Investigation of Water and Sulfur Tolerance of Precipitable Silver Compound Ag/Al_2O_3 Catalysts in H_2-Assisted C_3H_6-SCR of NOx

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ABSTRACT: Ag/Al_2O_3 catalysts containing different precipitable silver compounds (AgCl, Ag_2SO_4, and Ag_3PO_4) were synthesized and investigated for NOx reduction in H_2-assisted C_3H_6-selective catalytic reduction (SCR). The samples were systematically characterized by N_2 adsorption, X-ray diffraction (XRD), UV–Vis, X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HR-TEM). N_2 adsorption revealed that the introduction of anions (Cl\textsuperscript{-}, SO_4\textsuperscript{2-}, and PO_4\textsuperscript{3-}) did not significantly affect the surface and structural properties of the Al_2O_3 support. However, XRD patterns and HR-TEM images indicated that the addition of Cl\textsuperscript{-} anions caused the agglomeration of silver species to form large AgCl particles on the AgCl/Al_2O_3 catalysts. In contrast, the silver species dispersed well on Ag_2SO_4/Al_2O_3 and Ag_3PO_4/Al_2O_3 catalysts. Furthermore, similar suppression was also found on 5 wt % Ag/Al_2O_3 in H_2-C_3H_8-SCR. Moreover, similar suppression was also found on 5 wt % Ag/Al_2O_3 in H_2-C_3H_6-SCR. Besides, it was proposed that the valence state of silver species affected the performance of Ag/Al_2O_3 in H_2-C_3H_6-SCR containing moisture, which was related to the formation of inert surface formate.

1. INTRODUCTION

NOx emission from diesel engines causes severe environmental issues such as acid rain, photochemical smog, and haze. Selective catalytic reduction (SCR) of NOx is the commercial technology utilized for NOx elimination in heavy-duty diesel engine vehicles. In addition to the widely used reductant of ammonia (NH_3-SCR), hydrocarbons can also be employed in NOx reduction (HC-SCR). In particular, ethanol and propene have shown high efficiency for NOx reduction at moderate temperatures. In general, it is accepted that Ag/Al_2O_3 is the most efficient catalyst for HC-SCR. Moreover, traces of H_2 can significantly improve the catalytic activity of Ag/Al_2O_3 in HC-SCR.

Since diesel engine exhausts contain a lot of moisture, SCR catalysts must have excellent water resistance. Nevertheless, the effect of H_2O on the HC-SCR reaction has rarely been systematically studied. Shimizu et al. studied the influence of water vapor on HC-SCR using different alkanes, and they found that the alkanes with higher carbon numbers exhibited better water tolerance. Meunier et al. found that H_2O severely suppressed the performance of 1.2 wt % Ag/Al_2O_3 in C_3H_8-SCR. Moreover, similar suppression was also found on 5 wt % Ag/Al_2O_3 in H_2-C_3H_8-SCR. Besides, it was proposed that the valence state of silver species affected the performance of Ag/Al_2O_3 in H_2-C_3H_6-SCR containing moisture, which was related to the formation of inert surface formate.

Sulfur poisoning is another challenge for HC-SCR catalysts, although the amount of sulfur dioxide in diesel engine exhausts has gradually decreased. Ag/Al_2O_3 catalysts show moderate sulfur resistance in HC-SCR, related to the reaction conditions. In general, SO_2 can react with the active sites to produce stable sulfates, thus suppressing NOx reduction. Meunier et al. proposed that these sulfate species resulted in permanent deactivation of 1.2 wt % Ag/Al_2O_3 in C_3H_8-SCR. In contrast, Houel et al. and Park et al. found that Ag/Al_2O_3 catalysts could be regenerated after the removal of SO_2. It was also reported that the nature of the reductant affected the performance of Ag/Al_2O_3 in HC-SCR containing SO_2. More recently, it was proposed that the sulfur resistance of Ag/Al_2O_3 is affected by the mobility of sulfate species, which is closely related to the state of silver species.

Hence, both water and sulfur tolerance are important factors for SCR catalysts utilized in diesel engines after treatment. With this in mind, herein, we prepared Ag/Al_2O_3 catalysts containing different precipitated silver compounds (AgCl, Ag_2SO_4, and Ag_3PO_4) and investigated the water and sulfur tolerances of these catalysts in H_2-assisted C_3H_6-SCR. These samples were systematically investigated by Brunauer–
Emmett–Teller (BET), X-ray diffraction (XRD), UV–vis, X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM), and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). It was found that these samples showed distinct differences in their water and sulfur tolerances, which were nearly related to the state of silver species on these catalysts. Hence, this work provides some advice for designing efficient and stable SCR catalysts for NOx elimination in diesel engines.

2. RESULTS AND DISCUSSION

2.1. Activity Test. The water tolerance of Ag/Al2O3 catalysts in H2-C3H6-SCR is shown in Figure 1. The Ag/Al2O3 catalysts with 2 wt % silver loading showed high efficiency for NOx reduction in the range of 350–550 °C in the absence of water vapor, although the 2% Ag3PO4/Al2O3 catalyst showed slightly lower NOx conversion in the high-temperature region. In the presence of water vapor, the low-temperature activity of 2% AgCl/Al2O3 was suppressed to some extent. Nevertheless, the 2% Ag2SO4/Al2O3 and 2% Ag3PO4/Al2O3 catalysts still exhibited excellent deNOx performance at 350–550 °C. Clearly, the Ag3SO4/Al2O3 catalyst showed better deNOx performance than the AgCl/Al2O3 and Ag3PO4/Al2O3. Ag3SO4/Al2O3 catalysts with higher silver contents showed better low-temperature deNOx activity in the absence of water vapor, with >95% NOx conversion at 300–500 °C. Even in the presence of water vapor, these samples were efficient for NOx reduction at about 300–500 °C. It is worth noting that 3% Ag2SO4/Al2O3 exhibited the best catalytic performance regardless of the presence of water vapor. For AgCl/Al2O3 and Ag3PO4/Al2O3 with higher silver loading, their activities were severely suppressed by water vapor, especially in the low-temperature region (Figure S1). As shown in Figure 2, the trends for C3H6 conversion were
approximately consistent with the NO\textsubscript{x} conversion. For example, the increase of silver loading on the Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts gradually reduced the light-off temperature of C\textsubscript{3}H\textsubscript{6} conversion in the absence of water vapor. The presence of water vapor also reduced C\textsubscript{3}H\textsubscript{6} conversion to some extent over all samples, consistent with the NO\textsubscript{x} conversion results. By the way, the normal Ag/Al\textsubscript{2}O\textsubscript{3} catalysts have been systematically investigated in H\textsubscript{2}-C\textsubscript{3}H\textsubscript{6}-SCR in our previous work,\textsuperscript{14,15,27} including the catalytic performance, water tolerance, and sulfur resistance. For the sake of brevity, the water and sulfur tolerances of the normal sample have not been emphatically investigated in the present work.

As shown in Figure 3, the deNO\textsubscript{x} activity of Ag/Al\textsubscript{2}O\textsubscript{3} catalysts with 2 wt % silver loading was gradually suppressed after SO\textsubscript{2} exposure and the NO\textsubscript{x} conversion decreased from 99 to \sim 60% within 3 h. Among these samples, the 2% AgCl/Al\textsubscript{2}O\textsubscript{3} catalyst showed slightly better sulfur tolerance in this experiment. Nevertheless, the deactivation induced by SO\textsubscript{2} could be gradually recovered to some extent after the removal of SO\textsubscript{2}. As for the Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts with higher silver contents (3, 4, and 5 wt %), it should be noted that SO\textsubscript{2} exposure only had little effect on their deNO\textsubscript{x} performance. More importantly, such an effect could be completely recovered after SO\textsubscript{2} removal. Considering water tolerance and sulfur resistance, 3% Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} was the most efficient catalyst for NO\textsubscript{x} reduction in H\textsubscript{2}-C\textsubscript{3}H\textsubscript{6}-SCR.

### 2.2. Characterization

The surface and structural properties of Ag/Al\textsubscript{2}O\textsubscript{3} catalysts were characterized by N\textsubscript{2} adsorption and XRD. As shown in Table 1, these samples had specific surface areas of about 200–220 m\textsuperscript{2}/g, which were only slightly smaller than that of pure Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{27} The decrease in the surface area could be attributed to the blockage caused by the precipitated silver compounds in the channels of the Al\textsubscript{2}O\textsubscript{3} support. Also, these samples had a pore volume of \sim 0.55 cm\textsuperscript{3}/g and an average pore size of 10 nm. Generally, this slight difference in surface properties should not significantly affect the catalytic performance of the catalysts. XRD patterns showed that the \gamma-Al\textsubscript{2}O\textsubscript{3} phase (2\theta = 37.2, 45.8, and 66.9°) was observed for all Ag/Al\textsubscript{2}O\textsubscript{3} catalysts (Figure 4). Moreover, the AgCl phase (2\theta = 27.7, 32.2, and 46.2°) also emerged on the 2% AgCl/Al\textsubscript{2}O\textsubscript{3} and 5% AgCl/Al\textsubscript{2}O\textsubscript{3} samples (Figure S2), indicating the formation of large AgCl particles.\textsuperscript{28} In contrast, no silver phase was detected on the Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts even under high silver loadings, which indicated that the silver species had been well-dispersed on these samples.

![Figure 3](image-url) Conversions of NO\textsubscript{x} (A) and C\textsubscript{3}H\textsubscript{6} (B) in the sulfur tolerance experiment on Ag/Al\textsubscript{2}O\textsubscript{3} catalysts at 400 °C. Feed composition: 800 ppm NO, 1714 ppm C\textsubscript{3}H\textsubscript{6}, 1% H\textsubscript{2}, 50 ppm SO\textsubscript{2} (when added), 10% O\textsubscript{2}, N\textsubscript{2} balance. GHSV: 100 000 h\textsuperscript{-1}.

![Figure 4](image-url) XRD pattern of the 2% Ag/Al\textsubscript{2}O\textsubscript{3} catalysts containing different precipitable silver compounds (A) and the Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts with different silver loadings (B).

**Table 1. Structural Parameters of Ag/Al\textsubscript{2}O\textsubscript{3} Catalysts**

| sample                  | BET surface area (m\textsuperscript{2}/g) | pore volume (cm\textsuperscript{3}/g) | average pore size (nm) | surface Ag proportion\textsuperscript{a} (mass %) |
|-------------------------|------------------------------------------|----------------------------------------|------------------------|-----------------------------------------------|
| Al\textsubscript{2}O\textsubscript{3}\textsuperscript{27} | 237                                      | 0.51                                    | 9.8                    |                                               |
| 2% Ag/Al\textsubscript{2}O\textsubscript{3} | 196                                      | 0.51                                    | 10.5                   | 3.06                                          |
| 2% AgCl/Al\textsubscript{2}O\textsubscript{3} | 200                                      | 0.54                                    | 10.8                   | 1.33                                          |
| 5% AgCl/Al\textsubscript{2}O\textsubscript{3} | 220                                      | 0.53                                    | 9.6                    | 2.53                                          |
| 2% Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} | 218                                      | 0.54                                    | 9.9                    | 2.95                                          |
| 3% Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} | 218                                      | 0.56                                    | 10.3                   | 3.82                                          |
| 4% Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} | 215                                      | 0.53                                    | 9.9                    | 4.61                                          |
| 5% Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} | 236                                      | 0.55                                    | 9.4                    | 6.18                                          |
| 2% Ag\textsubscript{3}PO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} | 211                                      | 0.54                                    | 10.1                   | 3.32                                          |
| 5% Ag\textsubscript{3}PO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} | 215                                      | 0.56                                    | 10.4                   | 8.51                                          |

\textsuperscript{a}Obtained by the XPS spectra in Figures 6 and S4.
UV–Vis analysis was performed to investigate the valence state of silver species on these Ag/Al₂O₃ catalysts (Figures 5 and S3). Four adsorption peaks (220, 260, 290, and 350 nm) were observed on these samples. They could be attributed to dispersed silver cations (Ag⁺, 220 nm), partially oxidized silver clusters (Agₓ⁰⁺ₓ, 260 nm), and metallic silver clusters (Agₓ⁰, 290 and 350 nm), respectively. Moreover, a strong peak due to AgCl particles (260 nm) was also observed on 2% AgCl/Al₂O₃. On the Ag₂SO₄/Al₂O₃ samples with higher silver loadings, in addition to a large amount of dispersed silver cations, the amount of metallic silver clusters gradually increased with an increase in silver content. Besides, there was a wide band (400–600 nm) due to Ag₃PO₄ particles observed on 5% Ag₃PO₄/Al₂O₃.32

XPS analysis was further performed to study the valence state of silver species on these Ag/Al₂O₃ catalysts (Figure 6). The binding energy bands of the Ag 3d₅/₂ orbit were located at 367.4–368.0 eV, which is consistent with our previous work.11 Notably, the binding energy of the Ag 3d₅/₂ orbit on 2% AgCl/Al₂O₃ was significantly lower than 2% Ag₂SO₄/Al₂O₃ and 2% Ag₃PO₄/Al₂O₃. It might be due to the greater electronegativity of chloride ions, which reduced the electron cloud density around the Ag atoms. Similarly, the silver species on the 5% AgCl/Al₂O₃ sample also had a smaller binding energy than that on 5% Ag₃PO₄/Al₂O₃ (Figure S4). On Ag₂SO₄/Al₂O₃ catalysts, the increase of silver loading only increased the binding energy intensity but did not affect the value of the binding energy. Moreover, XPS analysis showed the surface silver proportion on 2% Ag/Al₂O₃ catalysts (Figure 6). The binding energy of the Ag 3d₅/₂ orbit were located at 367.4–368.0 eV, which is consistent with our previous work.11

Figure 5. UV–Vis spectra of the 2% Ag/Al₂O₃ catalysts containing different precipitable silver compounds (A) and the Ag₂SO₄/Al₂O₃ catalysts with different silver loadings (B).

Figure 6. XPS spectra of 2% Ag/Al₂O₃ catalysts containing different precipitable silver compounds (A) and Ag₂SO₄/Al₂O₃ catalysts with different silver loadings (B).

Ag₂SO₄/Al₂O₃ with higher silver loadings followed the same rule. In contrast, the surface silver concentrations on 2% AgCl/Al₂O₃ (1.33%) and 5% AgCl/Al₂O₃ (2.53%) were significantly lower than the setting values. One of the most important reasons is that XPS analysis could only detect surface elements with a depth of less than a few nanometers. As indicated by the XRD pattern and HR-TEM images (Figure 7), the silver species on the AgCl/Al₂O₃ catalysts were mainly presented as large nanoparticles. Consequently, the silver species in AgCl nanoparticles’ core could not be detected by XPS analysis, resulting in the underestimation of the surface silver concentration on AgCl/Al₂O₃ catalysts.

HR-TEM was further performed to investigate the morphology of the Ag/Al₂O₃ catalysts (Figure 7). On 2% AgCl/Al₂O₃, the Ag species aggregated and large AgCl particles with 40–60 nm in diameter were observed. Moreover, the AgCl particles on 5% AgCl/Al₂O₃ showed an even slightly larger diameter (50–80 nm). In contrast, the silver species dispersed well on 2% Ag₂SO₄/Al₂O₃, and the silver nanoparticles showed a diameter of about 5 nm. Besides, the increase of silver loading had little effect on the silver nanoparticles on 5% Ag₂SO₄/Al₂O₃. Similarly, the silver species on Ag₃PO₄/Al₂O₃ catalysts also dispersed well regardless of the silver loading. The TEM images were consistent with the XRD results that the silver species on the Ag₂SO₄/Al₂O₃ and Ag₃PO₄/Al₂O₃ catalysts were highly dispersed.

2.3. In Situ DRIFTS. The partial oxidation of C₃H₆ over Ag/Al₂O₃ catalysts was studied by in situ DRIFTS (Figures 8, S5, and S6). There were three intermediates obtained in this experiment, including formate (1375, 1394, and 1591 cm⁻¹), acetate (1460 and 1575 cm⁻¹), and enolic species (1408 and 1636 cm⁻¹). On 3% Ag₃SO₄/Al₂O₃, acetate was the predominant intermediate and a considerable amount of
enolic species was also observed. Notably, the formation of acetate and enolic species was hardly affected by H2O addition on 3% Ag2SO4/Al2O3. However, on 2% AgCl/Al2O3, formate was the primary intermediate at low temperature, and acetate was predominant at high temperature, while the enolic species was hardly observed (Figure S5). Besides, H2O addition slightly affected the partial oxidation of C3H6 on this sample. As for the 2% Ag3PO4/Al2O3 sample, considerable amounts of enolic species and acetate were produced (Figure S6). However, H2O addition significantly suppressed the partial oxidation of C3H6 on this sample, especially the formation of enolic species.

The effect of H2O on the H2-assisted C3H6-SCR reaction was also investigated by in situ DRIFTS (Figures 9, S7, and S8). In addition to the oxygenated hydrocarbons mentioned above, there were other intermediates produced during the SCR reaction, including nitrate species (1300 and 1540 cm⁻¹), −CN species (2160 and 2170 cm⁻¹), and −NCO species (2230 cm⁻¹). Among them, the −NCO species has been widely accepted as the most important precursor for the formation of N2. On 3% AgSO4/Al2O3, H2O addition inhibited the formation of oxygenated hydrocarbons, especially the inert formate (1591 cm⁻¹), which was consistent with our previous work. In contrast, the generation of reactive −NCO species was hardly affected by the moisture, indicating that the reduction of NOx was not inhibited by H2O addition. However, on 2% AgCl/Al2O3, the inert formate was the primary intermediate, and there were more −CN species than...
processes, H\textsubscript{2}O and SO\textsubscript{2} may affect the valence state and microstructure of silver species had an essential effect on the SCR reaction. BET analysis revealed that Cl\textsuperscript{−} anion addition could strongly affect the valence state of silver species on AgCl/Al\textsubscript{2}O\textsubscript{3} by reducing the electron cloud intensity around the Ag atoms.

During H\textsubscript{2}-C\textsubscript{3}H\textsubscript{6}-SCR, the Ag/Al\textsubscript{2}O\textsubscript{3} catalysts with low silver loading (2 wt %) showed similar deNO\textsubscript{x} activity to 2\% AgPO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} exhibiting slightly worse performance in the absence of water vapor, while 2\% AgCl/Al\textsubscript{2}O\textsubscript{3} showed worse water tolerance. This phenomenon was even more remarkable for the samples with higher silver loading (5 wt %). In contrast, the AgSO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts showed excellent water tolerance regardless of the silver loading. Besides, the addition of water vapor slightly shifted the reaction window of NO\textsubscript{x} reduction to a higher temperature, possibly due to its suppression on the low-temperature activation of C\textsubscript{3}H\textsubscript{6} and the high-temperature combustion of C\textsubscript{3}H\textsubscript{6}. In the sulfur tolerance experiment, all Ag/Al\textsubscript{2}O\textsubscript{3} catalysts with 2 wt % silver loading were deactivated to some extent after exposure to SO\textsubscript{2}, whereas such deactivation could be recovered gradually after SO\textsubscript{2} removal. It was proposed that the deactivation induced by SO\textsubscript{2} was attributed to the formation of sulfate species, which covered the catalyst surface and thus inhibited NO\textsubscript{x} reduction. It should be noted that AgSO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts, especially 3\% AgSO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3}, exhibited superior water tolerance and sulfur resistance during the H\textsubscript{2}-C\textsubscript{3}H\textsubscript{6}-SCR reaction. Incidentally, the amount of H\textsubscript{2} used in this reaction was slightly higher; hence, considering the fuel penalty, reducing the H\textsubscript{2} concentration required for the HC-SCR reaction is an important issue.

\textbf{2.4. Discussion.} It is widely accepted that HC-SCR starts with the partial oxidation of hydrocarbons to produce reactive oxygenated hydrocarbons such as enolic species and acetae. Then, the reactive oxygenated hydrocarbons further react with nitrate species or NO to yield -NCO species, which is the most important precursor for N\textsubscript{2}.\textsuperscript{2,5,8} During the above processes, H\textsubscript{2}O and SO\textsubscript{2} may affect the formation of reactive intermediates through competitive adsorption or changing the catalyst’s properties. For example, moisture could suppress inert formate formation and release active sites for NO\textsubscript{x} reduction on 2\% Ag/Al\textsubscript{2}O\textsubscript{3}.	extsuperscript{15} Besides, SO\textsubscript{2} could react with the dispersed silver cations to produce thermodynamically inert formate formation and release active sites for NO\textsubscript{x} reduction.	extsuperscript{27} According to our previous reports,\textsuperscript{14,15,27} the valence state and microstructure of silver species had an essential effect on the water and sulfur tolerance of Ag/Al\textsubscript{2}O\textsubscript{3} catalysts in H\textsubscript{2}-C\textsubscript{3}H\textsubscript{6}-SCR. Hence, accurately controlling the state of silver species on Ag/Al\textsubscript{2}O\textsubscript{3} catalysts is essential in improving the water and sulfur tolerances.

In the present work, anions (Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, and PO\textsubscript{4}\textsuperscript{3−}) were introduced to interfere with the valence state of silver species on Ag/Al\textsubscript{2}O\textsubscript{3} catalysts. BET analysis revealed that the introduction of anions did not significantly affect the surface and structural properties of Ag/Al\textsubscript{2}O\textsubscript{3} catalysts, which showed a similar specific surface area and crystal structure to that of pure γ-Al\textsubscript{2}O\textsubscript{3}. Nevertheless, XRD measurements showed that the introduction of Cl\textsuperscript{−} anions caused the agglomeration of silver species to form large AgCl particles on AgCl/Al\textsubscript{2}O\textsubscript{3} catalysts. In contrast, the silver species dispersed well on AgSO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} and AgPO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts. HR-TEM images further confirmed that the silver particles on AgCl/Al\textsubscript{2}O\textsubscript{3} catalysts were about 10 times larger than those on Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} and Ag\textsubscript{3}PO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts. Besides, XPS analysis revealed that Cl\textsuperscript{−} anion addition could strongly affect the valence state of silver species on AgCl/Al\textsubscript{2}O\textsubscript{3} by reducing the electron cloud intensity around the Ag atoms.

3. CONCLUSIONS

Ag/Al\textsubscript{2}O\textsubscript{3} catalysts containing different precipitable silver compounds (AgCl, Ag\textsubscript{2}SO\textsubscript{4}, and Ag\textsubscript{3}PO\textsubscript{4}) were synthesized and investigated for NO\textsubscript{x} reduction in H\textsubscript{2}-C\textsubscript{3}H\textsubscript{6}-SCR. The introduction of anions (Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, and PO\textsubscript{4}\textsuperscript{3−}) did not significantly affect the surface and structural properties of the Ag/Al\textsubscript{2}O\textsubscript{3} catalysts. Instead, the addition of Cl\textsuperscript{−} anions caused the agglomeration of silver species to form large AgCl particles on the AgCl/Al\textsubscript{2}O\textsubscript{3} catalysts. In contrast, the silver species dispersed well on the AgSO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} and AgPO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts regardless of the silver loading. Also, the partial oxidation of C\textsubscript{3}H\textsubscript{6} on Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} produced a large amount of reactive enolic species, while it tended to yield inert formate on AgCl/Al\textsubscript{2}O\textsubscript{3}. The above properties contributed to the better deNO\textsubscript{x} activity and water tolerance of the Ag\textsubscript{2}SO\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} catalysts.
4. EXPERIMENTAL SECTION

Ag/Al2O3 catalysts containing different precipitated silver compounds (AgCl, Ag2SO4, and Ag3PO4) were synthesized using an impregnation method. First, silver nitrate was added into the boehmite suspension. Afterward, NH4Cl, (NH4)2SO4, or (NH4)3PO4 was dripped into the above suspension. The suspension was then further stirred for 60 min, and the surplus water was evaporated in a rotary evaporator. Finally, these samples were baked at 120 °C overnight and then calcined in air at 600 °C for 5 h. These samples were labeled as AgCl/Al2O3, Ag2SO4/Al2O3, or Ag3PO4/Al2O3, where x represents the silver content.

Catalytic measurements were carried out in a horizontal reactor (7 mm). The typical reaction gas compositions consisted of NO (800 ppm), C2H2 (1714 ppm), H2 (1%), O2 (10%), and N2 balance (1000 mL/min). A 300 mg sample was employed, which corresponded to a GHSV of 100 000 h−1. Moisture was provided using a micropump and vaporized using an electric heater. The gas compositions were analyzed by a Fourier transform infrared (FT-IR) spectrometer (Nicolet iS10). The conversions of NOx and C2H2 were calculated according to previous work.

The N2 adsorption analysis was performed on a physisorption instrument (Quantachrome Autosorb-1C). XRD measurements were carried out on an X-ray diffractometer (Rigaku D/max-RB) using Cu Kα radiation. UV−vis analysis was carried out on a UV−vis spectrophotometer (Hitachi, U3100), utilizing BaSO4 as a reference. XPS analysis was performed on a scanning X-ray microprobe (PHI Quanta) with Al Kα radiation. The morphology of the catalysts was characterized by a high-resolution transmission electron microscope (TEM-2100 Plus, JEOL).

In situ DRIFTS experiments were carried out on a Nicolet FT-IR spectrometer (Nexus 670). The spectra were collected at a resolution of 4 cm−1 with an accumulation of 100 scans. Before measurement, the samples were pretreated in 10% O2/N2 at 400 °C for 0.5 h. Afterward, the temperature was ramped down to the desired temperature to collect a reference spectrum.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04631.

NOx conversion in H2-NH3-SCR, XRD patterns, UV−Vis spectra, XPS spectra, and in situ DRIFTS data (PDF)

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Notes

The authors declare no competing financial interest.

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