

Mechanism of the H₂ Effect on NH₃-Selective Catalytic Reduction over Ag/Al₂O₃: Kinetic and Diffuse Reflectance Infrared Fourier Transform Spectroscopy Studies

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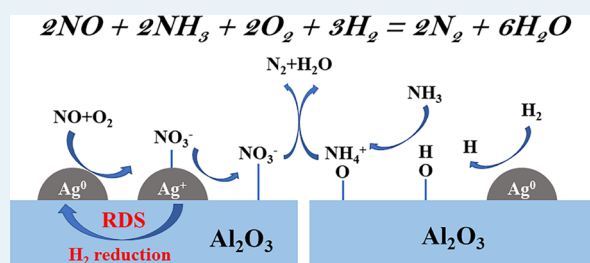
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Supporting Information

ABSTRACT: The mechanism of H₂-assisted NH₃-selective catalytic reduction (SCR) over Ag/Al₂O₃ was systematically investigated by kinetic measurements and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). H₂ was an essential reactant for the NH₃-SCR reaction over Ag/Al₂O₃, and the overall chemical reaction equation for this reaction was as follows: $2\text{NO} + 2\text{NH}_3 + 2\text{O}_2 + 3\text{H}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$. Kinetic studies indicated that this reaction obeyed the Langmuir–Hinshelwood mechanism, such that both NO and NH₃ adsorbed on the Ag/Al₂O₃ surface before their further reaction. In situ DRIFTS experiments showed that Ag species catalytically oxidized NO to yield nitrate species, which further migrated to the Al₂O₃ surface. Then, the bridging and bidentate nitrates reacted with the B_{NH3} species to produce N₂ and H₂O. Afterward, the –OH species consumed by the adsorption of B_{NH3} species were restored by H₂ dissociation on the metallic Ag species. Notably, the rate-determining step in the H₂-NH₃-SCR reaction was the reduction of oxidized Ag species, which further governed the formation of nitrate species. The reduction of NO_x primarily occurred at the surface of Al₂O₃, while Ag species and H₂ contributed to the oxidation of NO to generate nitrates and to the regeneration of –OH species.

KEYWORDS: NO_x, NH₃-SCR, H₂, Ag/Al₂O₃, reaction mechanism



1. INTRODUCTION

NO_x emissions from diesel vehicles can induce serious environmental problems such as acid rain, photochemical smog, and haze.^{1,2} To cope with the increasingly serious problems, the exhaust aftertreatment system is required to work efficiently at low temperatures below 200–250 °C. For NO_x removal from diesel vehicles, selective catalytic reduction (SCR) of NO_x by ammonia (NH₃-SCR) is the leading technology.^{3,4} Compared with NH₃-SCR, hydrocarbon (HC)-SCR technology exhibits unique advantages by utilizing on-board diesel or its additives as reductants and has thus been widely investigated.^{1,2} The alumina-supported silver catalyst (Ag/Al₂O₃) is generally recognized as one of the most promising catalysts for HC-SCR.¹ Furthermore, a small amount of H₂ addition significantly improves the catalytic activity of Ag/Al₂O₃ during HC-SCR, especially in low-temperature regions.^{5,6} During the NH₃-SCR, unexpectedly, H₂ addition was also found to greatly improve the deNO_x activity of Ag/Al₂O₃, which is almost inactive for this reaction in the absence of H₂.⁷ The H₂-assisted NH₃-SCR system (H₂-

NH₃-SCR) exhibited high efficiency for NO_x removal and achieved 100% NO_x conversion at a low temperature of 200 °C.⁷ Recent engine bench tests also revealed that this system exhibited moderate efficiency for NO_x removal even under very demanding practical conditions.⁸ Besides, since high concentrations of H₂ (~1000 ppm) and NH₃ (~200 ppm) were produced in ethanol-SCR on Ag/Al₂O₃,^{9,10} the H₂-NH₃-SCR reaction would also occur in the ethanol-SCR, thus contributing to a conjugated SCR system.

Since Richter et al.⁷ first found the unusual enhancement effect of H₂ on the NH₃-SCR over Ag/Al₂O₃, several groups^{8,11–23} have been working on this highly efficient catalytic system. Kondratenko et al.^{11,14} employed a transient isotopic approach and temporal analysis of products (TAP) reactor to investigate the effect of H₂ on the formation of N₂ during NH₃-SCR over Ag/Al₂O₃. They proposed that H₂

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contributed to the reduction of oxidized silver and that N_2 was yielded via direct or O_2 -induced decomposition of surface NH_2NO species. Shimizu et al.^{12,13} investigated the mechanism of H_2 - NH_3 -SCR by kinetic and spectroscopic methods and found that H_2 addition increased the relative amounts of Ag clusters and superoxide ion. They further proposed that Ag clusters were the active species for NO_x reduction and that superoxide ion was important for the activation of NH_3 . Doronkin et al.¹⁵ found that both Ag and Al_2O_3 were necessary components for the H_2 - NH_3 -SCR reaction, and they further proposed a "fast SCR"-like mechanism. Olsson et al.¹⁹ investigated the influence of gas composition on NO_x reduction during the above reaction and suggested that the global stoichiometry between $NO:NH_3:H_2$ was equal to 1:1:2. In addition, they found that H_2 promoted the transformation of nitrites and bidentate nitrate to monodentate and bridging nitrates over Al_2O_3 .²⁰ Besides, some groups investigated the sulfur tolerance of this catalytic system, which is an important factor in its practical applications.^{16,17,21}

According to the above literature, it was found that H_2 addition reduced the Ag^+ ion and increased the amount of $Ag_n^{\delta+}$ clusters, which might contribute to the reductive activation of molecular O_2 and thus improve the NO_x reduction. However, the complete mechanism of the H_2 - NH_3 -SCR reaction remains unclear, especially the rate-determining step (RDS) of this reaction. In addition, the roles of different intermediates such as nitrates and surface ammonia species have been barely investigated. Besides, the different roles of Ag and Al_2O_3 in the H_2 - NH_3 -SCR have not been totally confirmed. In the present work, the reaction mechanism of H_2 -assisted NH_3 -SCR over Ag/Al_2O_3 was systematically investigated by kinetic studies and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements. It was found that this reaction followed the Langmuir–Hinshelwood (L–H) mechanism, and the rate-determining step involved the reduction of oxidized silver species by H_2 . This study offers new insight into the mechanism of H_2 - NH_3 -SCR over Ag/Al_2O_3 and provides some advice for the design of highly efficient catalytic systems.

2. EXPERIMENTAL SECTION

Al_2O_3 and 2 wt % Ag/Al_2O_3 were prepared by an impregnation method, with boehmite (SASOL, SB-1) and silver nitrate as the precursors.^{9,24,25} These samples were further dried at 100 °C over night and calcined at 600 °C for 3 h. The catalytic activity was measured in a fixed-bed reactor (6 mm i.d.) with a 150 mg sample. The typical reaction gas consisted of 500 ppm NO (or NO_2), 520 ppm NH_3 , 1500 ppm H_2 , and 5% O_2 in N_2 balance. The total flow was 500 mL/min, which corresponded to a GHSV of 150,000 h^{-1} . The reactants and products including NO, NH_3 , NO_2 , N_2O were detected by an FTIR spectrometer (Nicolet iS 10). The conversions of NO_x and NH_3 were calculated based on the equations below (eqs 1 and 2).

$$NO_x \text{ conversion} = \frac{[NO + NO_2]_{in} - [NO + NO_2]_{out}}{[NO + NO_2]_{in}} \times 100\% \quad (1)$$

$$NH_3 \text{ conversion} = \frac{[NH_3]_{in} - [NH_3]_{out}}{[NH_3]_{in}} \times 100\% \quad (2)$$

The kinetic studies were carried out in the above fixed-bed reactor. The conversions of NO_x and NH_3 were kept below 30% by changing the amount of sample. To eliminate the effects of internal and external diffusion, a set of experiments were performed (Figure S1). Afterward, experiments were performed at a flow rate of 500 mL/min using samples of 40–60 mesh. Then, the reaction rate ($-R_{NO_x}$) was calculated based on the equation below (eq 3).

$$-R_{NO_x} (\text{mol/g/s}) = F_{NO_x} \times X_{NO_x} / W \quad (3)$$

where F_{NO_x} and X_{NO_x} represent the molar flow rate (mol/s) and NO_x conversion (%), respectively, and W is the sample weight. The Arrhenius plots for NO_x conversion were drawn according to the above results. Afterward, the activation energies of NO_x reduction were calculated based on the Arrhenius plots. Besides, the kinetic experiments have been repeated to ensure the reliability of the kinetic results.

In situ DRIFTS experiments were carried out on an FTIR spectrometer (Nicolet iS 50) as described in our previous works.^{9,24,25} The spectra were collected with an accumulation of 100 scans at a resolution of 4 cm^{-1} . Before measurements, the sample was pretreated in 5% O_2/N_2 (200 mL/min) at 350 °C for 0.5 h. The typical reaction gas was the same as that in the activity tests. UV–vis measurements were performed on a UV–vis spectrophotometer (LAMBDA 650, PerkinElmer) with barium sulfate as a reference with a resolution of 1 nm.

3. RESULTS AND DISCUSSION

3.1. Catalytic Studies. The effect of H_2 on the catalytic activity of Ag/Al_2O_3 during NH_3 -SCR was investigated (Figure 1). In the absence of H_2 , Ag/Al_2O_3 was completely inactive for

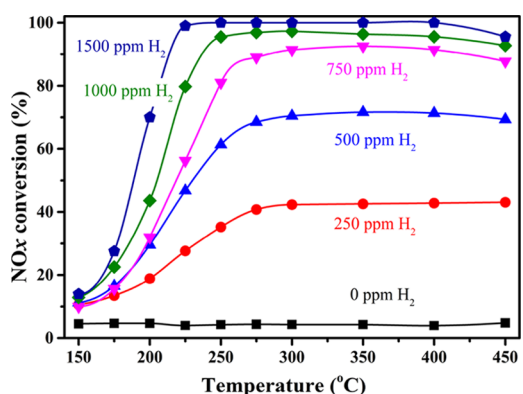


Figure 1. NO_x conversion over Ag/Al_2O_3 during H_2 -assisted NH_3 -SCR with various amounts of H_2 . Feed composition: 500 ppm NO, 520 ppm NH_3 , 0–1500 ppm H_2 , 5% O_2 , N_2 balance, and GHSV of 150,000 h^{-1} .

NO_x reduction during the NH_3 -SCR, which is in good agreement with the literature.^{7,13} On the contrary, H_2 addition greatly boosted the NO_x reduction over Ag/Al_2O_3 , and the NO_x conversion was quantitatively governed by the H_2 concentration. In addition, the NO_x conversion gradually increased as the reaction temperature increased from 150 to 300 °C and then remained constant as the temperature was further raised to 450 °C. The increase in NO_x conversion at low temperatures could be attributed to the light-off of H_2 , which was confirmed by the work of Olsson.¹⁹ More importantly, the constant NO_x conversion at high temperatures

revealed that NO_x reduction was governed by the H_2 concentration. In particular, the addition of 750 ppm H_2 increased the NO_x conversion to $\sim 92\%$ at temperatures above 300°C , while the incomplete reduction of NO_x might be due to nonselective oxidation of H_2 . The global stoichiometry between $\text{NO}:\text{NH}_3:\text{H}_2$ was approximately equal to 1:1:1.5, while further increasing the H_2 concentration helps to completely reduce NO_x .

The NH_3 conversion (Figure S2) exhibited the same trend as the NO_x conversion. The yield of N_2O was negligible over the whole temperature range and H_2 addition further inhibited its formation, consistent with the previous literature.^{11,14} Furthermore, the experiment of $\text{H}_2\text{-NH}_3\text{-SCR}$ with 2% H_2O was also performed over the $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts (Figure S3). The NO_x conversions were substantially the same as that in the absence of H_2O , revealing that H_2O had negligible influence on the total reaction over this catalyst. Besides, this catalytic system exhibited high efficiency for NO_x reduction at a high GHSV of $450,000\text{ h}^{-1}$ (Figure S4), which is beneficial for its practical applications. In contrast, Al_2O_3 was completely inactive for NO_x reduction with the coexistence of H_2 (Figure S5), revealing that the Ag species was a necessary component for NO_x reduction.

As NO_2 has been proposed as an important reactant for the $\text{NH}_3\text{-SCR}$ over $\text{Ag}/\text{Al}_2\text{O}_3$,^{15,22} the effect of H_2 addition on the NO oxidation to yield NO_2 was investigated (Figure 2A). Without the coexistence of H_2 , $\text{Ag}/\text{Al}_2\text{O}_3$ was inactive for the

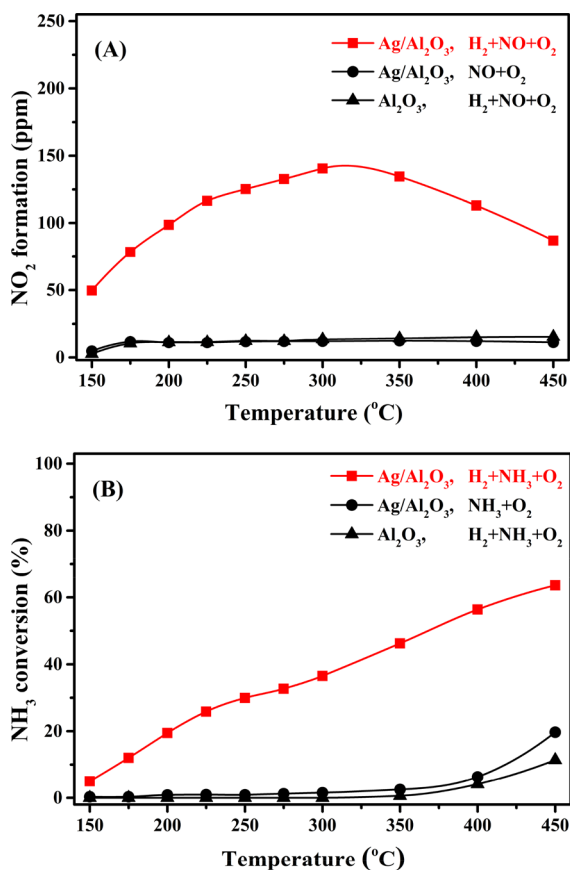


Figure 2. Effect of H_2 on (A) the oxidation of NO to yield NO_2 and (B) the oxidation of NH_3 over $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 . Typical feed composition: 500 ppm NO , 500 ppm NH_3 , 1500 ppm H_2 , 5% O_2 , N_2 balance, and GHSV of $150,000\text{ h}^{-1}$.

oxidation of $\text{NO} + \text{O}_2$ to yield NO_2 , while H_2 addition significantly boosted this reaction. The increase in NO_2 formation from 150 to 300°C could be attributed to the light-off of H_2 , while the decrease in NO_2 formation from 300 to 450°C might be due to the thermodynamic equilibrium between NO and NO_2 .¹ In contrast, Al_2O_3 was completely inactive for NO oxidation even in the presence of H_2 , revealing that the Ag species was critical for NO oxidation.

Considering that the activation of NH_3 has been suggested as an important step during the $\text{NH}_3\text{-SCR}$,^{3,4} the effect of H_2 addition on the oxidation of NH_3 was studied (Figure 2B). Similarly, $\text{Ag}/\text{Al}_2\text{O}_3$ was almost inactive for NH_3 oxidation in the absence of H_2 , while H_2 addition significantly enhanced the activation of NH_3 over the whole temperature range. The selectivity of N_2 was approximately equal to 85–95% with only a small amount of N_2O yielded (not shown). In contrast, Al_2O_3 was completely inactive for NH_3 oxidation with the coexistence of H_2 . Apparently, the Ag species was the essential component for the activation of NH_3 in the presence of H_2 .

Afterward, the different effects of NO and NO_2 on NO_x reduction during $\text{NH}_3\text{-SCR}$ were investigated (Figure 3). It

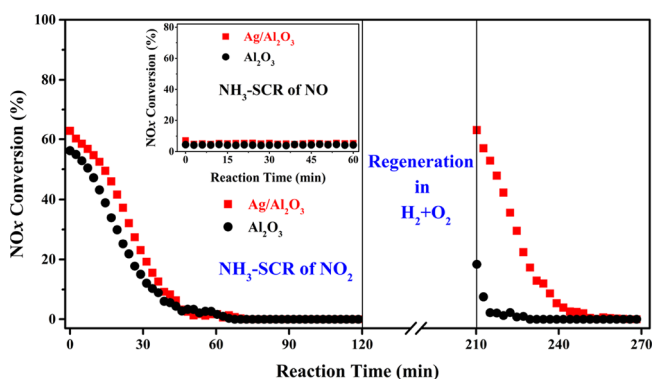


Figure 3. NO_x conversion over $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 during $\text{NH}_3\text{-SCR}$ of NO_2 or NO (inset figure) at 200°C . The regeneration was performed in $\text{H}_2 + \text{O}_2$ for 60 min followed by N_2 for 30 min. Feed composition: 500 ppm NO (or NO_2), 500 ppm NH_3 , 1500 ppm H_2 (when used), 5% O_2 , N_2 balance, and GHSV of $150,000\text{ h}^{-1}$.

was found that NO could not be reduced on either $\text{Ag}/\text{Al}_2\text{O}_3$ or Al_2O_3 during the above reaction in the absence of H_2 . In contrast, NO_2 could be reduced on both samples at the beginning of this reaction, although the NO_x conversion gradually decreased from ~ 60 to $\sim 5\%$ within 45 min. It should be highlighted that the NO_x conversions on $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 were approximately equal, indicating that NO_x reduction possibly occurred at the surface of Al_2O_3 . Besides, the amount of NO_2 adsorbed on these samples in a flow of $\text{NO}_2 + \text{O}_2$ (not shown) was much less than that in $\text{NO}_2 + \text{NH}_3 + \text{O}_2$, revealing that NO_x were reduced to N_2 rather than being adsorbed in the above SCR reaction. Furthermore, NO was detected in the effluent gas after the adsorption of NO_2 , indicating the occurrence of a disproportionation reaction. After complete inactivation, these samples were regenerated in $\text{H}_2 + \text{O}_2$ for 60 min followed by N_2 purge for 30 min. Interestingly, the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst was almost completely regenerated during this process, and the NO_x conversion curve exhibited the same trend as that on the fresh sample. Still, the activity of Al_2O_3 for NO_x reduction was hardly recovered during the above process, indicating that the Ag species was an essential component for the regeneration of $\text{Ag}/\text{Al}_2\text{O}_3$. In some sense, the above

reaction over Ag/Al₂O₃ could be considered as two procedures in which the reaction between NO₂ and NH₃ resulted in the deactivation of Al₂O₃, and H₂ + O₂ restored this sample with the assistance of Ag species.

It was reported that Al₂O₃ and Ag/Al₂O₃ facilitated the reduction of NO + NO₂ mixtures in the absence of H₂ via a “fast SCR”-like mechanism.¹⁵ In the present work, however, it was found that Ag/Al₂O₃ could not catalytically reduce NO_x during the fast NH₃-SCR reaction, especially at low temperatures (Figure S6A). Instead, the Ag/Al₂O₃ catalyst was gradually deactivated in this experiment, with the NO_x conversion gradually decreased from 49 to 4% within 3 h (Figure S6B), which was similar to that seen in Figure 3. Considering that the catalytic measurements in the earlier work were performed while changing the temperature from 400 to 150 °C at a rate of 2 °C/min with a total time of 125 min,¹⁵ it is cautiously speculated that those catalysts were efficient for NO_x reduction at the beginning of the experiment and then gradually deactivated throughout the process.

3.2. Kinetic Studies. Kinetic measurements were carried out to study the reaction mechanism of H₂-NH₃-SCR over Ag/Al₂O₃. As shown in Figure 4, the reaction orders for NO_x

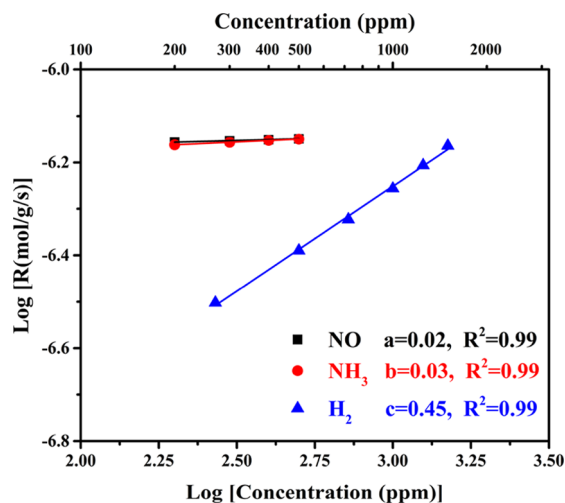


Figure 4. Reaction rates of NO_x conversion as a function of NO (solid square), NH₃ (red solid circle), and H₂ (blue solid triangle) concentrations over Ag/Al₂O₃ at 200 °C. Typical feed composition: 500 ppm NO, 500 ppm NH₃, 1500 ppm H₂, 5% O₂, N₂ balance, and GHSV of 300,000 h⁻¹.

reduction were zero for both NO and NH₃, indicating that this reaction obeyed the Langmuir–Hinshelwood mechanism (L–H mechanism), with both NO and NH₃ adsorbed on the Ag/Al₂O₃ surface before their further reaction. In contrast, the reaction order of H₂ was 0.45, revealing that the reduction rate of NO_x was quantitatively governed by the H₂ concentration. Since O₂ used in this experiment was in considerable excess, the reaction order for O₂ was not measured. Therefore, the reaction rate for NO_x reduction could be presented using the following power-law model (eq 4), where *k* is the apparent rate constant.

$$-R_{\text{NO}_x} = k \times [\text{H}_2]^{1/2} \quad (4)$$

The activation energies for NO oxidation and NO_x reduction were also measured (Figure 5). In a flow of H₂ + NO + O₂, the activation energy for NO oxidation to yield NO₂

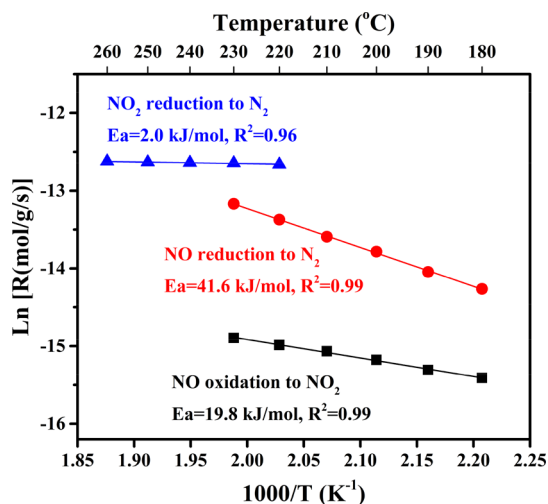


Figure 5. Arrhenius plots for the rate of NO_x reduction or NO oxidation over Ag/Al₂O₃ in different conditions: H₂ + NO + O₂ (solid square), H₂-NH₃-SCR of NO (red solid circle), H₂-NH₃-SCR of NO₂ (blue solid triangle). Feed composition: 500 ppm NO (or NO₂), 500 ppm NH₃, 1500 ppm H₂, 5% O₂, and N₂ balance.

was 19.8 kJ/mol, while the reaction rate was relatively low. Since the formation of NO₂ from NO at this temperature is thermodynamically favorable,²⁶ the reaction rate of NO oxidation was mainly controlled by kinetics, especially in this kinetic experiment where the NO conversion was kept below 15%. During the H₂-NH₃-SCR, the activation energy for NO reduction to produce N₂ was 41.6 kJ/mol, which was consistent with the result of Shimizu.¹² It should be highlighted that the reaction rate for NO_x reduction was much higher than the oxidation of NO to yield NO₂. When using NO₂ as reactant, notably, the reaction rate for NO_x reduction was extremely high, and the activation energy was as low as 2 kJ/mol. Therefore, the formation of NO₂ boosted by H₂ addition was beneficial for NO_x reduction during the H₂-NH₃-SCR. Nevertheless, as the oxidation of NO to produce NO₂ was much slower than the NO_x reduction, the formation of NO₂ and its further reaction with NH₃ should not be the main pathway for NO_x reduction.

Shimizu et al.¹² have also investigated the influence of the concentration of reactants on the NO_x reduction during H₂-NH₃-SCR. They found that increasing the concentrations of H₂, NO, NH₃, and O₂ could enhance the reduction of NO_x over Ag/Al₂O₃. It should be noted that a large amount of H₂ (1%) was used in that work, which was 10 times the NO concentration. As mentioned above, the H₂ concentration exhibited a critical effect on the NO_x reduction rate during the NH₃-SCR. Hence, having an excess of H₂ could greatly accelerate the rate-determining step as well as the overall reaction rate for NO_x reduction and even change the rate-determining step of that reaction.

3.3. In Situ DRIFTS Studies. **3.3.1. Formation of Intermediates.** Kinetic studies indicated that the H₂-NH₃-SCR reaction over Ag/Al₂O₃ obeyed the L–H mechanism, such that both NO and NH₃ adsorbed on the catalyst surface before their further reaction. Hence, in situ DRIFTS experiments were carried out to study the adsorption of these reactants as well as their further reactions. H₂O was not added in the reactant feed in the DRIFTS experiments because of its strong interference effects.^{27,28} Activity tests revealed that H₂O has negligible influence on the NH₃-SCR reaction on Ag/

Al₂O₃. Therefore, it is proposed here that H₂O does not alter the nature of the SCR reactions, and its absence does not affect the key conclusions of the DRIFTS results.^{6,29}

First, the oxidation of NO_x over Ag/Al₂O₃ and Al₂O₃ was investigated (Figure 6). In the absence of H₂, neither Ag/

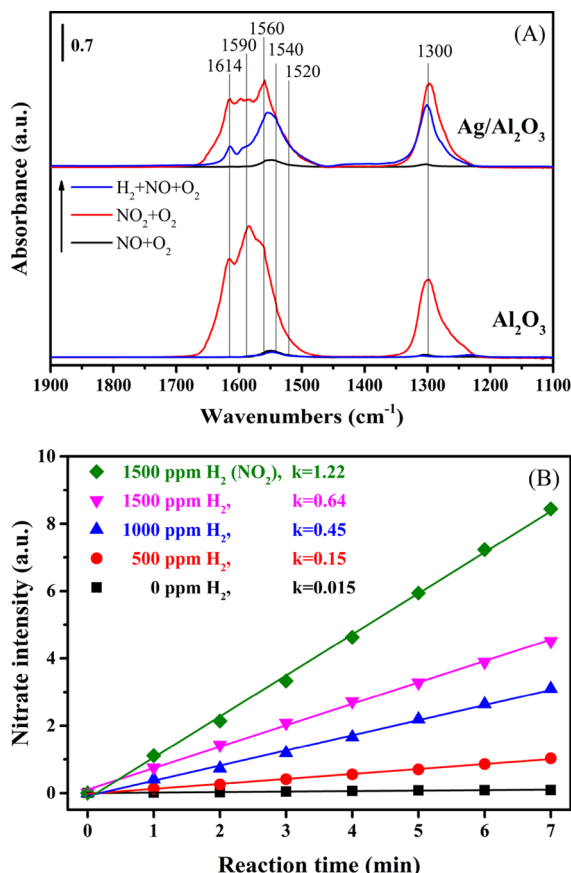
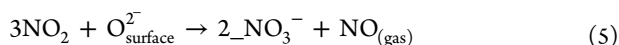


Figure 6. (A) In situ DRIFTS spectra of adsorbed nitrate species on Ag/Al₂O₃ and Al₂O₃ under different conditions (NO + O₂, NO₂ + O₂, or H₂ + NO + O₂) for 60 min. (B) Formation rate of bridging nitrate (1614 cm⁻¹) on Ag/Al₂O₃ in a flow of H₂ + NO + O₂ (or H₂ + NO₂ + O₂) with different amounts of H₂. Typical feed composition: 500 ppm NO (or NO₂), 5% O₂, 1500 ppm H₂, N₂ balance, and 200 °C.

Al₂O₃ nor Al₂O₃ could catalytically oxidize NO to yield nitrate species. In a flow of NO₂ + O₂, however, a large amount of nitrate species was produced on both these samples. According to the literature, these nitrate species could be attributed to bridging nitrates (1614 cm⁻¹),^{2,30} bidentate nitrates (1590 cm⁻¹),^{20,30,31} and monodentate nitrates (1560, 1540, 1520, and 1300 cm⁻¹).^{1,2,20} As mentioned above in the Catalytic Studies section, NO was generated after the adsorption of NO₂ on these samples. Hence, the formation of nitrate species possibly took place via the adsorption and disproportionation of NO₂ (eq 5).¹⁵



After exposure to a flow of H₂ + NO + O₂, a considerable amount of nitrates was observed on the surface of Ag/Al₂O₃, while little could be observed on Al₂O₃ even in the presence of H₂. Therefore, it was speculated that the oxidation of NO mainly occurred on the Ag species on Ag/Al₂O₃.²⁰ UV-vis measurement indicated that metallic silver species were

converted to oxidized ones in a flow of NO + O₂, possibly due to the formation of AgNO₃ (Figure S7). Afterward, H₂ reduced the oxidized silver species to metallic ones and thus induced the desorption and migration of nitrates. The effect of H₂ concentration on the generation rate of nitrates was also investigated (Figure S8). To quantitatively evaluate the formation rate of nitrate species, the spectra were fitted and deconvoluted into constituent peaks (with typical results shown in Figure S8). Then, the areas of peaks due to different nitrates were integrated. In particular, the formation rate of bridging nitrate was especially focused on due to its high reactivity (see below) and the lack of overlap of its characteristic band (1614 cm⁻¹) with the other bands. In the absence of H₂, nitrate species were hardly generated on Ag/Al₂O₃ (Figure 6B). However, 500 ppm H₂ addition significantly enhanced the oxidation of NO, making the formation rate of nitrates 10 times that without H₂ coexistence. Moreover, increasing the H₂ concentration further accelerated the formation of nitrate species. Clearly, H₂ played a critical role in the formation of nitrates,³² and the H₂ concentration quantitatively governed the generation rate of this species. Coincidentally, the effect of H₂ concentration on the formation rate of nitrate species exhibited the same trend as its effect on the NO_x reduction rate. Besides, the generation of nitrates in a flow of H₂ + NO₂ + O₂ was much faster than that in the case of H₂ + NO + O₂.

The adsorption of NH₃ on Ag/Al₂O₃ and Al₂O₃ was also investigated (Figure 7). Several kinds of adsorbed NH₃ species

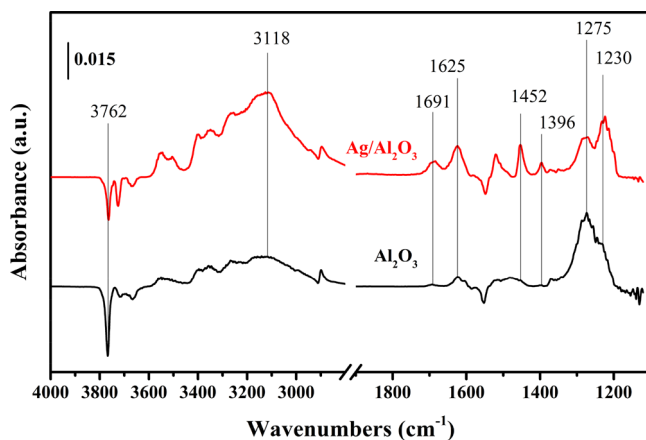


Figure 7. In situ DRIFTS of NH₃ adsorption over Ag/Al₂O₃ and Al₂O₃ for 60 min followed by N₂ purge for 30 min. Typical feed composition: 500 ppm NH₃, N₂ balance, and 200 °C.

were observed on both samples. According to the literature,^{33–36} the absorbance peaks at 1625, 1275, and 1230 cm⁻¹ could be assigned to NH₃ adsorption on Lewis acid sites (L_{NH₃} species), and the peaks at ~3118, 1691, 1452, and 1396 cm⁻¹ could be assigned to NH₄⁺ ions formed by chemisorption of NH₃ on Brønsted acid sites (B_{NH₃} species). In addition, the formation of NH₄⁺ ions resulted in the consumption of -OH species (3762 cm⁻¹). It should be highlighted that the adsorption of NH₃ species on both samples was much faster than the formation of nitrate species and reached saturation within 10 min (not shown). In addition, the amount of adsorbed B_{NH₃} species was significantly more than that of the L_{NH₃} species.

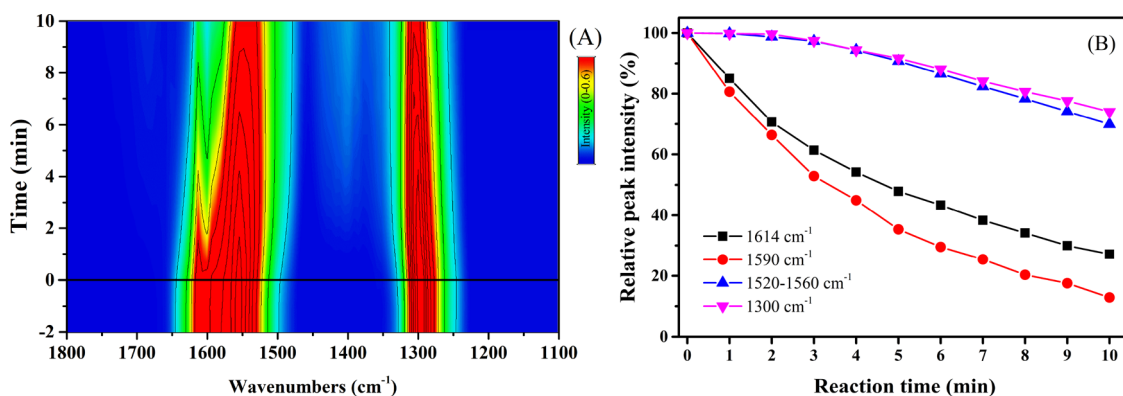


Figure 8. (A) Reactivity of nitrate species toward $\text{H}_2 + \text{NH}_3 + \text{O}_2$ at 200 °C. (B) Consumption rates of different peaks due to bridging nitrate (1614 cm^{-1}), bidentate nitrate (1590 cm^{-1}), and monodentate nitrate (1560 , 1540 , 1520 , and 1300 cm^{-1}).

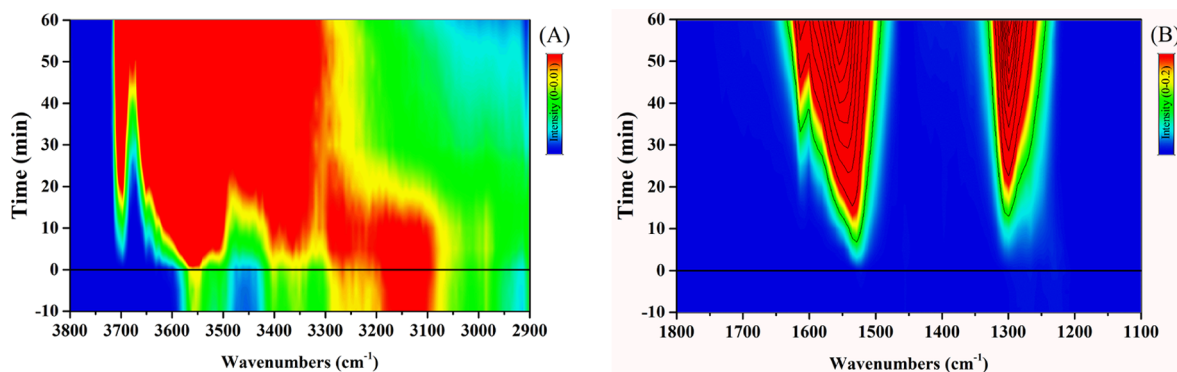


Figure 9. Reactivity of adsorbed NH_3 species toward $\text{NO}_2 + \text{O}_2$ over $\text{Ag}/\text{Al}_2\text{O}_3$ at 200 °C.

3.3.2. Reactivity of Intermediates. The reactivity of different nitrate species toward $\text{H}_2 + \text{NH}_3 + \text{O}_2$ was further studied (Figure 8). As mentioned above, the spectra were fitted and deconvoluted into constituent peaks, the areas of which were further integrated. As shown in Figure 8B, the bridging and bidentate nitrates were consumed rapidly in this reaction, exhibiting $\sim 50\%$ decrease in peak area within 5 min. In contrast, the monodentate nitrate exhibited low reactivity toward $\text{H}_2 + \text{NH}_3 + \text{O}_2$, with only $\sim 10\%$ decrease in the peak area during the above process. Clearly, the bridging and bidentate nitrates were much more reactive toward NH_3 species than the monodentate nitrate. Compared to the bidentate nitrate (1590 cm^{-1}), the peak due to bridging nitrate (1614 cm^{-1}) had less interference from other peaks and was thus chosen to represent the formation and reactivity of the nitrate species. It should be pointed out that the consumption of bridging nitrate in the flow of $\text{H}_2 + \text{NH}_3 + \text{O}_2$ was much faster than its formation in $\text{H}_2 + \text{NO} + \text{O}_2$ (Figure S10), revealing that the formation of this species was much slower than its further reaction with NH_3 species to yield N_2 . Therefore, the rate-determining step should occur during the generation of nitrates.

The reactivity of nitrate species toward $\text{NH}_3 + \text{O}_2$ over $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 was also studied (Figure S11). The bridging nitrate was rapidly consumed in the first 5 min on both samples. Quantitative measurements showed that the consumption rates of bridging nitrate on these samples were approximately equal, revealing that the reaction possibly occurred at the surface of Al_2O_3 , consistent with the results shown in Figure 3. Afterward, the reaction between nitrates and NH_3 species rapidly declined after 5 min, indicating that

the adsorption of NH_3 or its further reaction with nitrate species was suspended. Notably, the consumption rate of nitrates in the flow of $\text{H}_2 + \text{NH}_3 + \text{O}_2$ was only slightly higher than that in the flow of $\text{NH}_3 + \text{O}_2$, especially in the first few minutes, revealing that H_2 did not significantly accelerate the adsorption of NH_3 or its further reaction with nitrate species. Rather, H_2 addition possibly restored the adsorption of NH_3 or its further reaction with nitrates.

The reactivity of adsorbed NH_3 species toward $\text{NO}_2 + \text{O}_2$ was also investigated over $\text{Ag}/\text{Al}_2\text{O}_3$ (Figure 9). To eliminate the influence of H_2 on the catalysts and the adsorbed species, $\text{NO}_2 + \text{O}_2$ rather than $\text{H}_2 + \text{NO} + \text{O}_2$ was employed in this experiment. The B_{NH_3} species ($3100\text{--}3200\text{ cm}^{-1}$) continuously reacted with nitrate species in the flow of $\text{NO}_2 + \text{O}_2$, and it were completely consumed within 20 min. Correspondingly, bridging and bidentate nitrates were gradually observed after the complete consumption of B_{NH_3} species. In contrast, the monodentate nitrate was rapidly produced on the catalyst surface upon exposure to $\text{NO}_2 + \text{O}_2$. Besides, the consumption of L_{NH_3} species was hardly observed, which was possibly due to its low intensity or low reactivity. Therefore, it was proposed that the reaction of B_{NH_3} species with the bridging and bidentate nitrates was the main pathway for NO_x reduction.

3.3.3. Regeneration of the $\text{Ag}/\text{Al}_2\text{O}_3$ Catalyst. As mentioned above, both $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 were gradually deactivated in a flow of $\text{NO}_2 + \text{NH}_3 + \text{O}_2$, while $\text{Ag}/\text{Al}_2\text{O}_3$ could be regenerated in a flow of $\text{H}_2 + \text{O}_2$ (Figure 3). Hence, the effects of $\text{H}_2 + \text{O}_2$ regeneration on these samples were investigated by in situ DRIFTS (Figure 10). After exposure to a flow of $\text{NO}_2 + \text{NH}_3 + \text{O}_2$ for 60 min, large amounts of

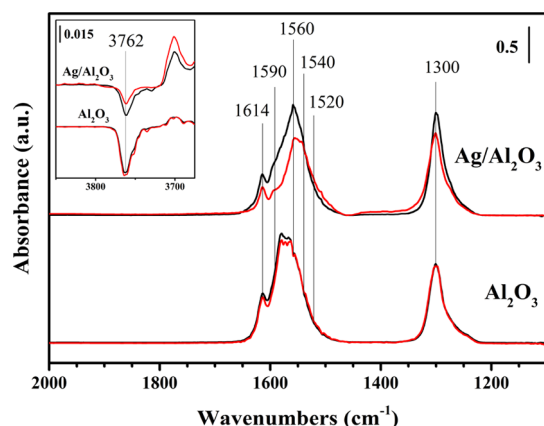


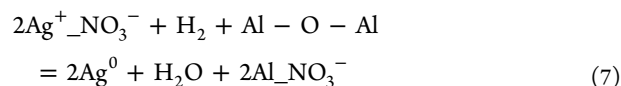
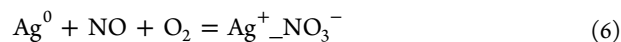
Figure 10. Effect of $\text{H}_2 + \text{O}_2$ regeneration on $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 . These samples were pre-exposed to a flow of $\text{NO}_2 + \text{NH}_3 + \text{O}_2$ at 200°C for 60 min (black lines) and then regenerated in a flow of $\text{H}_2 + \text{O}_2$ for 60 min (red lines).

nitrates were produced on these samples, while adsorbed NH_3 species were hardly observed. In addition, the absence of feature peak assignable to NH_4NO_3 ($1450\text{--}1350\text{ cm}^{-1}$)³⁷ further confirmed that NO_2 was reduced to N_2 instead of accumulating on the surface (Figure 3). Furthermore, a negative peak at 3762 cm^{-1} was observed for both samples, indicating the consumption of $-\text{OH}$ species. On $\text{Ag}/\text{Al}_2\text{O}_3$, regeneration promoted the desorption of nitrates and the recovery of $-\text{OH}$ species.³⁸ The oxidation of NO to yield NO_2 over $\text{Ag}/\text{Al}_2\text{O}_3$ (Figure 2A) possibly originated from the desorption of nitrate species induced by H_2 . Notably, the desorption rate of nitrate species in this experiment was much lower than the consumption rate shown in Figure 8, further revealing that NO oxidation to produce NO_2 was much slower than NO_x reduction. Considering that the $-\text{OH}$ species were critical for the formation of B_{NH_3} species, the recovery of $-\text{OH}$ species possibly contributed to the regeneration of $\text{Ag}/\text{Al}_2\text{O}_3$. On Al_2O_3 , however, regeneration showed little effect on the adsorbed nitrate species or $-\text{OH}$ species, further indicating that this sample could not be regenerated.

3.4. Proposed Reaction Mechanism. Generally, a redox reaction mechanism has been established for NO_x reduction in $\text{NH}_3\text{-SCR}$, where active metal species cycle between low and high oxidation states during this reaction.^{27,28,39–42} This reaction mechanism contains a reduction half-cycle and an oxidation half-cycle. During the reduction half-cycle, adsorbed NH_3 species reacts with nitrates or gaseous NO_x to yield nitrogen and water, resulting in the reduction of active metal species to a low oxidation state. In contrast, the active metal species are reoxidized by O_2 to a high oxidation state in the oxidation half-cycle. For the $\text{H}_2\text{-NH}_3\text{-SCR}$ over $\text{Ag}/\text{Al}_2\text{O}_3$, it was proposed that H_2 plays an important role in the redox cycling of Ag species during NO_x reduction.

As mentioned above, the $\text{H}_2\text{-NH}_3\text{-SCR}$ reaction over $\text{Ag}/\text{Al}_2\text{O}_3$ started with the oxidation of NO to produce nitrate species. Both the Ag species and H_2 coexistence were necessary for the formation of nitrate species. Therefore, redox cycling of the oxidation states of Ag species during NO oxidation to generate nitrates was proposed (eqs 6 and 7). First, metallic Ag (Ag^0) catalytically oxidized NO to produce nitrate species,¹¹ resulting in the formation of oxidized silver species. Afterward, H_2 reduced the oxidized Ag species to generate Ag^0 and H_2O ⁴³ and thus induced the desorption and migration of nitrates. The

formation of NO_2 was possibly due to the desorption of nitrates, and its further adsorption would contribute to the formation of nitrates to some extent. The adsorption of nitrates led to the cleavage of the Al-O-Al bond. Notably, since 1 mole of H_2 could reduce 2 moles of Ag^+ , the stoichiometry of $\text{Ag}:\text{NO}:\text{H}_2$ for the generation of nitrates was equal to $1:1:0.5$. Shimizu et al.^{12,44} proposed a reductive activation of O_2 by $\text{Ag}_n^{\delta+}$ clusters to produce superoxide ion. In the present work, indeed, it is also reasonable that superoxide ion would be produced on the Ag^0 site before it further reacted with NO to generate nitrates. Then, the oxidized Ag species would be reduced by H_2 via eq 7. Besides, Olsson et al.¹⁹ suggested that the effect of H_2 is to free Ag from the single O atom, which could be considered as another way to describe the reduction of oxidized Ag species.



There were two active sites on $\text{Ag}/\text{Al}_2\text{O}_3$ and Al_2O_3 for NH_3 adsorption, namely, the Brønsted acid site and the Lewis acid site, the former of which showed much higher intensity compared to the latter. More importantly, the B_{NH_3} species exhibited higher reactivity toward nitrate species during NO_x reduction compared to the L_{NH_3} species. Therefore, the $-\text{OH}$ species, which served as the adsorption sites for B_{NH_3} species, were critical for this reaction. On the other hand, the bridging and bidentate nitrates were more reactive toward adsorbed NH_3 species compared to monodentate nitrate. Hence, the main reaction path could be considered as B_{NH_3} species reacting with the bridging and bidentate nitrates to produce nitrosoamide (NH_2NO) or ammonium nitrite (NH_4NO_2), which are frequently suggested as important intermediates for the generation of N_2 and H_2O .^{39,40,45,46} Kondratenko et al.^{11,14} proposed that N_2 originated from the decomposition of surface NH_2NO species during $\text{H}_2\text{-NH}_3\text{-SCR}$ over $\text{Ag}/\text{Al}_2\text{O}_3$. Shimizu et al.¹² suggested that the superoxide ion was important for the activation of NH_3 to yield NH_4^+ , which further reacted with nitrates to yield N_2 and H_2O . Besides, the formation of NH_4NO_2 via NH_4^+ reacting with nitrates or gaseous NO_2 should also be considered as a possible route since NH_4NO_2 is highly unstable and easily decomposes to N_2 and H_2O even at low temperatures.⁴⁷ It is worth noting that Gao et al.⁴⁰ investigated the reaction pathway involving NH_2NO and NH_4NO_2 by DFT calculations and proposed that the “ NH_4NO_2 ” pathway was energetically more favorable and served as the main reaction pathway for NO_x reduction. Hence, it could not be unambiguously confirmed whether NH_4NO_2 or NH_2NO served as the precursor for the formation of N_2 and H_2O .

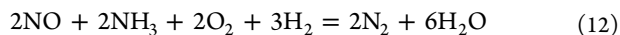
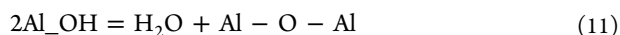
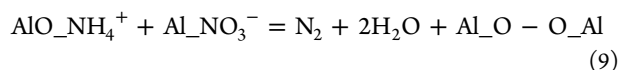
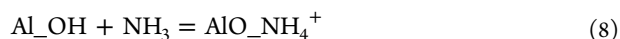
As neither $\text{Ag}/\text{Al}_2\text{O}_3$ nor Al_2O_3 were active for the oxidation of NO to produce nitrates in the absence of H_2 , NO could not be reduced on these samples during $\text{NH}_3\text{-SCR}$. In contrast, NO_2 could be reduced on both samples under similar conditions, although these samples were gradually deactivated during the overall process. After deactivation, $\text{Ag}/\text{Al}_2\text{O}_3$ could be almost completely regenerated in a flow of $\text{H}_2 + \text{O}_2$, while Al_2O_3 was hardly recovered during the same process. As NO_2 reduction occurred at the surface of Al_2O_3 , the deactivation should be related to the properties of Al_2O_3 , and $\text{H}_2 + \text{O}_2$

regeneration needed the assistance of Ag species. Several explanations exist for the deactivation of these catalysts. One possibility is that the adsorption of nitrate species gradually occupied the surface of Al_2O_3 , thereby reducing the active sites for NH_3 adsorption and its further reaction.¹⁵ However, this conflicts with the phenomenon that these samples were gradually deactivated despite the availability of more active sites after the consumption of nitrates (Figure S11). Although active oxygen species such as superoxide ions have been suggested as important intermediates for NH_3 activation, they should not be responsible for the deactivation of these catalysts because superoxide ions have not been detected on $\text{Ag}/\text{Al}_2\text{O}_3$ or Al_2O_3 in the absence of H_2 .^{12,44} Considering the critical effect of $-\text{OH}$ species on the adsorption of B_{NH_3} species, which served as an important intermediate for NO_x reduction, the consumption of $-\text{OH}$ species seemed to be the reason for the deactivation of these samples. More fundamentally, as N in NH_3 was in the valence state of -3 and N in NO_2 was in the valence state of $+4$, the formation of N_2 needed another electron, which could not be recovered under this reaction condition.

During the regeneration process (Figure 10), the nitrate species were desorbed and $-\text{OH}$ species were restored on $\text{Ag}/\text{Al}_2\text{O}_3$, while little effect was observed on Al_2O_3 . Shimizu et al.⁴⁴ employed an H/D isotopic exchange experiment to investigate the effect of H_2 reduction on the dehydrated $\text{Ag}/\text{Al}_2\text{O}_3$. They proposed that H_2 (D_2) dissociated on the Ag sites to produce acidic protons, which further spilled over to the Al_2O_3 surface. During the regeneration process, H atom transferred an electron to $\text{Ag}/\text{Al}_2\text{O}_3$ and thus restored the electron consumed in the formation of N_2 and simultaneously recovered the $-\text{OH}$ species. In our recent work,⁴⁸ it was found that B_{NH_3} species exhibited high reactivity toward O_2 to produce N_2 during the selective catalytic oxidation of NH_3 over $\text{Ag}/\text{Al}_2\text{O}_3$. Hence, the recovery of adsorption sites for B_{NH_3} species would also contribute to the improvement of the NH_3 oxidation over $\text{Ag}/\text{Al}_2\text{O}_3$ (Figure 2B).

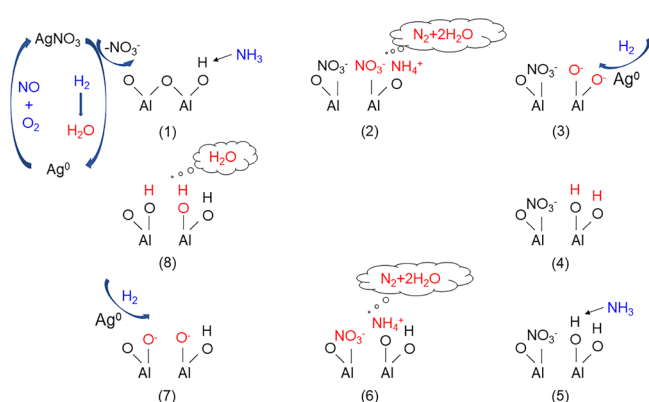
Based on the above discussion, a complete catalytic cycle for the H_2 - NH_3 -SCR reaction over $\text{Ag}/\text{Al}_2\text{O}_3$ was proposed (Scheme 1). First, Ag^0 catalytically oxidized NO to produce nitrates, which further migrated to the Al_2O_3 surface (eqs 6 and 7). Simultaneously, NH_3 adsorbed on the $-\text{OH}$ species to yield $-\text{NH}_4^+$, which further reacted with $-\text{NO}_3^-$ to produce N_2 and H_2O (eqs 8 and 9). Notably, as N in $-\text{NH}_4^+$ was in the

valence state of -3 and N in $-\text{NO}_3^-$ was in the valence state of $+5$, the reaction of N_2 generation needed another two electrons, thus resulting in the formation of two unsaturated O atoms. Afterward, H_2 dissociated on metallic Ag species, further spilled over to the Al_2O_3 surface, transferred electrons to the unsaturated O atoms, and simultaneously restored the $-\text{OH}$ species.⁴⁴ Subsequently, another catalytic cycle involved N_2 formation and $-\text{OH}$ recovery occurred (eqs 8–10). Ultimately, the $-\text{OH}$ species dehydrated to produce H_2O and restored the $\text{Al}-\text{O}-\text{Al}$ bond (eq 11), thus completing the catalytic cycle for NO_x reduction. To summarize the above reactions and consider the law of conservation of mass, the overall chemical reaction equation could be considered to follow eq 12. The Al_2O_3 surface provided the active sites for the reduction of NO_x , while Ag species contributed to the oxidation of NO to produce nitrates and to the dissociation of H_2 to restore the $-\text{OH}$ species. The global stoichiometry between $\text{NO}:\text{NH}_3:\text{H}_2$ was equal to $1:1:1.5$, where 1.5 H_2 contributed to the reduction of Ag^+ and the recovery of two electrons consumed in N_2 formation.



H_2 addition was important for the oxidation of NO to produce nitrate species. It should be highlighted that the formation rate of nitrate species was relatively low and was quantitatively governed by the H_2 concentration (Figure 6B). In contrast, the consumption of nitrates in the flow containing $\text{NH}_3 + \text{O}_2$ was much faster than its formation rate, regardless of the presence or absence of H_2 . As a result, the reactive nitrate species (bridging and bidentate nitrates) were not observed on $\text{Ag}/\text{Al}_2\text{O}_3$ during H_2 - NH_3 -SCR until a high concentration of H_2 was employed (Figure S12). This indicated that the cycle involving NH_3 adsorption and its further reaction with nitrates to produce N_2 and H_2O were faster than the cycle involved in the formation of nitrates. Hence, the rate-determining step for the H_2 - NH_3 -SCR reaction should occur during the formation of nitrate species, which included the oxidation of NO on Ag^0 and the reduction of Ag^+ by H_2 (eqs 6 and 7). The oxidation of NO could not be the rate-determining step because if so, the NO concentration rather than the H_2 concentration would quantitatively govern the formation rate of nitrates. The kinetic results showed that the reduction rate of NO_x was controlled by the H_2 concentration and that the reaction order of H_2 was approximately equal to 0.5, consistent with eq 7 in which the reduction of one Ag^+ ion consumed half of a H_2 molecule. This further confirmed that the reduction of Ag^+ by H_2 to yield Ag^0 was the intrinsic rate-determining step in the H_2 - NH_3 -SCR reaction. In the case of $\text{H}_2 + \text{NO}_2 + \text{O}_2$, nitrate species were produced much faster than in $\text{H}_2 + \text{NO} + \text{O}_2$ (Figure 6B), thus contributing to the rapid reduction of NO_2 with an extremely low activation energy of 2.0 kJ/mol (Figure 5).

Scheme 1. Proposed Mechanism for the H_2 -Assisted NH_3 -SCR over $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts



4. CONCLUSIONS

Ag/Al₂O₃ was completely inactive for NO_x reduction during NH₃-SCR, while H₂ addition significantly enhanced its deNO_x activity. The overall chemical reaction equation was as follows: 2NO + 2NH₃ + 2O₂ + 3H₂ = 2N₂ + 6H₂O. Kinetic results revealed that the reaction obeyed the Langmuir–Hinshelwood mechanism and that the reduction rate of NO_x was governed by the H₂ concentration. In situ DRIFTS experiments showed that Ag species catalytically oxidized NO to yield nitrate species, which further migrated to the Al₂O₃ surface. Then, the bridging and bidentate nitrates reacted with the B_{NH₃} species to produce N₂ and H₂O. Afterward, the –OH species consumed by the B_{NH₃} species adsorption were restored by H₂ dissociation over metallic Ag species. Notably, the rate-determining step in the H₂-NH₃-SCR reaction was the reduction of oxidized Ag species, which further governed the formation of nitrate species. In conclusion, the reduction of NO_x primarily occurred at the surface of Al₂O₃, while Ag species and H₂ contributed to the oxidation of NO + O₂ to generate nitrates and to the recovery of –OH species.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acscatal.9b04100](https://doi.org/10.1021/acscatal.9b04100).

NH₃ conversion and N₂O formation, H₂-NH₃-SCR reaction over Al₂O₃, fast NH₃-SCR reaction over Ag/Al₂O₃, UV–vis spectra of Ag/Al₂O₃, and detailed information of DRIFTS experiment (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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