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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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: 2NO + 2NH₃ + 2O₂ + 3H₂ = 2N₂ + 6H₂O. 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 nitrites 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 NOₓ primarily occurred at the surface of Al₂O₃, while Ag species and H₂ contributed to the oxidation of NO to generate nitrites and to the regeneration of −OH species.

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

1. INTRODUCTION

NOₓ emissions from diesel vehicles can induce serious environmental problems such as acid rain, photochemical smog, and haze. To cope with the increasingly serious problems, the exhaust aftertreatment system is required to work efficiently at low temperatures below 200–250 °C. For NOₓ removal from diesel vehicles, selective catalytic reduction (SCR) of NOₓ by ammonia (NH₃-SCR) is the leading technology. Compared with NH₃-SCR, hydrocarbon (HC)-SCR technology exhibits unique advantages by utilizing onboard diesel or its additives as reductants and has thus been widely investigated. The alumina-supported silver catalyst (Ag/Al₂O₃) is generally recognized as one of the most promising catalysts for HC-SCR. Furthermore, a small amount of H₂ addition significantly improves the catalytic activity of Ag/Al₂O₃ during HC-SCR, especially in low-temperature regions. During the NH₃-SCR, unexpectedly, H₂ addition was also found to greatly improve the deNOₓ activity of Ag/Al₂O₃ which is almost inactive for this reaction in the absence of H₂. The H₂-assisted NH₃-SCR system (H₂-NH₃-SCR) exhibited high efficiency for NOₓ removal and achieved 100% NOₓ conversion at a low temperature of 200 °C. Recent engine bench tests also revealed that this system exhibited moderate efficiency for NOₓ removal even under very demanding practical conditions. Besides, since high concentrations of H₂ (~1000 ppm) and NH₃ (~200 ppm) were produced in ethanol-SCR on Ag/Al₂O₃, the H₂-NH₃-SCR reaction would also occur in the ethanol-SCR, thus contributing to a conjugated SCR system.

Since Richter et al. found the unusual enhancement effect of H₂ on the NH₃-SCR over Ag/Al₂O₃, several groups have been working on this highly efficient catalytic system. Kondratenko et al. 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...
contributed to the reduction of oxidized silver and that N₂ was yielded via direct or O₂-induced decomposition of surface NH₃NO species. Shimizu et al.12,13 investigated the mechanism of H₂-NH₃-SCR by kinetic and spectroscopic methods and found that H₂ addition increased the relative amounts of Ag clusters and superoxide ion. They further proposed that Ag clusters were the active species for NO reduction and that superoxide ion was important for the activation of NH₃. Doronkin et al.15 found that both Ag and Al₂O₃ were necessary components for the H₂-NH₃-SCR reaction, and they further proposed a “fast SCR”-like mechanism. Olsson et al.19 investigated the influence of gas composition on NOx reduction during the above reaction and suggested that the global stoichiometry between NO:NH₃:H₂ was equal to 1:1:2. In addition, they found that H₂ promoted the transformation of nitrates and bidentate nitrate to monodentate and bridging nitrates over Al₂O₃.20 Besides, some groups investigated the sulfur tolerance of this catalytic system, which is an important factor in its practical applications.

According to the above literature, it was found that H₂ addition reduced the Ag⁺ ion and increased the amount of Agₙ clusters, which might contribute to the reductive activation of molecular O₂ and thus improve the NOx reduction. However, the complete mechanism of the H₂-NH₃-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 Al₂O₃ in the H₂-NH₃-SCR have not been totally confirmed. In the present work, the reaction mechanism of H₂-assisted NH₃-SCR over Ag/Al₂O₃ 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 H₂. This study offers new insight into the mechanism of H₂-NH₃-SCR over Ag/Al₂O₃ and provides some advice for the design of highly efficient catalytic systems.

2. EXPERIMENTAL SECTION

Al₂O₃ and 2 wt % Ag/Al₂O₃ 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 NOₓ), 520 ppm NH₃, 1500 ppm H₂, and 5% O₂ in N₂ balance. The total flow was 500 mL/min, which corresponded to a GHSV of 150,000 h⁻¹. The reactants and products including NO, NH₃, NO₂, N₂O were detected by an FTIR spectrometer (Nicolet iS 10). The conversions of NOₓ and NH₃ were calculated based on the equations below (eqs 1 and 2).

\[
\text{NO}_x \text{ conversion} = \frac{[\text{NO} + \text{NO}_2]_{\text{in}} - [\text{NO} + \text{NO}_2]_{\text{out}}}{[\text{NO} + \text{NO}_2]_{\text{in}}} \times 100\%
\]

\[
\text{NH}_3 \text{ conversion} = \frac{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \times 100\%
\]

The kinetic studies were carried out in the above fixed-bed reactor. The conversions of NOₓ and NH₃ 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 (\( -\frac{\Delta x}{\Delta t} \)) was calculated based on the equation below (eq 3).

\[
-\frac{\Delta x}{\Delta t} = \frac{F_{\text{NO}_x} \times X_{\text{NO}_x}}{W}
\]

where \( F_{\text{NO}_x} \) and \( X_{\text{NO}_x} \) represent the molar flow rate (mol/s) and NOx conversion (%), respectively, and W is the sample weight. The Arrhenius plots for NOx conversion were drawn according to the above results. Afterward, the activation energies of NOx 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% O₂/N₂ (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 H₂ on the catalytic activity of Ag/Al₂O₃ during NH₃-SCR was investigated (Figure 1). In the absence of H₂, Ag/Al₂O₃ was completely inactive for NOx reduction during the NH₃-SCR, which is in good agreement with the literature.7,13 On the contrary, H₂ addition greatly boosted the NOx reduction over Ag/Al₂O₃, and the NOx conversion was quantitatively governed by the H₂ concentration. In addition, the NOx 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 NOx conversion at low temperatures could be attributed to the light-off of H₂, which was confirmed by the work of Olsson.19 More importantly, the constant NOx conversion at high temperatures...
revealed that NO\textsubscript{2} reduction was governed by the H\textsubscript{2} concentration. In particular, the addition of 750 ppm H\textsubscript{2} increased the NO\textsubscript{2} conversion to ~92% at temperatures above 300 °C, while the incomplete reduction of NO\textsubscript{2} might be due to nonselective oxidation of H\textsubscript{2}. The global stoichiometry between NO:NH\textsubscript{3}:H\textsubscript{2} was approximately equal to 1:1:1.5, while further increasing the H\textsubscript{2} concentration helps to completely reduce NO\textsubscript{2}.

The NH\textsubscript{3} conversion (Figure S2) exhibited the same trend as the NO\textsubscript{2} conversion. The yield of N\textsubscript{2}O was negligible over the whole temperature range and H\textsubscript{2} addition further inhibited its formation, consistent with the previous literature.\textsuperscript{11,14} Furthermore, the experiment of H\textsubscript{2}-NH\textsubscript{3}-SCR with 2% H\textsubscript{2}O was also performed over the Ag/Al\textsubscript{2}O\textsubscript{3} catalysts (Figure S3). The NO\textsubscript{\textsubscript{2}} conversions were substantially the same as that in the absence of H\textsubscript{2}O, revealing that H\textsubscript{2}O had negligible influence on the total reaction over this catalyst. Besides, this catalytic system exhibited high efficiency for NO\textsubscript{2} reduction at a high GHSV of 450,000 h\textsuperscript{−1} (Figure S4), which is beneficial for its practical applications. In contrast, Al\textsubscript{2}O\textsubscript{3} was completely inactive for NO\textsubscript{2} reduction with the coexistence of H\textsubscript{2} (Figure S5), revealing that the Ag species was a necessary component for NO\textsubscript{2} reduction.

As NO\textsubscript{3} has been proposed as an important reactant for the NH\textsubscript{3}-SCR over Ag/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{15,22} the effect of H\textsubscript{2} addition on the NO oxidation to yield NO\textsubscript{2} was investigated (Figure 2A). Without the coexistence of H\textsubscript{2}, Ag/Al\textsubscript{2}O\textsubscript{3} was inactive for the oxidation of NO + O\textsubscript{2} to yield NO\textsubscript{2} while H\textsubscript{2} addition significantly boosted this reaction. The increase in NO\textsubscript{2} formation from 150 to 300 °C could be attributed to the light-off of H\textsubscript{2} while the decrease in NO\textsubscript{2} formation from 300 to 450 °C might be due to the thermodynamic equilibrium between NO and NO\textsubscript{2}. In contrast, Al\textsubscript{2}O\textsubscript{3} was completely inactive for NO oxidation even in the presence of H\textsubscript{2}, revealing that the Ag species was critical for NO oxidation.

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

Afterward, the different effects of NO and NO\textsubscript{2} on NO\textsubscript{x} reduction during NH\textsubscript{3}-SCR were investigated (Figure 3). It was found that NO could not be reduced on either Ag/Al\textsubscript{2}O\textsubscript{3} or Al\textsubscript{2}O\textsubscript{3} during the above reaction in the absence of H\textsubscript{2}. In contrast, NO\textsubscript{2} could be reduced on both samples at the beginning of this reaction, although the NO\textsubscript{2} conversion gradually decreased from ~60 to ~5% within 45 min. It should be highlighted that the NO\textsubscript{x} conversions on Ag/Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} were approximately equal, indicating that NO\textsubscript{x} reduction possibly occurred at the surface of Al\textsubscript{2}O\textsubscript{3}. Besides, the amount of NO\textsubscript{2} adsorbed on these samples in a flow of NO\textsubscript{2} + O\textsubscript{2} (not shown) was much less than that in NO\textsubscript{2} + NH\textsubscript{3} + O\textsubscript{2}, revealing that NO\textsubscript{2} were reduced to N\textsubscript{2} rather than being adsorbed in the above SCR reaction. Furthermore, NO was detected in the effluent gas after the adsorption of NO\textsubscript{2}, indicating the occurrence of a disproportionation reaction. After complete inactivation, these samples were regenerated in H\textsubscript{2} + O\textsubscript{2} for 60 min followed by N\textsubscript{2} purge for 30 min. Interestingly, the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst was almost completely regenerated during this process, and the NO\textsubscript{x} conversion curve exhibited the same trend as that on the fresh sample. Still, the activity of Al\textsubscript{2}O\textsubscript{3} for NO\textsubscript{x} reduction was hardly recovered during the above process, indicating that the Ag species was an essential component for the regeneration of Ag/Al\textsubscript{2}O\textsubscript{3}. In some sense, the above

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ FIGURE2.png}
\caption{Effect of H\textsubscript{2} on (A) the oxidation of NO to yield NO\textsubscript{2} and (B) the oxidation of NH\textsubscript{3} over Ag/Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}. Typical feed composition: 500 ppm NO, 500 ppm NH\textsubscript{3}, 1500 ppm H\textsubscript{2}, 5% O\textsubscript{2}, N\textsubscript{2} balance, and GHSV of 150,000 h\textsuperscript{−1}.}
\end{figure}
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. In the present work, however, it was found that Ag/Al₂O₃ could not catalytically reduce NO during the fast NH₂-SCR reaction, especially at low temperatures (Figure S6A). Instead, the Ag/Al₂O₃ catalyst was gradually deactivated in this experiment, with the NO₂ 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, it is cautiously speculated that those catalysts were efficient for NO₂ 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 NO₂ 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 during H₂-NH₃-SCR was much higher than the oxidation of NO to yield NO₂. When using NO₃ as reactant, notably, the reaction rate for NO₃ reduction was extremely high, and the activation energy was as low as 2 kJ/mol. Therefore, the formation of NO₃ boosted by H₂ addition was beneficial for NO₃ reduction during the H₂-NH₃-SCR. Nevertheless, as the oxidation of NO to produce NO₂ was much slower than the NO₃ reduction, the formation of NO₂ and its further reaction with NH₃ should not be the main pathway for NO₂ reduction.

Shimizu et al. have also investigated the influence of the concentration of reactants on the NO₂ reduction during H₂-NH₃-SCR. They found that increasing the concentrations of H₂, NO, NH₃, and O₂ could enhance the reduction of NO₂ over Ag/Al₂O₃. It should be noted that a large amount of H₂ was added in the reactant feed in the DRIFTS experiments because NH₃ 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, 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. It should be highlighted that the reaction rate for NO reduction was much higher than the oxidation of NO to yield NO₂. When using NO₂ as reactant, notably, the reaction rate for NO₂ 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 NO₂ reduction during the H₂-NH₃-SCR. Nevertheless, as the oxidation of NO to produce NO₂ was much slower than the NO₂ reduction, the formation of NO₂ and its further reaction with NH₃ should not be the main pathway for NO₂ reduction.

Shimizu et al. have also investigated the influence of the concentration of reactants on the NO₂ reduction during H₂-NH₃-SCR. They found that the concentration of NO₂ and NH₃ 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, 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. It should be highlighted that the reaction rate for NO reduction was much higher than the oxidation of NO to yield NO₂. When using NO₂ as reactant, notably, the reaction rate for NO₂ 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 NO₂ reduction during the H₂-NH₃-SCR. Nevertheless, as the oxidation of NO to produce NO₂ was much slower than the NO₂ reduction, the formation of NO₂ and its further reaction with NH₃ should not be the main pathway for NO₂ reduction.

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. Activity tests revealed that H₂O has negligible influence on the NH₃-SCR reaction on Ag/Al₂O₃.

Figure 4. Reaction rates of NO₂ 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 30,000 h⁻¹.

Figure 5. Arrhenius plots for the rate of NO₂ 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.

\[ \text{Rate} = k \times [\text{H}_2]^{0.45} \] (4)
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 NOₓ over Ag/Al₂O₃ and Al₂O₃ was investigated (Figure 6). In the absence of H₂, neither Ag/

![Figure 6](image)

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),²⁻⁵ bidentate nitrates (1590 cm⁻¹),²⁰,³⁰,³¹ and monodentate nitrates (1560, 1540, 1520, and 1300 cm⁻¹).¹,²²⁰ 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

3NO₂ + O²⁻ → 2NO₃⁻ + NO₂(gas)  (5)

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 6 B). 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 substitution 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 were observed on both samples. According to the literature, the absorbance peaks at 1625, 1275, and 1230 cm⁻¹ could be assigned to NH₃ adsorption on Lewis acid sites (LNH₃ 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 (BNH₃ 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 BNH₃ species was significantly more than that of the LₐNH₃ species.
3.3.2. Reactivity of Intermediates. The reactivity of different nitrate species toward H₂ + NH₃ + O₂ 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 ~50% decrease in peak area within 5 min. In contrast, the monodentate nitrate exhibited low reactivity toward H₂ + NH₃ + O₂, with only ~10% decrease in the peak area during the above process. Clearly, the bridging and bidentate nitrates were much more reactive toward NH₃ 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 H₂ + NH₃ + O₂ was much faster than its formation in H₂ + NO + O₂ (Figure S10), revealing that the formation of this species was much slower than its further reaction with NH₃ species. The reactivity of adsorbed NH₃ species toward NO₂ + O₂ was also investigated over Ag/Al₂O₃ (Figure 9). To eliminate the influence of H₂ on the catalysts and the adsorbed species, NO₂ + O₂ rather than H₂ + NO + O₂ was employed in this experiment. The B NH₃ species (3100–3200 cm⁻¹) continuously reacted with nitrate species in the flow of NO₂ + O₂, and it were completely consumed within 20 min. Correspondingly, bridging and bidentate nitrates were gradually observed after the complete consumption of B NH₃ species. In contrast, the monodentate nitrate was rapidly produced upon exposure to NO₂ + O₂. Besides, the consumption of L NH₃ species was hardly observed, which was possibly due to its low intensity or low reactivity. Therefore, it was proposed that the reaction of B NH₃ species with the bridging and bidentate nitrates was the main pathway for NOₓ reduction.

3.3.3. Regeneration of the Ag/Al₂O₃ Catalyst. As mentioned above, both Ag/Al₂O₃ and Al₂O₃ were gradually deactivated in a flow of NO₂ + NH₃ + O₂, while Ag/Al₂O₃ could be regenerated in a flow of H₂ + O₂ (Figure 3). Hence, the effects of H₂ + O₂ regeneration on these samples were investigated by in situ DRIFTS (Figure 10). After exposure to a flow of NO₂ + NH₃ + O₂ for 60 min, large amounts of
nitrates were produced on these samples, while adsorbed NH3 species were hardly observed. In addition, the absence of feature peak assignable to NH2NO3 (1450–1530 cm−1)37 further confirmed that NOx was reduced to N2 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 –OH species. On Ag/Al2O3, regeneration promoted the desorption of nitrates and the recovery of –OH species.39 The oxidation of NO to yield NO2 over Ag/Al2O3 (Figure 2A) possibly originated from the desorption of nitrate species induced by H2. Notably, the desorption rate of nitrate species in this experiment was much slower than the consumption rate shown in Figure 8, further revealing that NO oxidation to produce NO2 was much slower than NOx reduction. Considering that the –OH species were critical for the formation of B-NH3 species, the recovery of –OH species possibly contributed to the regeneration of Ag/Al2O3. On Al2O3, however, regeneration showed little effect on the adsorbed nitrate species or –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 NOx reduction in NH3-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 NH3 species react with nitrates or gaseous NOx 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 O2 to a high oxidation state in the oxidation half-cycle. For the H2-NH3-SCR over Ag/Al2O3, it was proposed that H2 plays an important role in the redox cycling of Ag species during NOx reduction.

As mentioned above, the H2-NH3-SCR reaction over Ag/Al2O3 started with the oxidation of NO to produce nitrate species. Both the Ag species and H2 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 (Ag0) catalytically oxidized NO to produce nitrate species, resulting in the formation of oxidized silver species. Afterward, H2 reduced the oxidized Ag species to generate Ag0 and H2O53 and thus induced the desorption and migration of nitrates. The formation of NO2 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 NO2 could reduce 2 moles of Ag+, the stoichiometry of Ag:NO:H2 for the generation of nitrates was equal to 1:1:0.5. Shimizu et al.12,24 proposed a reductive activation of O2 by Ag0 clusters to produce superoxide ion. In the present work, indeed, it is also reasonable that superoxide ion would be produced on the Ag0 site before it further reacted with NO to generate nitrates. Then, the oxidized Ag species would be reduced by H2 via eq 7. Besides, Olsson et al.59 suggested that the effect of H2 is to free Ag from the single O atom, which could be considered as another way to describe the reduction of oxidized Ag species.

\[
\text{Ag}^0 + \text{NO} + \text{O}_2 = \text{Ag}^+ \cdot_\text{NO}_3^- \tag{6}
\]

\[
2\text{Ag}^+ \cdot_\text{NO}_3^- + \text{H}_2 + \text{Al} - \text{O} - \text{Al} = 2\text{Ag}^0 + \text{H}_2\text{O} + 2\text{Al}_\text{NO}_3^- \tag{7}
\]

There were two active sites on Ag/Al2O3 and Al2O3 for NH3 adsorption, namely, the Bronsted acid site and the Lewis acid site, the former of which showed much higher intensity compared to the latter. More importantly, the B-NH3 species exhibited higher reactivity toward nitrate species during NOx reduction compared to the L-NH3 species. Therefore, the –OH species, which served as the adsorption sites for B-NH3 species, were critical for this reaction. On the other hand, the bridging and bidentate nitrates were more reactive toward adsorbed NH3 species compared to monodentate nitrate. Hence, the main reaction path could be considered as B-NH3 species reacting with the bridging and bidentate nitrates to produce nitrosoamide (NH2NO) or ammonium nitrite (NH4NO2), which are frequently suggested as important intermediates for the generation of N2 and H2O.39,40,45,46 Kondratenko et al.11,14 proposed that N2 originated from the decomposition of surface NH2-NO species during H2-NH3-SCR over Ag/Al2O3. Shimizu et al.22 suggested that the superoxide ion was important for the activation of NH3 to yield NH2., which further reacted with nitrates to yield N2 and H2O. Besides, the formation of NH2-NO2 via NH4+ reacting with nitrates or gaseous NOx should also be considered as a possible route since NH2-NO2 is highly unstable and easily decomposes to N2 and H2O even at low temperatures.47 It is worth noting that Gao et al.40 investigated the reaction pathway involving NH2-NO and NH2-NO2 by DFT calculations and proposed that the “NH2-NOx” pathway was energetically more favorable and served as the main reaction pathway for NOx reduction. Hence, it could not be unambiguously confirmed whether NH2-NO3 or NH2-NO served as the precursor for the formation of N2 and H2O.

As neither Ag/Al2O3 nor Al2O3 were active for the oxidation of NO to produce nitrates in the absence of H2, NO could not be reduced on these samples during NH3-SCR. In contrast, NO2 could be reduced on both samples under similar conditions, although these samples were gradually deactivated during the overall process. After deactivation, Ag/Al2O3 could be almost completely regenerated in a flow of H2 + O2, while Al2O3 was hardly recovered during the same process. As NO2 reduction occurred at the surface of Al2O3, the deactivation should be related to the properties of Al2O3 and H2 + O2.
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 Al2O3, thereby reducing the active sites for NH3 adsorption and its further reaction.35 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 NH3 activation, they should not be responsible for the deactivation of these catalysts because superoxide ions have not been detected on Ag/Al2O3 or Al2O3 in the absence of H2.12,44 Considering the critical effect of −OH species on the adsorption of BNH3 species, which served as an important intermediate for NO2 reduction, the consumption of −OH species seemed to be the reason for the deactivation of these samples. More fundamentally, as N in NH3 was in the valence state of −3 and N in NO2 was in the valence state of +5, the formation of N2 needed another electron, which could not be recovered under this reaction condition.

During the regeneration process (Figure 10), the nitrate species were desorbed and −OH species were restored on Ag/Al2O3, while little effect was observed on Al2O3. Shimizu et al.44 employed an H/D isotopic exchange experiment to investigate the effect of H2 reduction on the dehydrated Ag/Al2O3. They proposed that H2 (D2) dissociated on the Ag sites to produce acidic protons, which further spilled over to the Al2O3 surface. During the regeneration process, H atom transferred an electron to Ag/Al2O3 and thus restored the electron consumed in the formation of N2 and simultaneously recovered the −OH species. In our recent work,48 it was found that BNH3 species exhibited high reactivity toward O2 to produce N2 during the selective catalytic oxidation of NH3 over Ag/Al2O3. Hence, the recovery of adsorption sites for BNH3 species would also contribute to the improvement of the NH3 oxidation over Ag/Al2O3 (Figure 2B).

Based on the above discussion, a complete catalytic cycle for the H2-NH3-SCR reaction over Ag/Al2O3 was proposed (Scheme 1). First, Ag0 catalytically oxidized NO to produce nitrates, which further migrated to the Al2O3 surface (eqs 6 and 7). Simultaneously, NH3 adsorbed on the −OH species to yield −NH4+, which further reacted with −NO3− to produce N2 and H2O (eqs 8 and 9). Notably, as N in −NH4+ was in the valence state of −3 and N in −NO3− was in the valence state of +5, the reaction of N2 generation needed another two electrons, thus resulting in the formation of two unsaturated O atoms. Afterward, H2 dissociated on metallic Ag species, further spilled over to the Al2O3 surface, transferred electrons to the unsaturated O atoms, and simultaneously restored the −OH species.44 Subsequently, another catalytic cycle involved N2 formation and −OH recovery occurred (eqs 8–10). Ultimately, the −OH species dehydrated to produce H2O and restored the Al−O−Al bond (eq 11), thus completing the catalytic cycle for NOx 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 Al2O3 surface provided the active sites for the reduction of NOx, while Ag species contributed to the oxidation of NO to produce nitrates and to the dissociation of H2 to restore the −OH species. The global stoichiometry between NO: NH3:H2 was equal to 1:1:1.5, where 1.5 H2 contributed to the reduction of Ag0 and the recovery of two electrons consumed in N2 formation.

Scheme 1. Proposed Mechanism for the H2-Assisted NH3-SCR over Ag/Al2O3 catalysts

\[
\text{Al}_2\text{O}_3 + \text{NO} + \frac{3}{2}\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + 2\text{Ag}^+ + \frac{3}{2}\text{O}_2
\]
4. CONCLUSIONS

Ag/Al₂O₃ was completely inactive for NO₃ reduction during NH₃-SCR, while H₂ addition significantly enhanced its deNOₓ activity. The overall chemical reaction equation was as follows: 2NO + 2H₂ + O₂ + 3H₂ = 2N₂ + 6H₂O. Kinetic results revealed that the reaction obeyed the Langmuir–Hinshelwood mechanism and that the reduction rate of NOₓ 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 NOₓ 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
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ASSOCIATED CONTENT

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Notes
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