. On the basis of this result, we concluded that there is excellent agreement between the calculational vibration spectrum and the experimental spectrum, supporting our assignment of the structure of surface enolic species. Furthermore, a surface reaction mechanism was proposed for the formation of enolic species as shown in Scheme 1.

3.2. Reactivity of enolic species

The reactivity of the enolic species toward NO + O₂ was evaluated by the in situ DRIFTS method. As shown in Fig. 8, after Ag/Al₂O₃ was exposed to C₂H₅OH + O₂ for 60 min (curve a), very strong peaks assignable to the adsorbed enolic species (1633, 1416 and 1336 cm^{–1}), and acetate peaks (1579 and 1464 cm^{–1}) were observed. Switching the fed gas to NO + O₂ resulted in a sharp decrease in the intensity of enolic species peaks accompanied by a corresponding increase in the intensity of a new NCO peak at 2229 cm^{–1} [16,17,50], indicating that the enolic species contributes to the formation of NCO species. It is widely accepted that the NCO species could be a crucial intermediate in the SCR of NO_x over Ag/Al₂O₃, and its high productivity results in high efficiency of NO_x reduction by C₂H₅OH or hydrocarbons [19,48,59,60]. Since the enolic species plays an important role in NCO species formation, this species must also be another crucial intermediate in the SCR of NO_x by C₂H₅OH.

Many research groups have studied the formation and reactivity of acetate during NO + C₃H₆ + O₂ reactions on oxide catalysts and metal-supported catalysts such as Al₂O₃ [61,62] and Ag/Al₂O₃ [7], and have suggested that acetate, as a dominant adsorbed species at high temperatures, plays a crucial role in the formation of NCO species by reacting toward NO + O₂. The reaction can be described as follows: NO + O₂ + C₃H₆ → NO_x (nitrate in particular) + C_xH_yO_z (acetate in particular) → R–NO₂ + R–ONO → –NCO + –CN + NO + O₂ → N₂. In the case of the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃, Kameoka et al. [50] proposed that acetate also plays a key role in NCO species formation. Furthermore, they considered that more acetate and less

Fig. 7. Molecular structure and optimized geometries of the calculational model for absorbed enolic species from C_2H_5OH on Ag/Al_2O_3 by oxidation (A) and aldol condensation (B); (C) and (D) calculated vibrational IR spectra for models A and B at the DFT-B3P86/LANL2DZ level [38,41].

nitrate were observed in comparison with the SCR of NO_x by C_3H_6 , which probably explains why NCO species is more easily produced when C_2H_5OH is used as a reductant. If the acetate really plays a crucial role in NCO species formation during the SCR of NO_x by C_2H_5OH , it should have high reactivity with $NO + O_2$. However, as shown in Fig. 8(B), enolic species have much higher reactivity than acetate on Ag/Al_2O_3 towards $NO + O_2$ to form NCO species. Actually, the acetate did not react with $NO + O_2$ until the enolic species had nearly disappeared from the Ag/Al_2O_3 surface.

Scheme 1. The formation of an adsorbed enolic species on Ag/Al_2O_3 .

This means that enolic species, instead of acetate, play a crucial role in the NO_x reduction by C_2H_5OH .

3.3. Reaction pathway of the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3

Fig. 9 shows the DRIFTS spectra of Ag/Al_2O_3 during the $NO + C_2H_5OH + O_2$ reaction at various temperatures (200–550 °C) in a steady state. Surface species such as enolic species (1633, 1416 and 1336 cm^{-1}), acetate (1572 cm^{-1} and 1473–1462 cm^{-1}), and NCO (2229 cm^{-1}) were found. In addition, strong peaks at 1583, 1302 cm^{-1} and shoulders at 1612, 1560 and 1250 cm^{-1} were also observed, which were respectively assigned to unidentate (1560 cm^{-1}), bidentate (1583, 1302 cm^{-1}), and bridging (1612 cm^{-1}) nitrates according to the literature [31,50]. Kameoka et al. [50] reported that these nitrates were highly active in their reaction with $C_2H_5OH + O_2$ to form NCO species, which was also supported by our earlier study [38]. The intensity of each peak indicated that the enolic species and the nitrates are predominant at 200 °C. Heating the sample causes the intensity of the peaks to decrease for these two types of adsorbed species. In contrast, a sharp increase in the intensity of the NCO peak (2229 cm^{-1}) was observed. At 450 °C, the NCO

Fig. 8. (A) Dynamic changes of in situ DRIFTS spectra on Ag/Al₂O₃ as a function of time in a flow of NO + O₂ at 400 °C. Before measurement, the catalyst was pre-exposed to a flow of C₂H₅OH + O₂ for 60 min at 400 °C (a), in a flow of NO + O₂ (b) 1 min, (c) 5 min, (d) 10 min and (e) 30 min. (B) Time dependence of the integrated areas of the peak in the range of 2160–2305 cm⁻¹ ((Δ), NCO), 1612–1711 cm⁻¹ ((◇), enolic species), 1439–1508 cm⁻¹ ((□), acetate) and 1209–1321 cm⁻¹ ((○), nitrates). Conditions: 800 ppm NO, 1565 ppm C₂H₅OH, 10 vol.% O₂/N₂. [38].

peak reached a maximum, while the peaks of enolic species and nitrates became very weak at this temperature. Heating the sample in sequential increments to a final temperature of 550 °C, the enolic species and nitrate peaks were barely perceptible, and acetate became the predominant surface species. These results strongly suggest that the enolic species and nitrates are key intermediates in the formation of NCO species during the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃.

Taking our earlier works [16,17,36–45] into account, we proposed a mechanism for the NO_x reduction by C₂H₅OH,

which can be described by a simplified reaction scheme, as shown in Scheme 2. The reaction starts with the formation of both adsorbed nitrates via NO oxidation by O₂ and enolic species and acetate via the partial oxidation of C₂H₅OH over Ag/Al₂O₃. The reaction between the two kinds of adsorbed species then leads to the formation of NCO species directly, or via organo-nitrogen compounds (such as R-ONO and R-NO₂), which is widely accepted in studies of the SCR of NO_x [7,16,47,50,63]. Subsequently, NCO species reacts with NO + O₂ and nitrates to yield N₂. It should be pointed out

Fig. 9. In situ DRIFTS spectra of adsorbed species in steady states over Ag/Al₂O₃ in a flow of NO + C₂H₅OH + O₂ at (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C, (f) 450 °C, (g) 500 °C and (h) 550 °C. Conditions: 800 ppm NO, 1565 ppm C₂H₅OH, 10 vol.% O₂/N₂ [41].

that the acetate formed by the reaction of C₂H₅OH + O₂ also reacts toward NO + O₂ to produce NCO species. However, the relatively low activity of acetate toward NO + O₂ results in this parallel reaction not playing an important role in the formation of NCO species.

The enolic species has a higher reactivity with NO + O₂ on Ag/Al₂O₃ than acetate has, and the former is the main surface species during the partial oxidation of C₂H₅OH over Ag/Al₂O₃. As a result, high surface concentration of NCO species and high efficiency of NO_x reduction are obtained when C₂H₅OH is used as a reductant during the SCR of

NO_x. We also studied the partial oxidation of C₃H₆ and the SCR of NO_x by C₃H₆ over Ag/Al₂O₃. In both cases, only a small amount of enolic species was formed, accompanied by the formation of large amounts of acetate. This relates to a lower NCO species concentration over Ag/Al₂O₃ as well as relatively lower NO_x conversion when C₃H₆ is used as a reductant.

3.4. Influence of water vapor on the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃

In general, the SCR of NO_x by hydrocarbons is suppressed in the presence of water vapor, which makes utilization of the catalysts difficult because great amounts of water vapor inevitably exist in various exhausts. When C₂H₅OH is used as a reductant, however, Ag/Al₂O₃ was extremely effective in the NO_x reduction even in the presence of water vapor [10,11,17]. Our results showed that the addition of water vapor enhances the NO_x reduction by C₂H₅OH over Ag/Al₂O₃, especially in the low temperature range (Fig. 5). Up to now, however, the mechanism behind water vapor's influence on the SCR of NO_x by C₂H₅OH is still unclear.

Fig. 10 shows the influence of water vapor on the NO_x reduction by C₂H₅OH over Ag/Al₂O₃ at 300 °C. In the absence of water vapor, NCO species (2237 cm⁻¹), enolic species (1633, 1416 and 1336 cm⁻¹), acetate (1576 and 1470 cm⁻¹), and nitrate (1564 and 1304 cm⁻¹) were observed. It is apparent that the addition of water vapor inhibited the formation of acetate, while the concentration of enolic species changed little on the Ag/Al₂O₃ surface. Considering that the formation of enolic species is parallel to the formation of acetate and that the two intermediates compete for adsorption sites, a decrease in the concentration of acetate on Ag/Al₂O₃ means more adsorption sites are available for the enolic species formation and its subsequent reaction. As a consequence, the reaction of NCO species to form CO₂ was enhanced. This was confirmed by both a decrease in the concentration of NCO species and an increase in the intensity of gas phase CO₂

Scheme 2. A possible reaction mechanism of the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃.

Fig. 10. Dynamic changes of in situ DRIFTS spectra in the flow of $\text{NO} + \text{O}_2 + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ over $\text{Ag}/\text{Al}_2\text{O}_3$ at 300°C after exposure to $\text{NO} + \text{O}_2 + \text{C}_2\text{H}_5\text{OH}$ for 60 min. Conditions: 800 ppm NO , 1565 ppm $\text{C}_2\text{H}_5\text{OH}$, 10 vol.% O_2/N_2 , 0 or 10 vol.% H_2O .

peaks (2361 and 2339 cm^{-1}). Since the formation of enolic species and its subsequent reaction play a dominant role in the SCR of NO_x by $\text{C}_2\text{H}_5\text{OH}$ over $\text{Ag}/\text{Al}_2\text{O}_3$, it is reasonable to conclude that the presence of water vapor enhances this process as shown in Scheme 2 which has been proved by activity test in Fig. 5.

4. Improvement of the low temperature activity and sulphur tolerance of $\text{Ag}/\text{Al}_2\text{O}_3$

At the low temperature range, $\text{Ag}/\text{Al}_2\text{O}_3$ is not active for the SCR of NO_x by C_3H_6 , and extensive studies have been performed focusing on this. He et al. first reported at the 69th Annual Meeting of JCS [64] that the SCR of NO_x by C_3H_6 over an $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst was effectively enhanced by co-impregnating with a small amount of Pd, whereas it was reduced by the addition of Pt and Au. The effect of adding Pd on $\text{Ag}/\text{mordenite}$ was also reported by Masuda et al. [65] using $(\text{CH}_3)_2\text{O}$ as a reductant, although the durability of $\text{Ag}/\text{Pd}/\text{mordenite}$ decreased in the presence of water vapor. Seker et al. [66] showed the negative effect of Au on $\text{Ag}/\text{Al}_2\text{O}_3$ for the NO reduction with C_3H_6 . In our earlier study [37], we reported that the addition of trace Pd (0.01 wt.%) to $\text{Ag}/\text{Al}_2\text{O}_3$ is favorable for the partial oxidation of C_3H_6 to form enolic species, resulting in an increase in NO_x conversion.

Fig. 11. (A) Catalytic activity for NO_x reduction by C_3H_6 over $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ catalysts respectively at various temperatures in the presence of water vapor. (B) Conversions of C_3H_6 into CO_x over $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Al}_2\text{O}_3$ respectively at various temperatures in the presence of water vapor. Conditions: 800 ppm NO , 1714 ppm C_3H_6 , 10 vol.% O_2/N_2 , 10 vol.% H_2O , catalyst weight = 1.2 g, $W/F = 0.018\text{ g s cm}^{-3}$ [37].

Fig. 11(A) shows the SCR of NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ catalysts by C_3H_6 at various temperatures. Both NO_x conversions increased with increase in the reaction temperature and reached a maximum at 437°C for $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ and at 470°C for $\text{Ag}/\text{Al}_2\text{O}_3$. The NO_x conversions then decreased with further increases in the reaction temperature. The highest rate of NO_x conversion was 82% over $\text{Pd-Ag}/\text{Al}_2\text{O}_3$, which was higher than the 73% rate over $\text{Ag}/\text{Al}_2\text{O}_3$. Obviously, a trace amount of Pd added into $\text{Ag}/\text{Al}_2\text{O}_3$ can enhance the NO_x conversion in the presence of excess oxygen and water vapor. This effect of adding metals is considered to be favorable for activating reductant molecules, for example, the scission of a C–C bond and partial oxidation. Fig. 11(B) shows the conversions of C_3H_6 into CO_x over $\text{Pd-Ag}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Al}_2\text{O}_3$. Similar to NO_x conversion, the curve of C_3H_6 conversion for $\text{Ag}/\text{Al}_2\text{O}_3$ shifted to lower temperatures after the addition of Pd.

This result suggests that Ag–Pd/Al₂O₃ can activate C₃H₆ to react with NO + O₂.

According to the tests using Ag–Pd/Al₂O₃ catalysts and contrastive Ag/Al₂O₃, we found that loading trace amounts of Pd on Ag/Al₂O₃ led to a significant improvement of NO_x conversion during the SCR of NO_x by C₃H₆, especially at low temperatures. In situ DRIFTS results suggested that Pd addition catalyzes the partial oxidation of C₃H₆ into a surface enolic species, and the surface enolic species is quite reactive towards NO₃[−] and NO₂ to form surface NCO species. This is in good agreement with the new reaction mechanism proposed above.

As SO₂ usually exists in lean-burn engine exhaust, the sulphur tolerance of oxide and base metal catalysts has been widely investigated [67]. An inhibition of the SCR of NO_x by SO₂ was observed in essentially all cases, originating from the reaction among SO₂, O₂ and the catalyst surface to form thermodynamically stable sulphate phases under reaction conditions [27]. The formation of these sulphate species brings about a reduction in the number of ‘strong’ chemisorption sites for NO_x [28,68]. Our results showed that Ag/Al₂O₃ is highly effective for the SCR of NO_x by C₃H₆ even in the presence of SO₂, while the addition of Pd to this catalyst results in an obvious loss in activity, especially in the low temperature range. On the other hand, our results demonstrated that Ag₂SO₄/Al₂O₃ performs well in NO_x reduction; thus the formation of some aluminum sulphate phases might be responsible for the activity loss [7]. Based on this prediction, we attempted to enhance the sulphur tolerance of Ag–Pd/Al₂O₃ by modifying the supporter to reduce the adsorption and accumulation of sulphate species, a technique which was also supported by our recent experiments [69]. Furthermore, DRIFTS spectra suggested that the presence of SO₂ inhibited the formation of enolic species and NCO species, which are the key intermediates of the SCR of NO_x by C₃H₆ over Ag–Pd/Al₂O₃.

Burch [7] reported that the inhibition extent of the SCR of NO_x by SO₂ is dramatically dependent on the nature of the

Fig. 12. Activity of Ag/Al₂O₃ for the SCR of NO_x by C₂H₅OH on an actual engine bench (GHSV: (■) 30,000, (●) 50,000 and (▲) 80,000).

reductant and the SO₂ concentration. When using alcohols as reductants, the loss in activity due to SO₂ is usually only a limited fraction of the initial activity [70]. We also observed similar phenomena during the NO_x reduction by C₂H₅OH over Ag/Al₂O₃. In addition, our DRIFTS results showed that the presence of SO₂ hardly changed the formation of enolic species originating from the partial oxidation of C₂H₅OH, which probably explains why the inhibition of SO₂ largely depends on the nature of the reductant.

As discussed above, Ag/Al₂O₃ is a promising candidate for the NO_x reduction from diesel engine exhaust. However, Eränen et al. [35] noticed that a considerable amount of CO was produced during the SCR of NO with octane over Ag/Al₂O₃. In their study, a commercial Pt-oxidation catalyst was extremely effective for the removal of CO when placed after Ag/Al₂O₃, while a drastic decrease of NO_x conversion was observed. We also found that a large amount of CO was produced during the NO_x reduction by either propene or

Fig. 13. Performance of NO_x catalytic converter in the European Economic Community's 13-mode test cycle.

Table 2
NO_x emission and EURO standards

Average NO _x emission (g kW ⁻¹ h)	Initial outlet	Catalytic converter outlet	NO _x conversion	Euro III standard	Euro IV standard
NO _x (steady state)	5.82	1.74	70.0%	5.0	3.5
NO _x (transient state)	6.02	2.67	55.6%	5.0	3.5

ethanol over Ag/Al₂O₃. In order to eliminate undesired by-products, a two-component composite catalyst, Ag/Al₂O₃ + Cu/Al₂O₃, was employed, which was proved to be quite effective for both NO_x reduction and CO removal. In addition, it has been reported that a substantial amount of nitrogen-containing by-products such as N₂O, NH₃, CH₃CN, and HCN are produced during the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃. Further studies are planned to attempt to develop the composite catalyst system, combining placing an oxidation catalyst behind the Ag/Al₂O₃, to remove these nitrogen-containing by-products without losing any activity of the SCR of NO_x by C₂H₅OH.

5. Diesel NO_x reduction test with an actual engine bench

The results shown in Fig. 12 demonstrate that the Ag/Al₂O₃–C₂H₅OH system was extremely effective for the NO_x reduction on a four-cylinder direct injection engine bench [71]. At the typical diesel engine exhaust temperature range, the conversion of NO_x remained rather high at each space velocity tested (GHSV: 30,000, 50,000 and 80,000 h⁻¹). In the case of a space velocity of 30,000 h⁻¹, the light-off temperature of NO_x conversion was 270 °C and the highest NO_x conversion reached 92.3% at an operating temperature of 400 °C (C₂H₅OH/NO_x = 3:1 on a mass basis). This result was similar to our results of the laboratory scale test, indicating the most realistic potential in reducing NO_x under real diesel engine exhaust conditions.

Our Ag/Al₂O₃–C₂H₅OH NO_x catalytic converter satisfied the NO_x emission requirements of the Euro III standard using the European Economic Community's 13-mode test cycle (Fig. 13). Table 2 shows the average NO_x emission of diesel engines with and without de-NO_x catalytic converter aftertreatment. It is obvious that the NO_x emission from a diesel engine, which was at the level of Euro II, was greatly improved, meeting the requests for the Euro III standard by the use of a catalytic converter. In fact, the average NO_x emission on the catalytic converter outlet also satisfied the requirements for the Euro IV standard.

6. Continuing and future work

Diesel engines have a number of advantages including a high power/weight ratio, more than 50% thermal efficiency,

infrequent engine problems, and high fuel economy. However, the nitrogen oxides (NO_x) and particulate matter (PM) emitted from diesel engines constitute two major air pollution sources. Our previous research focused on the NO_x reduction in lean-burn exhausts. Our recently results showed that using Ethanol–diesel blend fuel could greatly reduce the PM emission [71,72]. Ethanol–diesel blend fuel partly replaces petroleum with a renewable resource and it is a promising alternative fuel for diesel engines. Therefore, employing the Ethanol–diesel blend fuel with our Ag/Al₂O₃–C₂H₅OH NO_x catalytic converter can reduce NO_x and PM emissions in diesel engine exhaust simultaneously.

In the near future, we plan to make further attempts to optimize the blend of Ethanol–diesel fuels and develop a corresponding catalytic converter system for reducing both NO_x and PM in diesel engine exhaust. The Ethanol–diesel blend fuel and corresponding NO_x catalytic converter systems will first be demonstrated on the urban transit system of buses, which is considered a major source of air pollution in urban regions.

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