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## Applied Catalysis B: Environmental

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# A cyclic reaction pathway triggered by ammonia for the selective catalytic reduction of NO<sub>x</sub> by ethanol over Ag/Al<sub>2</sub>O<sub>3</sub>



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## ABSTRACT

Alumina-supported silver catalysts (Ag/Al<sub>2</sub>O<sub>3</sub>) prepared using nordstrandite as a precursor exhibited excellent activity for the selective catalytic reduction of NO<sub>x</sub> by ethanol (ethanol-SCR). During the ethanol-SCR, the formation of NH<sub>3</sub> was observed over all Ag/Al<sub>2</sub>O<sub>3</sub> catalysts, the amount of which was related to silver loading, reaction temperature, and the concentration of ethanol used, even when water was excluded from the inlet gas. Transient activity testing and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis showed that the reaction between isocyanate species (–NCO) and water is the main pathway of NH<sub>3</sub> formation. Addition of NH<sub>3</sub> enhanced the NO<sub>x</sub> conversion for ethanol-SCR and the oxidation of ethanol over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub>. DRIFTS analysis revealed for the first time that NH<sub>3</sub> reacted with enolic species to form –NCO over Ag/Al<sub>2</sub>O<sub>3</sub>, thus resulting in a novel and cyclic reaction pathway for ethanol-SCR.

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## 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) cause a variety of health and environmental impacts, such as the formation of photochemical smog and acid rain. Consequently, NO<sub>x</sub> removal has become an important issue for environmental protection. The diesel engine has the advantages of low fuel consumption and low emissions of CO<sub>2</sub>, CO, and HC, while NO<sub>x</sub> removal is one of the major challenges for its commercial application. Among the NO<sub>x</sub> reduction technologies being developed to control diesel engine emissions, selective catalytic reduction by hydrocarbons (HC-SCR) has attracted much attention as a possible alternative to urea/NH<sub>3</sub>-SCR, the latter of which has been commercially used in Europe, the United States, and Japan [1–5].

Hitherto, numerous catalysts such as zeolitic oxide, base metal/oxide and noble metal catalysts have been found to be effective for the HC-SCR of NO<sub>x</sub> in the presence of excess oxygen [3,4,6–9]. Among them,  $\gamma$ -alumina-supported silver (Ag/Al<sub>2</sub>O<sub>3</sub>) is known as one of the most effective catalysts [10–17]. When using oxygenated hydrocarbons as reductants, particularly ethanol, Ag/Al<sub>2</sub>O<sub>3</sub> shows high activity even in the presence of SO<sub>2</sub> and H<sub>2</sub>O [18]. Over Ag/Al<sub>2</sub>O<sub>3</sub>, though NO<sub>x</sub> was mainly converted to N<sub>2</sub>, there was still an unexpected production of ammonia, the concentration of which varied with the silver loading of the catalyst, the Lewis acidity of the support, reaction temperature, water

vapor, the employed reductant and its concentration [8,19,20]. During C<sub>3</sub>H<sub>6</sub>-SCR carried out by Meunier et al. [8], NH<sub>3</sub> selectivity was 5% on pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which decreased to 3% over 1.2 wt% Ag/Al<sub>2</sub>O<sub>3</sub>, and further increasing the silver loading to 10 wt% resulted in the disappearance of NH<sub>3</sub>. Miyadera [19] observed that the concentration of NH<sub>3</sub> increased with the amount of ethanol employed over 2 wt% Ag/Al<sub>2</sub>O<sub>3</sub>, and also increased with the growing space velocity. Moreover, a correlation between NH<sub>3</sub> yield and acidic surface properties of the alumina support was likewise established for ethanol-SCR over Ag/Al<sub>2</sub>O<sub>3</sub>, such that the selectivity of NH<sub>3</sub> varied between 6% and 27% at 723 K with increasing numbers of strong Lewis acid sites [20]. In addition, water vapor plays a crucial role in NH<sub>3</sub> formation, as confirmed by the result that the NH<sub>3</sub> concentration promptly increased from 10 to 90 ppm at 773 K over 2.0 wt% Ag/Al<sub>2</sub>O<sub>3</sub> as soon as 10% H<sub>2</sub>O was added into the feed gas of NO+ethanol+O<sub>2</sub> [19].

Since ammonia is one of the main basic species commonly present in the atmosphere, it readily reacts with strongly acidic species such as NO<sub>x</sub> and SO<sub>x</sub>, leading to smog formation. As a result, minimizing the release of ammonia during the HC-SCR process should be given much more attention. With this aim, it will be helpful to recall the mechanism of the reduction of NO<sub>x</sub> by hydrocarbons.

Generally, HC-SCR of NO<sub>x</sub> can be considered as follows: NO+O<sub>2</sub>+HC→NO<sub>x</sub> (adsorbed nitrate in particular)+ad-C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>→R-ONO+R-NO<sub>2</sub>→–NCO+–CN→N<sub>2</sub> [5,12,21]. Among the intermediates mentioned above, the isocyanate species (–NCO) was considered to be highly reactive toward NO+O<sub>2</sub> and/or surface

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nitrate to produce  $N_2$ , and thus play a critical role in HC-SCR over  $Ag/Al_2O_3$ . Back in 1973, Unland [22] found that  $-NCO$  species adsorbed on the  $Pt/Al_2O_3$  surface reacted with  $H_2O$  to yield  $NH_3$  and  $CO_2$ . Such hydrolysis of  $-NCO$  on  $Ag/Al_2O_3$  catalysts was further demonstrated by DRIFTS and mass spectrometry (MS) measurements [23].

As a reduced form of nitrogen, ammonia can react with oxidized species of this element (e.g. surface-bound nitrates,  $NO + O_2$ ) to form the final product of  $N_2$ , thus ammonia has been regarded as a reactive intermediate for HC-SCR over  $Ag/Al_2O_3$  [1,18,19,23]. However, as reported by Richter et al. [24], the  $Ag/Al_2O_3$  catalyst was not active for  $NO_x$  reduction by  $NH_3$  in the absence of  $H_2$  (only reaching approximately 30%  $NO_x$  conversion at high temperature above 823 K), which was further confirmed by Kondratenko et al. [25] through a transient isotopic approach. Consequently, the intermediacy of  $NH_3$  for the HC-SCR over  $Ag/Al_2O_3$  needs to be further clarified.

In this study,  $\gamma$ -alumina-supported silver catalysts prepared using nordstrandite as a precursor were employed to evaluate their performance in the ethanol-SCR. Particular attention was paid on the formation of  $NH_3$  and its role in the  $NO_x$  reduction process. Combined with the results of DRIFTS measurements, the intermediacy of  $NH_3$  in ethanol-SCR was clarified. A novel reaction pathway concerning  $NH_3$  participating in ethanol-SCR by reaction with enolic species over  $Ag/Al_2O_3$  was proposed.

## 2. Experimental

### 2.1. Catalyst preparation

The precursor of  $\gamma$ - $Al_2O_3$  was synthesized by the following procedure. 4.8 g  $Al(NO_3)_3$  was added into 100 mL distilled water under vigorous stirring, followed by dropwise addition of anhydrous ethylenediamine, adjusting the pH value of the solution to  $\sim 8.5$ . After stirring for another 2 h, the gel was covered by PE film and aged at 303 K for 12 h. To obtain the final product, the precipitate was separated from the solution by centrifuging, and then dried at 363 K in air for 12 h.

$Ag/Al_2O_3$  catalysts with different silver loadings were prepared by an impregnation method [13], immersing the support synthesized by the above procedure into an aqueous solution of silver nitrate. After impregnation, the excess water was removed in a rotary evaporator at 333 K, and then the product was calcined in air at 873 K for 3 h.

### 2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a Rigaku D/max-RB X-ray Diffractometer (Japan) using  $CuK\alpha$  radiation and operating at 40 kV and 40 mA. The patterns were taken over the  $2\theta$  range from  $10^\circ$  to  $90^\circ$  at a scan speed of  $4^\circ \text{ min}^{-1}$ .

$N_2$  adsorption-desorption isotherms over the series of  $Ag/Al_2O_3$  catalysts were obtained at 77 K using a Quantachrome Autosorb-1C instrument. Prior to  $N_2$  physisorption, the catalysts were degassed at 573 K for 3 h. Surface areas were determined by the multi-point BET equation in the 0.05–0.35 partial pressure range. Pore volumes, average pore diameters and pore size distributions were determined by the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms.

The morphology and the particle size distribution of the prepared samples were examined by transmission electron microscopy (TEM, HITACHI H-7500) with 80 kV acceleration voltage.

### 2.3. Activity test

The activity test was carried out in a fixed-bed reactor by passing a gaseous mixture of  $NO$  (800 ppm),  $NH_3$  (150 ppm) (when added),  $C_2H_5OH$  (1565 ppm),  $O_2$  (10%) and water vapor (10%) (when added) in  $N_2$  balance at a total flow rate of  $1000 \text{ mL min}^{-1}$  ( $GHSV = 50,000 \text{ h}^{-1}$ ). An aqueous  $C_2H_5OH$  solution was supplied with a micropump and vaporized by a coiled heater. The concentrations of  $NO$ ,  $NO_2$ ,  $N_2O$  and  $NH_3$  were analyzed on-line by an FTIR spectrometer (Nicolet is10) equipped with a gas cell of volume  $0.2 \text{ dm}^3$ . In this case, the gas cell of the FTIR spectrophotometer and the gas line were heated to 393 K to avoid water condensation. The spectra were collected with a resolution of  $0.5 \text{ cm}^{-1}$  and with an accumulation of 16 scans when the SCR process reached a steady state. The concentration of  $C_2H_5OH$  and  $CH_3CHO$  was monitored by periodically injecting the outlet gas into a gas chromatograph (Shimadzu, GC-2014C) equipped with two TCDs and one FID. In our case, the concentration of  $N_2O$  was negligible during the reduction of  $NO_x$  by ethanol over  $Ag/Al_2O_3$ . Based on this,  $NO_x$  conversion and  $N_2$  ( $NH_3$ ) selectivity were calculated by the following equations:

$$NO_x \text{ conversion (\%)} = \frac{[NO]_{in} - [NO + NO_2]_{out}}{[NO]_{in}} \times 100$$

$$N_2 \text{ selectivity (\%)} = \frac{[NO]_{in} - [NO + NO_2 + NH_3]_{out}}{[NO]_{in}} \times 100$$

$$NH_3 \text{ selectivity (\%)} = \frac{[NH_3]_{out}}{[NO]_{in}} \times 100$$

### 2.4. In situ DRIFTS measurement

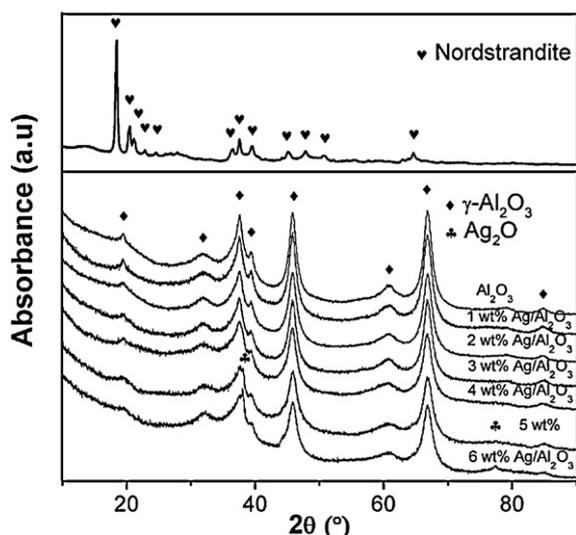
In situ DRIFTS spectra were recorded on a Nexus 670 FT-IR (Thermo Nicolet), equipped with an in situ diffuse reflection chamber and a high sensitivity MCT/A detector. In this case,  $Ag/Al_2O_3$  catalyst (3 wt%) was finely ground and placed in ceramic crucibles in the in situ chamber. Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions, such as mixture of gases, pressure and sample temperature. Prior to recording each DRIFTS spectrum, the sample was heated in situ in 10%  $O_2/N_2$  flow at 823 K for 1 h, then cooled to the desired temperature to measure a reference spectrum. All gas mixtures were fed at a flow rate of  $300 \text{ mL min}^{-1}$ . All spectra were measured with a resolution of  $4 \text{ cm}^{-1}$  and with an accumulation of 100 scans.

## 3. Results

### 3.1. Structural properties

The XRD pattern of uncalcined precursor prepared by a mixture of  $Al(NO_3)_3$  and anhydrous ethylenediamine is shown as the top curve of Fig. 1. The peaks of the uncalcined sample were identified as nordstrandite (JCPDS No. 24-0006), one of the four aluminum trihydroxide ( $Al(OH)_3$ ) polymorphs [26]. After being calcined at 873 K for 3 h, the sample demonstrated distinct peaks assigned to  $\gamma$ - $Al_2O_3$  (JCPDS No. 29-0063). Fig. 1 also exhibits the XRD patterns of  $Ag/Al_2O_3$  catalysts with different silver loadings, all of which presented the characteristic peaks of  $\gamma$ - $Al_2O_3$ . No peaks indexed to silver species could be found when silver loadings were below 5 wt%, indicating its high dispersion. However, further increasing the silver content resulted in an appearance of peaks attributable to silver oxides, indicating aggregation of silver species.

As listed in Table 1, calcining the prepared nordstrandite resulted in notable increases in the surface area and the pore volume, while the pore diameter remained almost the same. It should



**Fig. 1.** XRD patterns of nordstrandite and Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with different silver loadings.

be noted that silver loading further increased the surface area, while the pore volume decreased. The catalysts with moderate silver loading content (3–5 wt%) exhibited the highest surface area, 302.7–303.4 m<sup>2</sup>/g, indicating a favorable interaction between silver species and the support of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The TEM images gave a visual understanding of the morphology and particle size distribution of the prepared samples (Fig. 2). The nordstrandite prepared by precipitation was in the form of irregular sheets with smooth surfaces (Fig. 2A). After calcination, plentiful pore structures clearly appeared on the surface and were conserved even after impregnation with the active component, which may contribute to the increase in surface area arising from the calcination process (Fig. 2B and C). In addition, Ag particles with diameter of around 15 nm could be observed uniformly distributed over 4 wt% Ag/Al<sub>2</sub>O<sub>3</sub> (Fig. 2C).

### 3.2. Catalytic activity for NO<sub>x</sub> reduction by ethanol and ammonia formation on Ag/Al<sub>2</sub>O<sub>3</sub> catalysts

Fig. 3 displays the conversion of NO<sub>x</sub> by ethanol, NH<sub>3</sub> yield, and N<sub>2</sub> selectivity over Ag/Al<sub>2</sub>O<sub>3</sub> with different silver loadings. Over the whole temperature region of 473–823 K, increasing the silver content from 1 wt% to 2 wt% significantly enhanced the NO<sub>x</sub> conversion, the latter of which exhibited NO<sub>x</sub> conversion above 95% with a wide temperature window of 200 K (594–793 K). Increasing silver loading to 3 wt% further enhanced NO<sub>x</sub> conversion in the low temperature region, while it decreased NO<sub>x</sub> reduction at temperatures above 713 K. However, further increasing silver loading significantly decreased NO<sub>x</sub> conversion in the high temperature

**Table 1**  
Structural parameters of nordstrandite and Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with different silver loadings derived from N<sub>2</sub> physisorption results.

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
Nordstrandite	180.5	0.22	3.82
Al <sub>2</sub> O <sub>3</sub>	242.0	0.42	3.82
1 wt% Ag/Al <sub>2</sub> O <sub>3</sub>	269.1	0.40	3.41
2 wt% Ag/Al <sub>2</sub> O <sub>3</sub>	289.4	0.38	3.40
3 wt% Ag/Al <sub>2</sub> O <sub>3</sub>	303.4	0.35	3.41
4 wt% Ag/Al <sub>2</sub> O <sub>3</sub>	303.3	0.32	3.40
5 wt% Ag/Al <sub>2</sub> O <sub>3</sub>	302.7	0.27	3.40
6 wt% Ag/Al <sub>2</sub> O <sub>3</sub>	271.3	0.25	3.40

region while only slightly enhancing the NO<sub>x</sub> reduction at low temperatures.

As shown in Fig. 3C, the formation of NH<sub>3</sub> was also significantly enhanced when silver loading increased from 1 wt% to 2 wt%, while it gradually decreased when the silver loading continued to increase. Noticeably, ammonia was present over all the catalysts tested at temperatures above 548 K. Compared to the 2 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> showed a similar temperature range for 100% NO<sub>x</sub> conversion, except that it was shifted toward lower temperature. However, the production of NH<sub>3</sub> on 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> was much lower than that on the 2 wt% sample at temperatures above 600 K, exhibiting a high N<sub>2</sub> selectivity (Fig. 3B). Within a wide temperature range of 570–750 K, indeed, the 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> showed almost the highest N<sub>2</sub> selectivity. Thus, the following experiments were performed on the sample of 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub>.

A comparison of catalytic activity and NH<sub>3</sub> selectivity between our research and others in the literature is given in Table S1 [18,19,27,28]. Apparently, the catalysts prepared from nordstrandite in our research showed advantages in terms of lower T<sub>50</sub> (temperature required for 50% NO<sub>x</sub> conversion) and higher N<sub>2</sub> selectivity. However, NH<sub>3</sub> formation was a widespread phenomenon during HC-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with different reductants, the amount of which varied with the catalysts used and reaction conditions.

Fig. S1 further shows the concentrations of NO, NO<sub>2</sub>, N<sub>2</sub>O, and NH<sub>3</sub> in the outlet gas during NO<sub>x</sub> reduction by ethanol over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> at different temperatures. Sharp decreases in the concentration of NO and NO<sub>2</sub> were observed when the reaction temperature gradually increased to 600 K, which was accompanied by a gradual increase in NH<sub>3</sub> concentration. Over the temperature region of 600–700 K, NO<sub>x</sub> were almost totally consumed while the amount of NH<sub>3</sub> went on increasing; whereas at temperatures above 700 K, NO appeared again and its concentration increased with increasing temperature. Within this temperature range, a decreased NH<sub>3</sub> concentration was observed simultaneously. The coexistence of NO<sub>x</sub> and NH<sub>3</sub> indicated that the silver catalyst was not efficient for NH<sub>3</sub>-SCR in the absence of promoters (such as H<sub>2</sub>) over the tested temperature region, which was in agreement with the results of Kondratenko et al. [25] and Shimizu et al. [29]. As reported by Meunier et al. [8], it should be noted, however, that the presences of NO<sub>2</sub> and NH<sub>3</sub> during propene-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> in the absence of water vapor were mutually exclusive, i.e., NO<sub>2</sub> could be observed only when NH<sub>3</sub> was absent and vice versa, which is contrast to the data reported in the present work. This discrepancy may be possibly explained by differences in the nature of the reductant (propene vs ethanol) and reaction conditions (without water vapor vs with water vapor) employed in experiments. Indeed, the coexistence of NH<sub>3</sub> and NO<sub>2</sub> was also observed by Lee et al. [27] during ethanol-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> in the presence of water vapor.

Fig. 4 shows the influence of ethanol concentration on the NO<sub>x</sub> conversion and the formation of ammonia over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalyst. When 783 ppm ethanol was introduced (giving a molar ratio of C/N around 2), the Ag/Al<sub>2</sub>O<sub>3</sub> was not highly active for NO<sub>x</sub> conversion, exhibiting a maximum value of 65% at 659 K, during which the highest concentration of ammonia (78 ppm) was observed at 763 K. Gradually increasing the ethanol concentration from 783 to 1252 ppm notably enhanced NO<sub>x</sub> conversion at temperatures above 525 K, during which the same trend was also observed for the NH<sub>3</sub> and N<sub>2</sub> selectivities. Further increased feeding of ethanol slightly improved NO<sub>x</sub> conversion at temperatures above 700 K, while the production of NH<sub>3</sub> was still significant over the whole temperature region. Miyadera [19] also adjusted the ethanol inlet concentration (C/N = 1.5–2.5) in ethanol-SCR over 2 wt% Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, and a higher C/N ratio gave higher NO<sub>x</sub> conversion, N<sub>2</sub> selectivity, and NH<sub>3</sub> yield even without water.

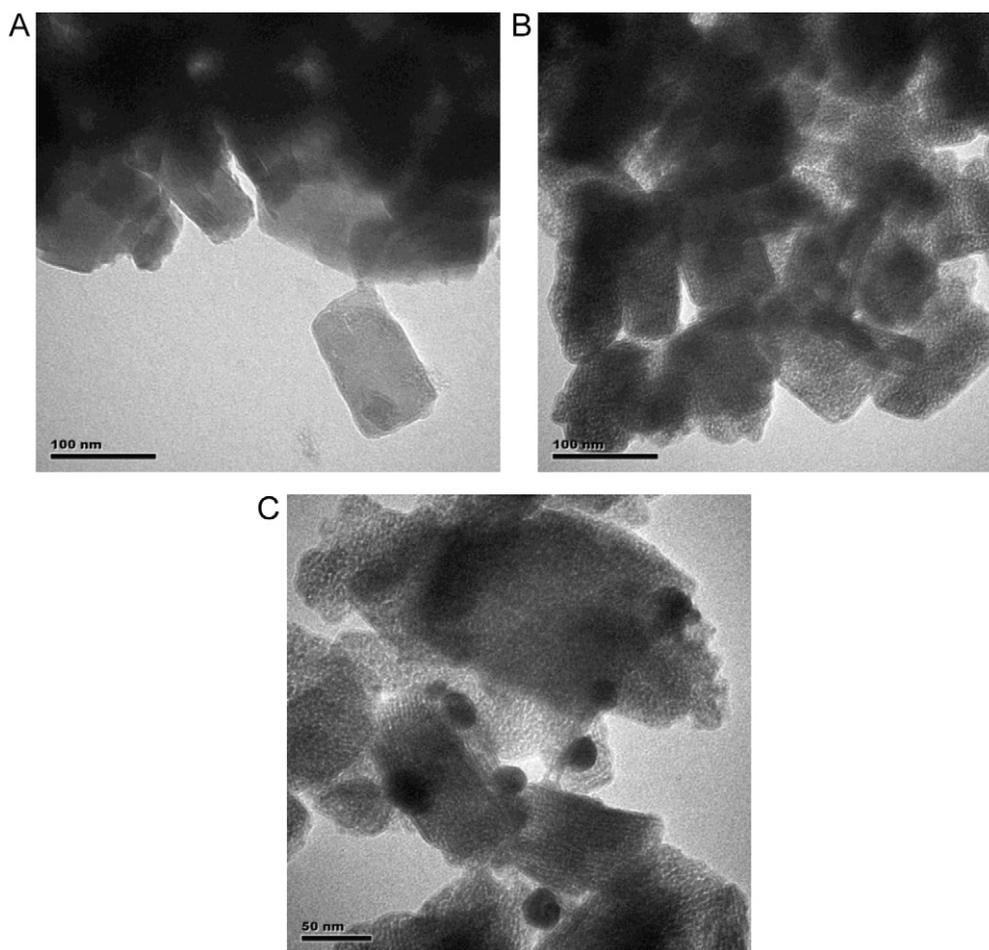


Fig. 2. TEM images of nordstrandite (A), Al<sub>2</sub>O<sub>3</sub> (B), and 4 wt% Ag/Al<sub>2</sub>O<sub>3</sub> (C).

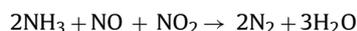
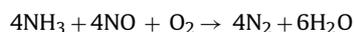
It has been proposed that the presence of water vapor triggered the hydrolysis of –NCO formed during the HC-SCR process, and thus enhanced the production of NH<sub>3</sub> [19,23]. To highlight this issue, we compared NO<sub>x</sub> conversion and NH<sub>3</sub> formation on 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> with and without water vapor. As shown in Fig. S2A, the addition of water in the reaction gas slightly enhanced NO<sub>x</sub> conversion at temperatures above 650 K. However, it should be noted that water vapor drastically increased the concentration of NH<sub>3</sub>, particularly at temperatures above 550 K (giving a maximum of 166 ppm, 1.5 times higher than that in the absence of water vapor), which results in a decrease of N<sub>2</sub> selectivity (Fig. S2B). Noticeably, the formation of NH<sub>3</sub> was still observed even when water vapor was switched out from the inlet gas, suggesting that surface-adsorbed species formed during the reduction of NO<sub>x</sub> by ethanol readily react with water to produce NH<sub>3</sub> (Fig. S2C).

### 3.3. The promotion of NO<sub>x</sub> conversion by ammonia addition

The reduction of NO<sub>x</sub> by ammonia over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> was also carried out in our research. Results given in Fig. S3A showed that the maximum conversion of NO<sub>x</sub> was 17% at temperatures above 673 K in standard SCR, and even in fast SCR the maximum conversion was only around 25%, similar to the results reported by Richter et al. [24]. What's more, up to 175 ppm N<sub>2</sub>O was formed even at the low temperature of 570 K during fast SCR, which is much higher than that detected during the ethanol-SCR process.

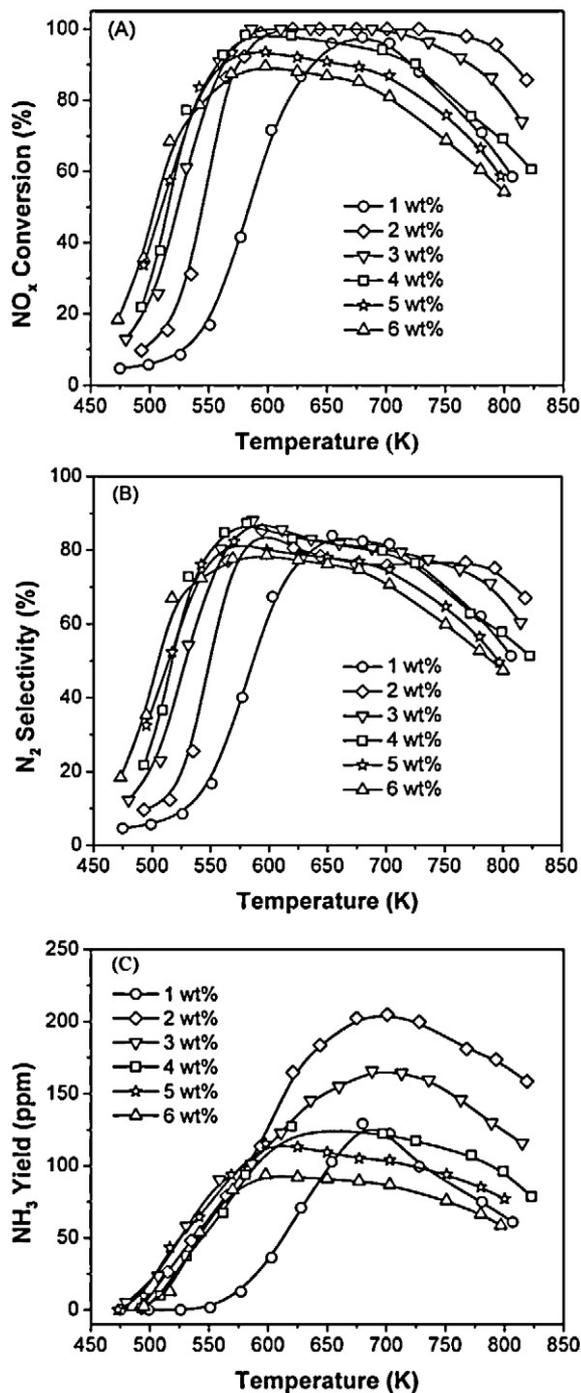
Furthermore, 150 ppm NH<sub>3</sub> was added into the inlet gas of the SCR of NO<sub>x</sub> by ethanol over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> at 523 K, during which the concentration of NO<sub>2</sub> decreased 112 ppm (from 184 ppm to

72 ppm), as shown in Fig. 5. At the same time, the concentration of NO decreased about 30 ppm and that of N<sub>2</sub>O remained almost the same (below 5 ppm). With the decreases of NO and NO<sub>2</sub> concentrations, the concentration of NH<sub>3</sub> in the outlet increased from 64 ppm to 123 ppm, giving a net change of 91 ppm considering the addition of 150 ppm NH<sub>3</sub> in the feed gas. These results suggest that further NO<sub>x</sub> reduction occurred after NH<sub>3</sub> was introduced into the ethanol-SCR system. Assuming that the reaction among NO, NO<sub>2</sub> and NH<sub>3</sub> over Ag/Al<sub>2</sub>O<sub>3</sub> follows the typical standard and/or fast NH<sub>3</sub>-SCR process [2,5,30]:



The theoretical consumption of NO should be equal to or higher than that of NO<sub>2</sub>, while in our case, the decrease of NO was 73% lower than that of NO<sub>2</sub>, clearly indicating the occurrence of a reaction pathway different to that of the NH<sub>3</sub>-SCR process.

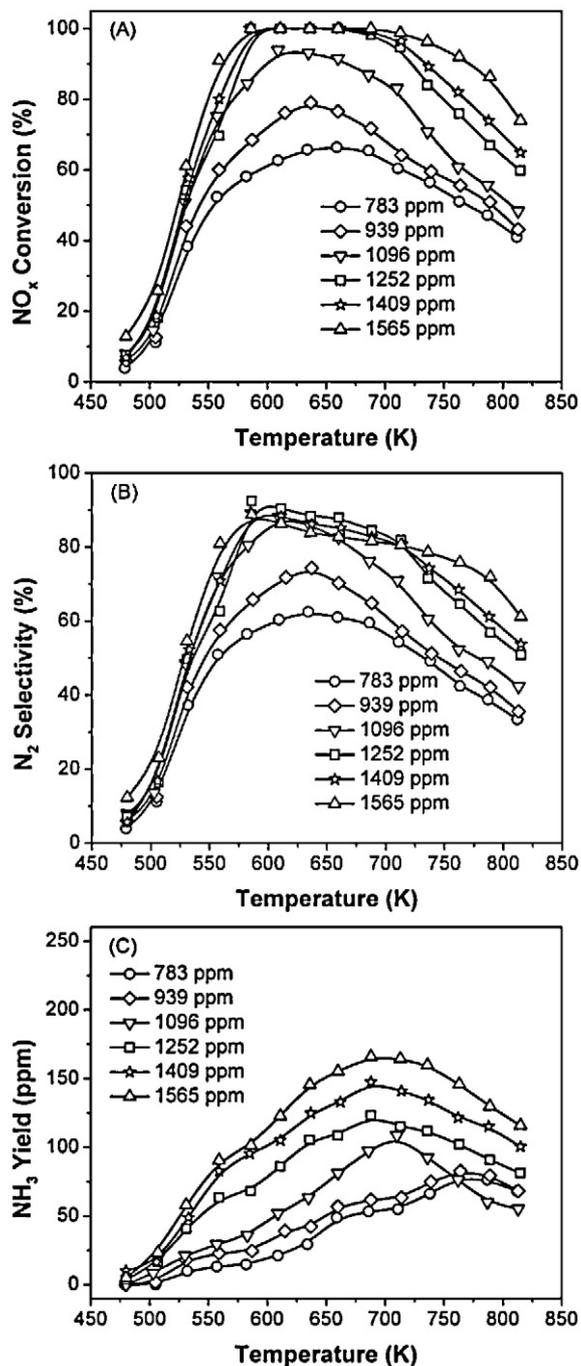
The role of NH<sub>3</sub> in the oxidation of ethanol over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> was further investigated (Fig. 6). At 498 K, adding NH<sub>3</sub> resulted in an increase of ethanol conversion from 45% to 54% (141 ppm decrease). Meanwhile, it should be noted that the concentration of acetaldehyde also increased about 120 ppm, indicating an enhancement of the partial oxidation of ethanol. As temperature increased, the enhancements of ethanol conversion and acetaldehyde formation induced by NH<sub>3</sub> addition gradually decreased, and disappeared above 598 K.



**Fig. 3.** NO<sub>x</sub> conversion (A), N<sub>2</sub> selectivity (B), and NH<sub>3</sub> yield (C) for the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub> catalysts with different silver loading. Conditions: NO 800 ppm, O<sub>2</sub> 10%, H<sub>2</sub>O 10%, N<sub>2</sub> balance, GHSV: 50,000 h<sup>-1</sup>.

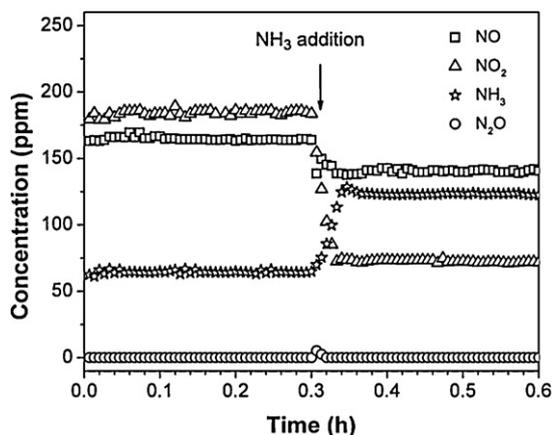
#### 3.4. In situ DRIFT studies

At the heart of HC-SCR of NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub> is the surface mechanism [1,13]. With this in mind, in situ DRIFTS measurements were performed to reveal the influence of NH<sub>3</sub> addition on the partial oxidation of ethanol and on its further reaction with NO + O<sub>2</sub> over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub>, with the result shown in Fig. 7 A. After exposing the catalyst to C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> at 548 K for 60 min, strong peaks at 1633, 1409 and 1338 cm<sup>-1</sup> were clearly observed, which have been assigned to enolic species [21,31–33]. Over Ag/Al<sub>2</sub>O<sub>3</sub>, this surface species prefers to adsorb on or close to silver sites,



**Fig. 4.** NO<sub>x</sub> conversion (A), N<sub>2</sub> selectivity (B), and NH<sub>3</sub> yield (C) for the SCR of NO<sub>x</sub> over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> by different amount of C<sub>2</sub>H<sub>5</sub>OH. Conditions: NO 800 ppm, O<sub>2</sub> 10%, H<sub>2</sub>O 10%, N<sub>2</sub> balance, GHSV: 50,000 h<sup>-1</sup>.

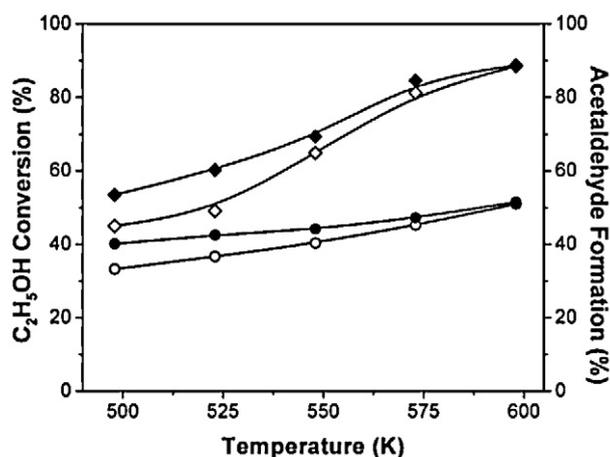
exhibiting an intimate contact with the active phase. Surface acetate also formed during this process, giving the characteristic frequencies at 1570 and 1466 cm<sup>-1</sup> [8,31,34]. Switching the feed gas to NH<sub>3</sub> + O<sub>2</sub> led to a gradual decrease in the intensity of enolic species, which was accompanied by the appearance of peaks at 2253 and 2233 cm<sup>-1</sup>. Many studies have been devoted to the assignment of these two peaks, which have been attributed to isocyanate species (–NCO) and play a crucial role in HC-SCR over Ag/Al<sub>2</sub>O<sub>3</sub> [1,13,35,36]. Meanwhile, it should be noted that the intensity of the acetate peaks hardly changed upon introduction of NH<sub>3</sub> + O<sub>2</sub>, indicating its lower reactivity. As proposed by Yan et al. [21] recently, the enolic species bound on or close to



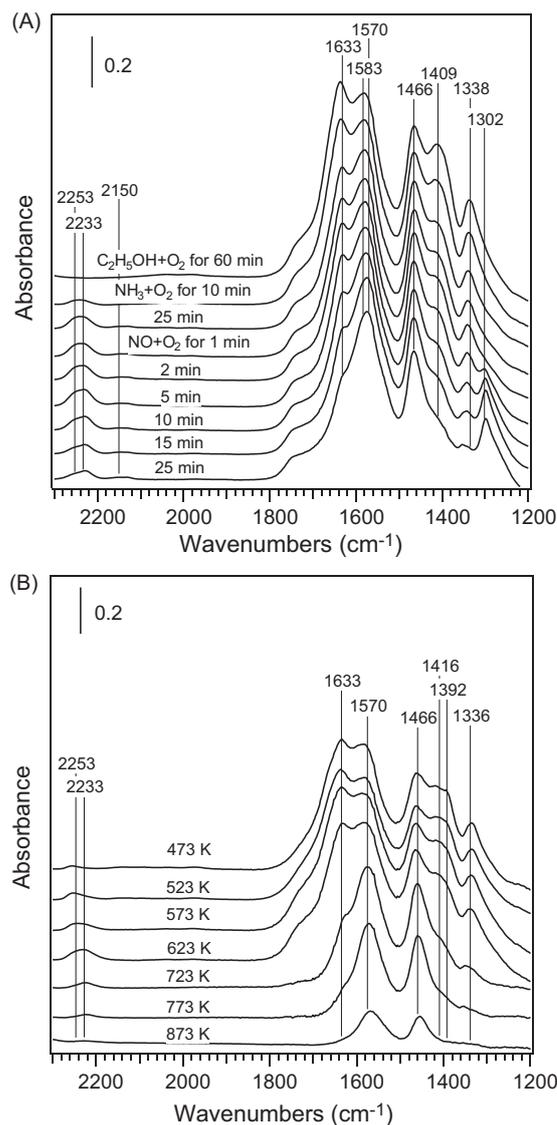
**Fig. 5.** The change of the concentration of nitrogen-containing gas composition in the outlet during the addition of 150 ppm NH<sub>3</sub> over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> at 548 K. Conditions: NO 800 ppm, O<sub>2</sub> 10%, H<sub>2</sub>O 10%, C<sub>2</sub>H<sub>5</sub>OH 1565 ppm, NH<sub>3</sub> 150 ppm (when added), N<sub>2</sub> balance, GHSV: 50,000 h<sup>-1</sup>.

Ag sites exhibits high activity for the formation of –NCO and thus contributes to the final product N<sub>2</sub> during the reduction of NO<sub>x</sub> by ethanol over Ag/Al<sub>2</sub>O<sub>3</sub>. Acetate, as another species originating from the partial oxidation of ethanol over Ag/Al<sub>2</sub>O<sub>3</sub>, prefers to interact with Al sites, resulting in a lower activity for –NCO formation. In the present study, the same situation was also observed when the two species were exposed to NH<sub>3</sub> + O<sub>2</sub>. In other words, the enolic species exhibits higher reactivity toward NH<sub>3</sub> + O<sub>2</sub> to form –NCO than acetate.

After 25 min, the gas flow was changed to NO + O<sub>2</sub>, leading to a further increase of the intensity of –NCO peaks, reaching its maximum after another 5 min, and then gradually decreasing to a much lower level than that before the introduction of NO + O<sub>2</sub>. At the same time, obvious significant consumption of enolic species was observed, contributing to the formation of –NCO. Finally, the intensity of –NCO peaks became weaker than that before the introduction of NO, indicating that the –NCO formed by NH<sub>3</sub> reacting with enolic species is also active for reaction with NO + O<sub>2</sub>. In addition, peaks assigned to nitrates were observed at 1583 and 1302 cm<sup>-1</sup> [31,37,38]. The appearance of a weak peak at around 2150 cm<sup>-1</sup> indicates the formation of a small amount of –CN species [1,12].



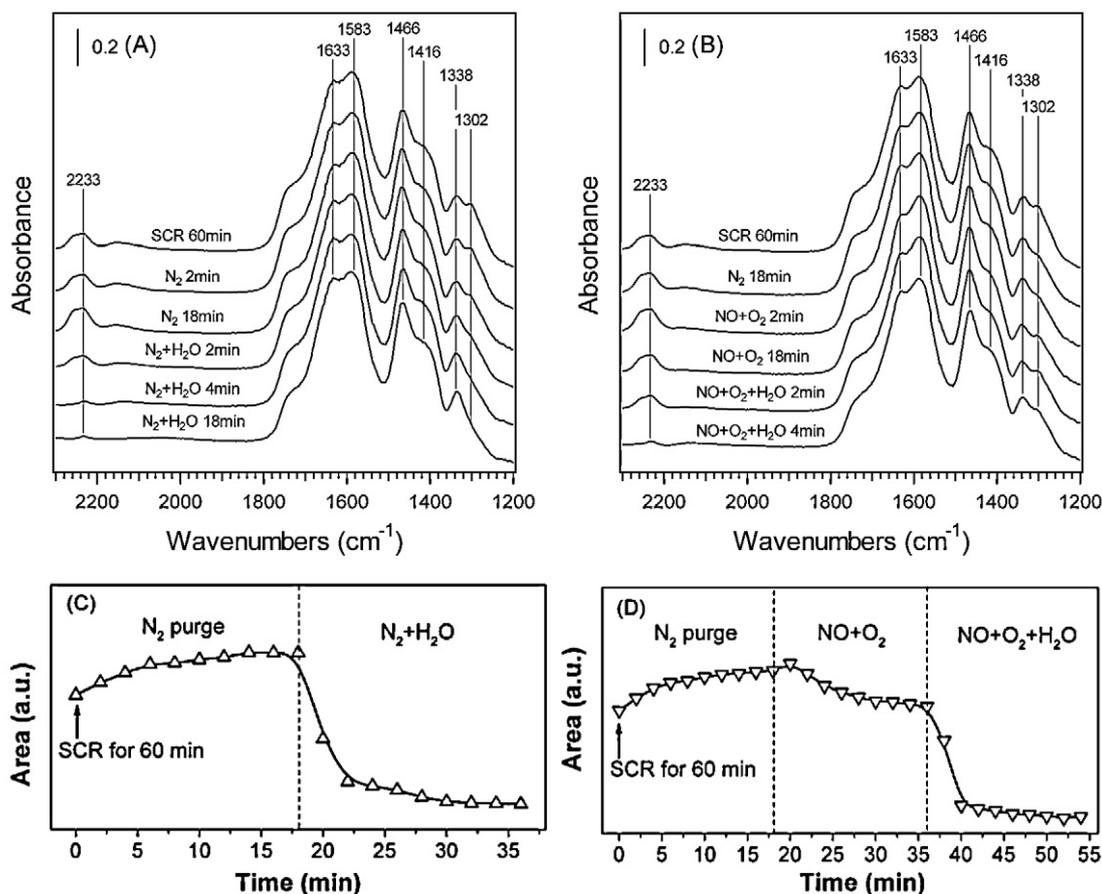
**Fig. 6.** The total conversions of ethanol (left axis) and the percentage of ethanol converted into acetaldehyde (right axis) in the presence of NH<sub>3</sub> (solid symbols) or in the absence of NH<sub>3</sub> (open symbols) over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub>. Conditions: NO 800 ppm, C<sub>2</sub>H<sub>5</sub>OH 1565 ppm, O<sub>2</sub> 10%, H<sub>2</sub>O 10%, NH<sub>3</sub> 150 ppm (when added), N<sub>2</sub> balance, GHSV: 50,000 h<sup>-1</sup>.



**Fig. 7.** Dynamic changes of in situ DRIFTS spectra over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 573 K (A). Before measurement, the catalyst was pre-exposed to a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> for 60 min at 673 K and subsequently exposed to a flow of NH<sub>3</sub> + O<sub>2</sub> for 25 min. In situ DRIFTS spectra of adsorbed species on 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> in steady states in a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> + NH<sub>3</sub> at different temperatures (B). Conditions: NO 800 ppm, C<sub>2</sub>H<sub>5</sub>OH 1565 ppm, NH<sub>3</sub> 150 ppm, O<sub>2</sub> 10%, N<sub>2</sub> balance.

Fig. 7B further shows the in situ DRIFTS spectra of 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> during the reaction of C<sub>2</sub>H<sub>5</sub>OH + NH<sub>3</sub> + O<sub>2</sub> at steady state within the temperature range of 473–873 K. Similar to our previous result in the absence of NH<sub>3</sub> [32,33], the enolic species was predominant within the low temperature range of 473–623 K, while acetate was dominant at temperatures above 623 K. In contrast, the peaks assignable to –NCO were observed over the whole temperature range during the partial oxidation of ethanol in the presence of NH<sub>3</sub>, indicating a critical role of NH<sub>3</sub> in –NCO formation in this case.

As identified in Fig. S2C, surface adsorbed species formed during the reduction of NO<sub>x</sub> by ethanol readily react with water to produce NH<sub>3</sub>. To reveal the species contributing to the formation of NH<sub>3</sub>, a similar experiment was performed by in situ DRIFTS (Fig. 8). After 60 min steady SCR reaction in a flow of C<sub>2</sub>H<sub>5</sub>OH + NO + O<sub>2</sub> at 548 K, the peak at 2233 cm<sup>-1</sup> ascribed to –NCO species was stabilized (Fig. 8A). The intensity of –NCO peaks exhibited a slight increment due to further transformation from enolic species during



**Fig. 8.** Dynamic changes of in situ DRIFTS spectra over 3 wt% Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in N<sub>2</sub> purging followed by exposure to water vapor balanced by N<sub>2</sub> (A) and N<sub>2</sub> purging followed by exposure to NO + O<sub>2</sub> and NO + O<sub>2</sub> + H<sub>2</sub>O in sequence (B) at 548 K; (C) and (D): time dependence of the corresponding integrated areas of the peaks of –NCO in the cases of (A), and (B), respectively. Before measurement, the catalyst was pre-exposed to a flow of C<sub>2</sub>H<sub>5</sub>OH + NO + O<sub>2</sub> for 60 min at 548 K. Conditions: NO 800 ppm, C<sub>2</sub>H<sub>5</sub>OH 1565 ppm, O<sub>2</sub> 10%, H<sub>2</sub>O 1%, N<sub>2</sub> balance.

N<sub>2</sub> purging for 18 min. Once 1% H<sub>2</sub>O was introduced, the peak area of –NCO species (Fig. 8C) was reduced sharply in 4 min, and almost disappeared in 10 min, certifying high activity of –NCO toward H<sub>2</sub>O. Actually, the consumption of –NCO in a feed of NO + O<sub>2</sub> + H<sub>2</sub>O was close to that of H<sub>2</sub>O carried by N<sub>2</sub> (Fig. 8B and D). This result indicates that the reaction rate of –NCO hydrolysis is much higher than that of the reaction between –NCO and NO + O<sub>2</sub> (or surface nitrates), which is in good agreement with the results of Bion et al. [12] and Tamm et al. [23].

### 3.5. NO<sub>x</sub> reduction by ethanol over Ag/Al<sub>2</sub>O<sub>3</sub> + Cu based catalyst

In consideration of the inactivity of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst for NH<sub>3</sub>-SCR, an additional oxidation catalyst might be needed to decrease NH<sub>3</sub> emission from the ethanol-SCR process. Previous studies revealed that Cu-based catalysts were active for selective catalytic oxidation (SCO) of NH<sub>3</sub> to produce N<sub>2</sub> [39]. With this in mind, a combination of Ag/Al<sub>2</sub>O<sub>3</sub> with Cu/TiO<sub>2</sub> (or Cu/Al<sub>2</sub>O<sub>3</sub>) was employed in NO<sub>x</sub> reduction by ethanol, giving 100% NO<sub>x</sub> conversion between 575 and 725 K. As shown in Fig. S4, the dual-bed system of Ag/Al<sub>2</sub>O<sub>3</sub> + Cu/TiO<sub>2</sub> decreased the NH<sub>3</sub> concentration from 165 ppm to 20 ppm at 700 K while the N<sub>2</sub> selectivity increased up to 96%, more effectively than Ag/Al<sub>2</sub>O<sub>3</sub> or the system of Ag/Al<sub>2</sub>O<sub>3</sub> + Cu/Al<sub>2</sub>O<sub>3</sub>. The above result is comparable to the results of He et al. [40] and other dual-bed systems, such as a combination of Ag/Al<sub>2</sub>O<sub>3</sub> and Cu-ZSM5 catalysts [28]. However, the combination of SCR and NH<sub>3</sub>-SCO catalysts could not completely eliminate

the NH<sub>3</sub> formed. Thus, more efforts are needed to eliminate the potential hazard of NH<sub>3</sub> emission.

## 4. Discussion

The Ag/Al<sub>2</sub>O<sub>3</sub> catalysts prepared using nordstrandite as a precursor of alumina exhibited excellent activity for reduction of NO<sub>x</sub> by ethanol. With a moderate silver loading (2–3 wt%), NO<sub>x</sub> conversion above 95% was obtained within a wide temperature window of 200 K. It has been widely accepted that the surface property of γ-Al<sub>2</sub>O<sub>3</sub> relating to hydroxyl groups (–OH) is fundamental in governing the dispersion of the supported active phases, and thus contributes to the reactivity of the final catalyst [41–43]. Nordstrandite, as one of the four aluminum trihydroxide (Al(OH)<sub>3</sub>) polymorphs, contains more abundant –OH groups than γ-Al<sub>2</sub>O<sub>3</sub>. With this in mind, it can be expected that an abundance of anchoring sites are available for dispersion of an active phase if nordstrandite is used as a precursor of the support. Such a feature may contribute to the high activity for NO<sub>x</sub> reduction of Ag/Al<sub>2</sub>O<sub>3</sub> prepared from nordstrandite in our research. Calcining the sample of nordstrandite results in the formation of γ-Al<sub>2</sub>O<sub>3</sub> (Fig. 1), the occurrence of which also results in an increase in the specific surface area (Table 1). This tendency is more noticeable when the samples with moderate silver loadings are calcined, possibly suggesting the formation of a strong interaction between silver species and the support during the phase transformation of the nordstrandite. Generally, a strong interaction of the active phase of silver

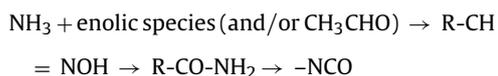
with the support is beneficial for HC-SCR of  $\text{NO}_x$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  [17,21,44].

During this process, however, the unexpected product of ammonia was formed, the amount of which varied with reaction conditions and silver loadings. A decrease of the concentration of ethanol employed significantly lowered the release of ammonia at the expense of  $\text{NO}_x$  conversion, although not enough to eliminate the  $\text{NH}_3$  production.

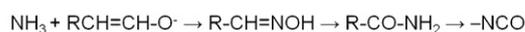
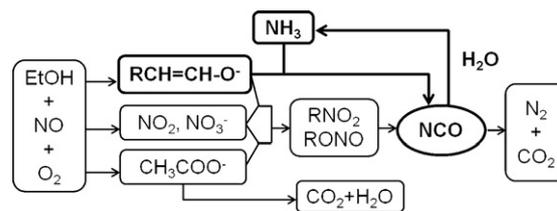
As confirmed by previous studies [12,35,45], the surface  $-\text{NCO}$  species possesses high reactivity toward  $\text{NO} + \text{O}_2$  to form  $\text{N}_2$ , and thus contributes to  $\text{NO}_x$  reduction by hydrocarbons and oxygenated hydrocarbons over  $\text{Ag}/\text{Al}_2\text{O}_3$ . This species also exhibits even much higher activity toward water vapor to produce  $\text{NH}_3$  [12,23]. The release of  $\text{NH}_3$  during ethanol-SCR in the presence of  $\text{H}_2\text{O}$  was mainly attributed to the hydrolysis of  $-\text{NCO}$  species over  $\text{Ag}/\text{Al}_2\text{O}_3$ , which has been identified by activity testing and FTIR analysis (Figs. 4 and 7). During ethanol-SCR over  $\text{Ag}/\text{Al}_2\text{O}_3$ , the final products of ethanol oxidation are  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . With this in mind, it is reasonable that, even in dry feed gas,  $\text{NH}_3$  was also produced during the ethanol-SCR (Fig. S2A).

As a reducing species of nitrogen,  $\text{NH}_3$  has been considered to have the potential to react with  $\text{NO}_x$  to produce  $\text{N}_2$  during HC-SCR over  $\text{Ag}/\text{Al}_2\text{O}_3$ , following the mechanism of  $\text{NH}_3$ -SCR [18,28,46]. By adding  $\text{NH}_3$  into the feed gas of ethanol-SCR over  $\text{Ag}/\text{Al}_2\text{O}_3$  (Fig. 5), however, the consumption of  $\text{NO}$  was much lower than that of  $\text{NO}_2$ , which is not in agreement with the theoretical value based on the typical  $\text{NH}_3$ -SCR processes, strongly suggesting the occurrence of a reaction pathway quite different to that of  $\text{NH}_3$ -SCR. Further evidence can be found when  $\text{NH}_3$  served as a reductant: the fed  $\text{NO}_x$  was mainly converted to  $\text{N}_2\text{O}$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  (Fig. S3B), significantly different from ethanol-SCR. During ethanol-SCR over 3 wt%  $\text{Ag}/\text{Al}_2\text{O}_3$  (Fig. S1), meanwhile, the co-existence of  $\text{NO}$  and  $\text{NH}_3$  was observed at temperatures above 673 K. Moreover, at temperatures below 573 K,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{NH}_3$  are all present in the outlet gas, and their concentrations meet the requirement for fast-SCR [47,48]. The above results further demonstrated the inactivity of  $\text{Ag}/\text{Al}_2\text{O}_3$  for the  $\text{NH}_3$ -SCR reaction.

Interestingly, the presence of  $\text{NH}_3$  enhanced the partial oxidation of ethanol over  $\text{Ag}/\text{Al}_2\text{O}_3$  (Fig. 6), particularly at the light-off temperature for the ethanol-SCR reaction. As a result, a higher concentration of  $\text{CH}_3\text{CHO}$  was measured in the gas phase. During the hydrocarbon oxidation, the produced  $\text{CH}_3\text{CHO}$  readily isomerizes to ethanol [49]. On the  $\text{Ag}/\text{Al}_2\text{O}_3$  surface,  $\text{CH}_3\text{CHO}$  may mainly be present as enolic species, by isomerization to enol and then hydrogen extraction [46]. In organic synthesis, it is well known that aldehydes and their isomers of enols easily react with ammonia to produce oxime, giving a structure of  $-\text{CH}=\text{N}(\text{OH})$ , which possibly occurs on the surface of  $\text{Ag}/\text{Al}_2\text{O}_3$  during the ethanol-SCR. The oxime then transforms to amide via Beckmann rearrangement, from which  $-\text{NCO}$  species can be produced by dehydrogenation [8,46,50]. Further in situ DRIFTS results presented here reveal that  $\text{NH}_3$  can react with surface enolic species to form  $-\text{NCO}$  species (Fig. 7), the reaction pathway of which can be proposed as follows:



Based on all the observations presented in this study and available literature reports, plausible reaction pathways for ethanol-SCR over  $\text{Ag}/\text{Al}_2\text{O}_3$  are proposed, as shown in Scheme 1. In a typical reaction process, partial oxidation of ethanol results in the formation of enolic species and acetate. The surface enolic species can react with  $\text{NO} + \text{O}_2$  and/or  $\text{NO}$  to produce  $-\text{NCO}$  species, possibly via the formation of organic nitroso and nitro compounds. Further reaction between  $-\text{NCO}$  and  $\text{NO} + \text{O}_2$  results in the formation of the final product of  $\text{N}_2$ . The acetate also participates in this process, while



Scheme 1. The mechanism of the SCR of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  over  $\text{Ag}/\text{Al}_2\text{O}_3$ .

its lower activity toward  $\text{NO} + \text{O}_2$  (and/or  $\text{NO}$ ) results in its minor role in  $-\text{NCO}$  formation, and thus in the  $\text{NO}_x$  reduction process.

Water vapor is inevitably present in the ethanol-SCR system, by addition and/or as produced from the oxidation of ethanol over  $\text{Ag}/\text{Al}_2\text{O}_3$ . On the surface of  $\text{Ag}/\text{Al}_2\text{O}_3$ , water vapor triggers the hydrolysis of  $-\text{NCO}$  species to produce  $\text{NH}_3$ , the latter of which in turn can react with enolic species to form  $-\text{NCO}$ , providing a new and cyclic pathway during the  $\text{NO}_x$  reduction by ethanol.

If compared with the reaction of  $-\text{NCO}$  with  $\text{NO} + \text{O}_2$  and with water vapor over  $\text{Ag}/\text{Al}_2\text{O}_3$ , we can estimate that the reaction rate of the latter is much higher than that of the former. Such a high reaction rate of  $-\text{NCO}$  hydrolysis may result in a significant decrease in  $\text{N}_2$  selectivity for ethanol-SCR over  $\text{Ag}/\text{Al}_2\text{O}_3$ . However, as shown in Fig. S2B, the practical  $\text{N}_2$  selectivity during  $\text{NO}_x$  reduction by ethanol does not decrease so much, which in turn demonstrates the crucial role of  $\text{NH}_3$  in  $\text{NO}_x$  reduction by cyclic reaction with enolic species. Yet, it should be pointed out that it is difficult to do accurate measurements on the contribution of  $\text{NH}_3$  for  $\text{NO}_x$  reduction by ethanol, with consideration of the following facts. The fact that  $\text{NH}_3$  was still released even in ethanol-SCR with dry feed gas, indicates that it is hard to create reaction conditions without the formation of  $\text{NH}_3$ . In the absence of  $\text{NO}_x$ , the contribution of  $\text{NH}_3$  to the partial oxidation of ethanol is limited, while this contribution will be prompted in the presence of  $\text{NO}_x$ .

## 5. Conclusions

Ammonia was inevitably produced over  $\text{Ag}/\text{Al}_2\text{O}_3$  catalysts during the SCR of  $\text{NO}_x$  by ethanol, the release of which derived from the high reaction rate of  $-\text{NCO}$  hydrolysis. Ammonia also participates in  $\text{NO}_x$  reduction during ethanol-SCR while it cannot be accounted for by the typical  $\text{NH}_3$ -SCR process. Ammonia originating from the hydrolysis of  $-\text{NCO}$  species can in turn react with enolic species, to produce  $-\text{NCO}$ . The reaction between ammonia and enolic species thus creates a cyclic pathway for  $\text{NO}_x$  reduction by ethanol, which may guarantee the high efficiency of the ethanol-SCR system.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.01.048>.

## References

- [1] R. Burch, J.P. Breen, F.C. Meunier, *Appl. Catal. B* 39 (2002) 283.
- [2] M.A. Gómez-García, V. Pitchon, A. Kiennemann, *Environ. Int.* 31 (2005) 445.
- [3] Z. Liu, S. Ihl Woo, *Catal. Rev.* 48 (2006) 43.
- [4] S. Roy, M.S. Hegde, G. Madras, *Appl. Energy* 86 (2009) 2283.
- [5] P. Granger, V.I. Parvulescu, *Chem. Rev.* 111 (2011) 3155.
- [6] F. Poignant, J.L. Freysz, M. Daturi, J. Saussey, *Catal. Today* 70 (2001) 197.
- [7] K. Sato, T. Yoshinari, Y. Kintaichi, M. Haneda, H. Hamada, *Appl. Catal. B* 44 (2003) 67.
- [8] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, *J. Catal.* 187 (1999) 493.
- [9] J. Li, J. Hao, L. Fu, T. Zhu, Z. Liu, X. Cui, *Appl. Catal. A* 265 (2004) 43.
- [10] Y. Ukisu, T. Miyadera, A. Abe, K. Yoshida, *Catal. Lett.* 39 (1996) 265.
- [11] K.A. Bethke, H.H. Kung, *J. Catal.* 172 (1997) 93.
- [12] N. Bion, J. Saussey, M. Haneda, M. Daturi, *J. Catal.* 217 (2003) 47.
- [13] H. He, Y.B. Yu, *Catal. Today* 100 (2005) 37.
- [14] K.-I. Shimizu, A. Satsuma, *Phys. Chem. Chem. Phys.* 8 (2006) 2677.
- [15] Y.B. Yu, X.P. Song, H. He, *J. Catal.* 271 (2010) 343.
- [16] V.I. Pârvulescu, B. Cojocaru, V. Pârvulescu, R. Richards, Z. Li, C. Cadigan, P. Granger, P. Miquel, C. Hardacre, *J. Catal.* 272 (2010) 92.
- [17] X. She, M. Flytzani-Stephanopoulos, *J. Catal.* 237 (2006) 79.
- [18] T. Miyadera, *Appl. Catal. B* 16 (1998) 155.
- [19] T. Miyadera, *Appl. Catal. B* 13 (1997) 157.
- [20] F. Can, A. Flura, X. Courtois, S. Royer, G. Blanchard, P. Marecot, D. Duprez, *Catal. Today* 164 (2011) 474.
- [21] Y. Yan, Y.B. Yu, H. He, J.J. Zhao, *J. Catal.* 293 (2012) 13.
- [22] M.L. Unland, *J. Phys. Chem.* 77 (1973) 1952.
- [23] S. Tamm, H.H. Ingelsten, A.E.C. Palmqvist, *J. Catal.* 255 (2008) 304.
- [24] M. Richter, R. Fricke, R. Eckelt, *Catal. Lett.* 94 (2004) 115.
- [25] E.V. Kondratenko, V.A. Kondratenko, M. Richter, R. Fricke, *J. Catal.* 239 (2006) 23.
- [26] R.A.V. Nordstrand, W.P. Hettinger, C.D. Keith, *Nature* 177 (1956) 713.
- [27] J.H. Lee, S.J. Schmiege, S.H. Oh, *Appl. Catal. A* 342 (2008) 78.
- [28] M.K. Kim, P.S. Kim, J.H. Baik, I.-S. Nam, B.K. Cho, S.H. Oh, *Appl. Catal. B* 105 (2011) 1.
- [29] K.-I. Shimizu, A. Satsuma, *Appl. Catal. B* 77 (2007) 202.
- [30] P.G. Savva, C.N. Costa, *Catal. Rev.* 53 (2011) 91.
- [31] Y.B. Yu, H. He, Q.C. Feng, H.W. Gao, X. Yang, *Appl. Catal. B* 49 (2004) 159.
- [32] Y.B. Yu, H.W. Gao, H. He, *Catal. Today* 93–95 (2004) 805.
- [33] Y.B. Yu, H. He, Q.C. Feng, *J. Phys. Chem. B* 107 (2003) 13090.
- [34] K.-I. Shimizu, J. Shibata, H. Yoshida, A. Satsuma, T. Hattori, *Appl. Catal. B* 30 (2001) 151.
- [35] S. Chansai, R. Burch, C. Hardacre, J. Breen, F. Meunier, *J. Catal.* 276 (2010) 49.
- [36] S. Chansai, R. Burch, C. Hardacre, J. Breen, F. Meunier, *J. Catal.* 281 (2011) 98.
- [37] S. Kameoka, Y. Ukisu, T. Miyadera, *Phys. Chem. Chem. Phys.* 2 (2000) 367.
- [38] K.-I. Shimizu, A. Satsuma, T. Hattori, *Appl. Catal. B* 25 (2000) 239.
- [39] X.P. Song, C.B. Zhang, H. He, *Chin. J. Catal.* 29 (2008) 524.
- [40] S. He, C. Zhang, M. Yang, Y. Zhang, W. Xu, N. Cao, H. He, *Sep. Purif. Technol.* 58 (2007) 173.
- [41] C. Morterra, G. Magnacca, *Catal. Today* 27 (1996) 497.
- [42] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, *J. Catal.* 226 (2004) 54.
- [43] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, *J. Catal.* 211 (2002) 1.
- [44] R. Zhang, S. Kaliaguine, *Appl. Catal. B* 78 (2008) 275.
- [45] F. Thibault-Starzyk, E. Seguin, S. Thomas, M. Daturi, H. Arnolds, D.A. King, *Science* 324 (2009) 1048.
- [46] P.S. Kim, M.K. Kim, B.K. Cho, I.-S. Nam, *J. Catal.* 292 (2012) 44.
- [47] M. Koebel, G. Madia, F. Raimondi, A. Wokaun, *J. Catal.* 209 (2002) 159.
- [48] E. Tronconi, I. Nova, C. Ciardelli, D. Chatterjee, M. Weibel, *J. Catal.* 245 (2007) 1.
- [49] C.A. Taatjes, N. Hansen, A. McIlroy, J.A. Miller, J.P. Senosiain, S.J. Klippenstein, F. Qi, L.S. Sheng, Y.W. Zhang, T.A. Cool, J. Wang, P.R. Westmoreland, M.E. Law, T. Kasper, K. Kohse-Hoinghaus, *Science* 308 (2005) 1887.
- [50] E. Joubert, X. Courtois, P. Marecot, C. Canaff, D. Duprez, *J. Catal.* 243 (2006) 252.