

Nanosize Effect of Al_2O_3 in Ag/Al_2O_3 Catalyst for the Selective Catalytic Oxidation of Ammonia

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Supporting Information

ABSTRACT: Ammonia (NH₃) has potentially harmful effects on human health and has recently been found to be an important factor in the formation of haze; thus, its emission control is urgent, especially during haze pollution periods. In this work, two kinds of Ag/Al₂O₃ catalysts with different Al₂O₃ particle sizes (micro-Al₂O₃ and nano-Al₂O₃) were prepared and tested for the selective catalytic oxidation of ammonia (NH₃-SCO). It was shown that Ag/nano-Al₂O₃ was much more active than Ag/micro-Al₂O₃ for NH₃-SCO in the low-temperature range. The results of characterization by BET, TEM, NH₃-TPD, XRD, H₂-TPR, UV–vis, and XAFS revealed that Ag/nano-Al₂O₃ possesses much smaller Ag particles and more metallic Ag species (Ag_{NPs}) and also contains abundant acid sites, which facilitate the adsorption and dissociation of NH₃, therefore resulting in much higher NH₃-SCO activity. In addition, on the basis of in situ DRIFTS, kinetic measurements, and DFT calculation results, we discovered that the NH₃-SCO reaction over Ag/nano-Al₂O₃ follows a reaction pathway we call the N₂⁻ mechanism.



KEYWORDS: ammonia (NH₃), Ag/Al₂O₃, low-temperature oxidation, reaction pathway, N_2^- mechanism

1. INTRODUCTION

Gaseous ammonia (NH₃), mainly emitted from agricultural sources, from industrial sources, or as a gas slip from the process of selective catalytic reduction of NO_x using NH₃ or urea (SCR) in deNO_x applications,¹ has potentially harmful effects on both human health and the environment. Importantly, it was recently reported that gaseous NH₃ greatly contributes to the formation of haze in China.¹⁻⁴ Thus, the control of NH₃ emissions is urgent, especially during periods of haze pollution.

There are a variety of techniques to eliminate gaseous ammonia, such as adsorption, absorption, biofiltration, catalytic combustion, catalytic oxidation, and so on.^{5–7} Considering the technical and/or economic limitations of treatment technologies, selective catalytic oxidation of ammonia (NH₃-SCO) into nitrogen and water is a highly promising process to reduce ammonia emissions. Various types of catalysts have been studied for NH₃-SCO and can be divided into three main groups, including supported noble metals (Ag, Pt, Au, Ir, etc.),^{8–14} supported transition-metal oxides (Fe₃O₄, Co₃O₄, NiO, CuO, etc.),^{15–22} and noble-/transition metal-modified zeolites (Cu-ZSM-5, Pd-Y, Rh-ZSM-5, Fe-Beta, etc.).^{23–26} Each category of catalysts has both advantages and disadvantages. Noble metals tend to possess high activity at low temperatures (110–280 °C),^{8–14} while their high cost and relatively low N₂

selectivity has restrained their widespread application. Transition-metal oxides and zeolites show high selectivity toward N₂; however, both of them need significantly higher operating temperatures (300-500 °C).^{15-21,23-26}

NH₃-SCO mechanisms have been also widely investigated, and three major reaction pathways have been proposed. One is often called the imide mechanism,^{27–30} in which NH₃ transforms to N₂ and N₂O as final products, with nitrosyl (HNO) as an intermediate. The second mechanism is called the hydrazine mechanism, with the formation of a hydrazinetype (N₂H₄) intermediate.^{30–32} The i-SCR mechanism (internal selective catalytic reduction) is the third mechanism of ammonia oxidation. This mechanism consists of ammonia oxidation to NO_x and NH₃-SCR in two main steps.^{15,33–35}

Ag-based catalysts used for NH₃ oxidation have been investigated in a number of studies.^{8,29,36–41} It was shown that alumina-supported Ag (Ag/Al₂O₃) catalysts had extremely high activity for NH₃ oxidation at low temperatures, even superior to that of noble-metal catalysts.^{37,38} Our previous work revealed that both the valence state and particle size of Ag species had a significant influence on the activity and N₂

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selectivity for the SCO of NH₃. Ag/Al₂O₃ catalysts with high surface areas and well-dispersed Ag⁰ particles favor greater activity at low temperature.⁸ The NH₃-SCO mechanisms over Ag-based catalysts were also studied, and both imide and i-SCR mechanisms were proposed.^{29,36}

It has been reported that nanosized supports have a significant influence on the dispersion of active sites, and nanosized supported catalysts tend to have relatively high activity.^{42–44} Therefore, in order to further improve the activity of Ag/Al₂O₃ catalysts for NH₃-SCO, we prepared an Ag/Al₂O₃ catalyst by using nanosized γ -Al₂O₃ as a support and then compared its activity with that of Ag/Al₂O₃ synthesized with microsized Al₂O₃. The results indicate that nanosized γ -Al₂O₃ supported Ag exhibited much higher catalytic performance in comparison to that of microsized Ag/Al₂O₃. Characterization techniques including BET, TEM, NH₃-TPD, XRD, H₂-TPR, UV-vis, and XAFS were utilized to elucidate the relationship between the catalytic performance and physicochemical properties. In addition, on the basis of in situ DRIFTS analysis and kinetic studies, we proposed a novel NH₃-SCO reaction mechanism.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. Nanosized γ -Al₂O₃ (Aladdin, average particle size 10 nm) supported Ag (Ag/Al₂O₃ nano) and microsized γ -Al₂O₃ (Sigma-Aldrich, average size 5 um) supported Ag (Ag/Al₂O₃ micro) samples were prepared by the impregnation method, with Ag loadings of 10 wt %. Typically, the same amounts of nano-Al₂O₃ and micro-Al₂O₃ powders were combined with Ag nitrate aqueous solutions having the same concentration and stirred for 3 h. The samples were dried at 120 °C overnight and then calcined at 500 °C for 3 h in air. The catalysts were sieved to 40–60 mesh powders before testing.

2.2. Sample Characterization. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL JEM 2010 TEM instrument with 200 kV acceleration voltage. The Ag dispersion was calculated on the basis of the average Ag particle size from the HR-TEM images. The specific surface area and pore size distribution of samples were determined by the Brunauer–Emmett–Teller (BET) method. The measurements were performed using a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co.). Prior to the nitrogen adsorption at -196 °C, the samples were outgassed under a nitrogen atmosphere at 300 °C for 4 h.

The elemental compositions of nano and micro-Al₂O₃ supports were analyzed by X-ray photoelectron spectra (XPS) and X-ray fluorescence (XRF) methods. The XPS measurements were recorded in a scanning X-ray microprobe (PHI Quantera, ULVAC-PHI, Inc.) using Al K α radiation. XRF measurements were performed on an Oxford ED 2000 X-ray fluorescence spectrometer. Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a computerized Bruker D8 ADVANCE diffractometer with Cu K α radiation source ($\lambda = 0.15406$ nm). The patterns were taken over the 2θ range from 10 to 90° at a scan speed of 6° min⁻¹. Diffuse-reflectance UV/vis spectra (UV/vis) were measured at room temperature in air with $BaSO_4$ as reference (U-3100 UV-vis spectrophotometer, Hitachi Co., Japan). All spectra were collected in the range of 190-800 nm with a resolution of 1 nm. IR spectra of nano- and micro-Al₂O₃ were collected through a NEXUS 670-FTIR spectrometer. About 2 mg of the

sample was mixed with 100 mg of KBr followed by drying under a heat lamp, and then the mixture was pressed into a transparent pellet die before FTIR measurement.

NH₃ temperature-programmed desorption (NH₃-TPD) experiments were performed in a Micromeritics AutoChem II 2920 apparatus, equipped with a computer-controlled CryoCooler, a thermal conductivity detector (TCD), and a quadrupole mass spectrometer (MKS Cirrus) to record the signals of NH₃ (m/z 17). Prior to TPD experiments, the samples (100 mg) were first pretreated with 20% O₂/Ar (50 mL/min) at 300 °C for 30 min and cooled to 50 °C. After purging with Ar for 30 min, the gas was switched to NH₃ for 60 min, followed by purging for another 30 min, and then the temperature was increased to 400 °C at a heating rate of 10 °C min⁻¹. To avoid the influence of H₂O, a cold trap was set before the MS detector.

 $\rm H_2$ temperature-programmed reduction (H₂-TPR) was performed in the same instrument as the NH₃-TPD. The samples (100 mg) were pretreated at 300 °C in a flow of 20% O₂/Ar (50 mL min⁻¹) for 30 min and cooled to 20 °C followed by Ar purging for 0.5 h. Then reduction profiles were obtained by passing a flow of 10% H₂/Ar (50 mL/min) through the sample from 20 to 700 °C at a ramp rate of 50 mL min⁻¹. The consumption of H₂ was continuously monitored using a thermal conductivity detector (TCD).

XANES and EXAFS analyses of the Ag K edges were respectively measured in transmission mode at room temperature on the BL14W1 XAFS beamline at the Shanghai Synchrotron Radiation Facility (SSRF). The PE storage ring was operated at 3.5 GeV with 200 mA as average storage current. The EXAFS data reduction and analysis were performed using the Athena program that is part of the IFFEFIT software package.⁴⁵ The filtered k^2 -weighted $\chi(k)$ was Fourier-transformed into *R* space (*k* range 2.2–12.8 Å⁻¹ for Ag K EXAFS).

The NH₃-SCO reaction mechanism was investigated by in situ DRIFTS in a NEXUS 670-FTIR instrument equipped with a smart collector and an MCT/A detector cooled with liquid nitrogen. A mixture containing 500 ppm of NH₃ and 10% O₂ at a total flow rate of 300 mL min⁻¹ was employed to investigate the behavior of the catalysts. All spectra presented here were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹. A background spectrum was subtracted from each spectrum.

2.3. Catalytic Test. The catalysts were tested for the NH₃-SCO reaction in a fixed-bed flow reactor (i.d. 4 mm) under atmospheric pressure. The composition of the gas mixture at the reactor inlet was NH₃ (500 ppm), O₂ (10 vol %), and balance N₂. The total flow rate of the reaction mixture was 100 mL/min, with a space velocity of 28000, 69000, 86000, or 115000 h⁻¹. The concentrations of inlet and outlet NH₃ and NO_x were analyzed with an online FTIR spectrometer equipped with a 2 m gas cell and a DTGS detector. Turnover frequency (TOF) was defined as the number of NH₃ molecules converted per surface Ag atom per second. Measurements of the turnover frequency (TOF) were obtained in a separate experiment, where the conversion of NH₃ was kept below 20% by varying the GHSV, and the computational formula is

$$\Gamma OF = \frac{\eta_{\rm NH_3} Q / (60V_{\rm m})}{(mw_{\rm Ag} D_{\rm Ag}) / M_{\rm Ag}}$$

where $\eta_{\rm NH_3}$ is the NH₃ conversion rate (<20%), *Q* is the gas flow rate (L/min), $V_{\rm m}$ is equal to 22.4 L/mol, *m* is the mass of Ag (g), $w_{\rm Ag}$ is the loading rate of Ag (%), $D_{\rm Ag}$ is the dispersion of Ag on Al₂O₃ (%) (calculated on the basis of the average Ag particle size from the HR-TEM images), and $M_{\rm Ag}$ is the relative molecular weight (g/mol).

2.4. Kinetic Measurements. Before kinetic measurements, two kinds of experiments were carried out to select suitable reaction conditions to eliminate both internal diffusion and external mass transfer resistances. The experimental details are presented in the Supporting Information, and the results are shown in Figure S3. It was shown that the external diffusion and internal diffusion limitation could be eliminated in a flow rate of 500 mL/min and with a grain size of Ag/Al₂O₃ samples of 0.25-0.43 mm. Therefore, the kinetic measurements were performed under the condition of 500 mL/min flow rate and 0.25–0.43 mm Ag/Al₂O₃ samples, and the NH₃ conversion was kept below 20% by adjusting the GHSVs in the range of $100000-2300000 \text{ h}^{-1}$. When the reaction order with respect to O₂ was measured, the concentration of NH₃ was kept constant at 500 ppm, while the concentration of O_2 was varied from 8% to 16% (8, 10, 12, 14, and 16 vol %).

2.5. DFT Calculations. DFT calculations were performed to confirm the infrared spectroscopy assignments. The Gaussian 03 program was used to optimize the structures and calculate the vibrational frequencies for the calculated models. The 3-21G basis set was employed to carry out the B3LYP calculations. Stationary points were identified as true local minima of the potential energy surface (PES) because no imaginary frequencies were found. The scaling factor 0.9614 was used in order to correct the frequency values.⁴⁶

3. RESULTS

3.1. Pore Structure and Particle Size. The morphologies of micro-/nano-Al₂O₃ loaded Ag catalysts were investigated by TEM measurements, and the TEM images are presented in Figure 1. From the image with low magnification shown in Figure 1A1, the micro-Al₂O₃ shows a large particle size of 500-1000 nm. From the image with high magnification shown in Figure 1A2, a wide distribution of Ag particles with nonuniform shapes were clearly observed on micro-Al₂O₃, and the average Ag particle size on micro- Al_2O_3 is about 7.5 nm. In contrast, the particle size of nano-Al₂O₃ is much smaller (about a tenth the size of micro-Al₂O₃ (Figure 1B1)). The Ag/nano-Al₂O₃ sample presents a narrower distribution of Ag size with more uniform shapes, and the average Ag particle size on nano-Al₂O₃ is 3.7 nm (Figure 1B2). The dispersion of Ag on nano-Al₂O₃ and micro-Al₂O₃ was then calculated on the basis of the average particle size and is summarized in Table 1. The results indicated that nano-Al₂O₃ was beneficial for Ag dispersion.

The elemental composition of the two types of Al_2O_3 was analyzed by using the XPS and XRF methods, and the results are summarized in Table S1. It can be seen that there is not much difference in elemental composition between the two kinds of Al_2O_3 . XRD patterns, UV–vis spectra, and IR spectra of two types of Al_2O_3 were also measured, and the results are shown in Figure S1. It can be seen that there are no obvious differences in the XRD, UV–vis, and IR spectra of the two supports. These findings suggest that the two types of Al_2O_3 have similar elemental compositions and identical crystal structures.



Figure 1. HRTEM of (A) Ag/micro-Al $_2O_3$ and (B) Ag/nano-Al $_2O_3$ catalysts.

Brunauer-Emmett-Teller (BET) measurements were next conducted to examine the pore properties of the samples. The data of the specific surface area, pore size, and pore volume are summarized in Table 1. As can be seen, the micro- Al_2O_3 and nano-Al₂O₃ supports showed similar BET specific surface areas (S_{BET}) , while presenting very different pore sizes and pore volumes. The N2 adsorption-desorption isotherms of the micro-Al₂O₃ and nano-Al₂O₃ samples are presented in Figure 2A,B. As shown in Figure 2A, the isotherm of the micro-Al₂O₃ sample belonged to type IV with a type H2 hysteresis loop. The Barrett-Joyner-Halenda (BJH) pore size distribution curve (inset in Figure 2A) shows that the pore distribution of micro-Al₂O₃ was narrow (around 3-10 nm) and the peak with highest probability appeared at 5.7 nm, which means that the pore sizes of micro- Al_2O_3 were relatively uniform. This result along with the V-t plot⁴⁸ in Figure 2C show that small-sized internal pores comprised the majority in micro-Al₂O₃, and thus the internal surface dominated the overall surface area. In contrast, the isotherm of the nano- Al_2O_3 sample (Figure 2B) is of type III with a type H3 hysteresis loop,⁴³ indicating the existence of plentiful piled holes between loose assemblages of particles. The pore size distribution of nano-Al₂O₃ is relatively broad, with two peaks in the pore size distribution. The small peak with the most probable size of 4.2 nm would correspond to the internal pores of Al₂O₃ particles, while another broad peak in the range of 6-60 nm corresponds to the piled pores between the nanoparticles. Meanwhile, it can also be seen in Table 1 that the pore volume of nano- Al_2O_3 is almost 3 times larger than that of micro-Al₂O₃. Therefore, the piled pores of nano-Al₂O₃ particles make up the majority, and correspondingly most of the nanosized Al₂O₃ surface area is external surface area. The Al₂O₃ surface exhibits a high population of diverse surface Al-OH groups as well as surface defect sites, which cause high metal dispersion.⁴⁹ Thus, the Al₂O₃ surface, especially the external surface, plays an important role in the loading and dispersion of active components. This may explain the huge difference in Ag particle size between Ag/nano-Al₂O₃

Table	e 1.	Ag	Particle	Size,	Dispersion,	BET	Surface 1	Area,	Pore	Size,	and	TOF	of the	Catalysts
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sample	Ag mean particle size $(nm)^a$	Ag dispersion (%) ^b	BET (m^2/g)	pore volume (mL/g)	pore diameter (nm)	TOF $(s^{-1})^c$
micro-Al ₂ O ₃			222.6	0.29	5.7	
nano-Al ₂ O ₃			216.1	0.86	18.9	
Ag/micro-Al ₂ O ₃	7.5	17.9	147.2	0.23	3.8	0.24
$Ag/nano-Al_2O_3$	3.7	36.2	161.6	0.78	17.9	1.11

^{*a*}Determined by HR-TEM. ^{*b*}Spherical Ag crystallites are assumed; the relationship between crystallite diameter (*d*) size and dispersion *D* is *d* (nm) = 1.31/D.⁷⁴ ^{*c*}TOF is calculated on the basis of Ag dispersion with the NH₃ conversion kept below 20%.



Figure 2. N_2 adsorption–desorption isotherms and pore-size distribution curves (insets) of the (A) micro-Al₂O₃ and (B) nano-Al₂O₃ catalysts and (C) *V*–*t* plot of micro-Al₂O₃ and nano-Al₂O₃ catalysts.

and Ag/micro-Al₂O₃. The N₂ adsorption–desorption isotherms of the Ag/micro-Al₂O₃ and Ag/nano-Al₂O₃ are also shown in Figure 2A,B. The results indicated that the isotherms of Ag/Al₂O₃ catalysts were similar to those of unloaded Al₂O₃ samples, and the types of pores in Al₂O₃ were not changed after Ag loading. The BET data for the Al₂O₃-supported Ag catalysts are also summarized in Table 1. It can be seen that the surface area, pore size, and average pore size of both catalysts clearly dropped with Ag loading, which might be due to pore blocking by Ag particles on the Al₂O₃ surface.

3.2. Results of Activity Tests. The catalytic performance of Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃ in the NH₃-SCO is shown in Figure 3. Figure 3A shows the NH₃ conversion as a function of temperature over the two samples at a GHSV of 28000 h⁻¹ and with an NH₃ inlet concentration of 500 ppm. It can be seen that the Ag/micro-Al₂O₃ was inactive until 120 °C, and T_{90} (the temperature of 90% conversion) was as high as 160 °C. In contrast, the Ag/nano-Al₂O₃ was highly active for NH₃-SCO in the low-temperature range, and 90% conversion of NH₃ was obtained at 90 °C. Furthermore, the TOFs at 120 °C were calculated and are summarized in Table 1, and the results revealed that the TOF of Ag/nano-Al₂O₃ was almost 5 times higher than that of Ag/micro-Al₂O₃. In addition, the N_2 selectivity results in Figure 3B revealed that the Ag/micro-Al₂O₃ catalyst possesses a higher N₂ selectivity in comparison to $Ag/nano-Al_2O_3$.

We next investigated the influence of space velocity on the reaction, and the results are shown in Figure S2. With increasing space velocity, the profiles of NH₃ conversions clearly shifted to higher temperatures on both Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃ catalysts, while the N₂ selectivity showed little change. Regardless of the space velocity, the Ag/nano-Al₂O₃ still showed much higher activity than Ag/micro-Al₂O₃. To the best of our knowledge, the performance of Ag/nano- Al_2O_3 for SCO-NH₃ is superior to that of all catalysts previously reported.^{21,41,50,51} We have also tested the Ag/ nano-Al₂O₃ catalyst under harsh reaction conditions with high water content (5%), high GHSV (136000 h^{-1}), and wide temperature window (150-400 °C). The results (Figure S4) show that the NH₃ conversion could maintain a level of 100% with 80% N₂ selectivity in the temperature range of 250-400 $^{\circ}C$ on the Ag/nano-Al₂O₃ catalyst, showing its promise for practical applications.

3.3. Characterization. *3.3.1. Surface Acidity.* The amount and strength of the acid sites of the catalysts and supports were studied by NH_3 -TPD experiments, and the results are shown in Figure 4. The overlapped NH_3 -TPD peaks were deconvoluted into three sub-bands located at approximately 93, 133, and 220 °C, which can be attributed to physisorbed NH_3 , and NH_3 bound to weak and strong acid sites, ⁵² respectively. As shown in Figure 4, the nano- Al_2O_3 and micro- Al_2O_3 supports contributed the most proportion of acidity (86% and 85%, respectively) to the catalysts. In addition, the peak area of nano- Al_2O_3 was 1.56



Figure 3. (A) NH_3 conversion and (B) N_2 selectivity at different temperatures over Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃.

times that of micro-Al₂O₃, and that of the Ag/nano-Al₂O₃ was 1.55 times more than that of Ag/micro-Al₂O₃, which may have resulted from the abundant defect sites and OH groups of the nanosized material. The results indicated that the acid sites of Ag/nano-Al₂O₃ were more abundant than those of Ag/micro-Al₂O₃, which is therefore beneficial for the adsorption, activation, and oxidation of NH₃.

3.3.2. State of Active Component (Ag). The XRD patterns of the samples are shown in Figure 5. All samples showed diffraction peaks at 31.5, 37.5°, 39.3, 45.7, 60.5, 66.6, and 84.5° corresponding to (220), (311), (222), (400), (511), (440), and (444) lattice planes of γ -Al₂O₃ (JCPDS 02-1420), respectively. As for the Ag-loaded samples, diffraction peaks at 38.1, 44.3, 64.5, and 77.4° corresponding to (111), (200), (220), and (311) lattice planes of Ag metal (JCPDS 87-0717) appeared alongside the peaks of γ -Al₂O₃, confirming the presence of metallic Ag on both types of Ag/Al₂O₃ samples. No Ag₂O diffraction peaks were observed in the patterns of either of the two catalysts, possibly due to a lack of Ag₂O or the fact that it was present at low surface concentration or in highly dispersed form.



Figure 4. TPD profiles of NH_3 from nano-Al_2O_3, micro-Al_2O_3, Ag/ nano-Al_2O_3, and Ag/micro-Al_2O_3 catalysts.



Figure 5. XRD profiles of $Ag/nano-Al_2O_3$ and $Ag/micro-Al_2O_3$ catalysts.

H₂-TPR experiments were conducted to investigate the reducibility of Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃ catalysts, and the results are shown in Figure 6. The overlapped H₂ reduction peaks were deconvoluted into several sub-bands by searching for the optimal combination of Gaussian bands with correlation coefficients (r^2) above 0.99 without fixing the sub-band positions (PeakFit software package, Version 4.12, SeaSolve Software Inc.). The sub-bands are designated as T₁, T₂, T₃, and T₄ from low to high temperature. As has been reported,⁵³ the T₁ sub-band is due to the reduction of surface oxygen on Ag, and the peak at around 100 °C (T₂ sub-band) is caused by large Ag₂O clusters, the peak at around 200 °C (T₃ sub-band) is assigned to small Ag₂O clusters, and the peak at around 530 °C (T_4 sub-band) is assigned to stable and well-



Figure 6. H_2 -TPR profiles of Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃ catalysts.

dispersed Ag⁺ ions. These results show that Ag oxide species were also present on both catalysts and that the amount of Ag oxides on Ag/micro-Al₂O₃ should be much higher than that on Ag/nano-Al₂O₃ according to the areas of H₂ consumption peaks corresponding to Ag₂O clusters (T₂-T₃) on these two catalysts.

Figure 7 shows the UV–vis DRS spectra of $Ag/nano-Al_2O_3$ and $Ag/micro-Al_2O_3$ catalysts with different Ag loadings. The spectra were obtained by subtracting the spectrum of the bare Al_2O_3 .⁸ As can be seen in Figure 7A,B, both Ag/Al₂O₃ samples exhibited a broad absorption band ranging from 200 to 600 nm. The bands at 215 and 235 nm can be attributed to the $4d^{10}$ -4d⁹5s¹ transition of Ag⁺ ions.⁵⁴ The band at 300 nm is assigned to the UV absorption of $Ag_n^{\delta+}$. Strong bands around 350 and 450 nm were observed when the silver loading was increased to 4% and were assigned to the surface plasmon absorption of Ag $(Ag_n^0 \text{ and } Ag_{NPs})$.^{53,55,56} It is obvious that, with an increase in Ag loading, the intensities of Ag_n^0 and Ag_{NPs} bands are enhanced in both Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃. These findings indicate that high Ag loading induces the formation of metallic Ag species. When the Ag loading was 10%, the metallic Ag $(Ag_n^0 \text{ and } Ag_{NPs})$ band intensities of Ag/nano-Al₂O₃ were much stronger than those of Ag/micro-Al₂O₃, indicating that the content of Ag in the metallic state on Ag/nano-Al₂O₃ is much higher than that on $Ag/micro-Al_2O_3$ (Figure 7C), which is in agreement with the H₂-TPR results.

Figure 8 displays XAFS data for Ag/nano-Al₂O₃, Ag/micro-Al₂O₃, Ag foil, and AgNO₃. It can be seen from the normalized near-edge structure (XANES) of the samples in Figure 8A that the white line positions of both Ag/Al₂O₃ samples are located between those of Ag foil and AgNO₃, indicating that Ag in Ag/Al₂O₃ exists in a mixed form of Ag⁰ and Ag⁺. The first-order derivatives of Ag K XANES were used to distinguish the valence states.⁵⁷ The results shown in Figure 8B reveal that first-order derivative peaks appeared at 25516.6, 25519.1, 25517.5, and 25518.6 eV, respectively, for Ag foil, AgNO₃, Ag/nano-Al₂O₃ is predominantly in or near the metallic state, while Ag in Ag/micro-Al₂O₃ is present mainly in the +1 oxidation state. Fourier transforms of k^2 -weighted EXAFS spectra of samples are shown in Figure 8C. An intense peak at



Figure 7. UV-vis profiles of (A) Ag/nano-Al₂O₃ and (B) Ag/micro-Al₂O₃ catalysts and (C) comparison between the two catalysts.



Figure 8. Ag K edge XAFS spectra: (A) normalized near-edge structure (XANES) of catalysts and standard samples; (B) first-order derivatives of Ag K XANES; (C) k^2 weighted EXAFS spectra of samples (Fourier transform k range 2.2–12.8 Å⁻¹).

2.67 Å appeared for the Ag/nano-Al₂O₃ sample, which could be attributed to the Ag–Ag shell,^{58,59} similar to that of Ag foil. However, the peak for the Ag–Ag shell at 2.67 Å is not obvious on Ag/micro-Al₂O₃. In addition, a peak at about 1.64 Å assigned to the Ag–O shell⁵⁹ can be observed clearly on both Ag/Al₂O₃ samples. These results confirm the presence of Ag⁰ species on the Ag/nano-Al₂O₃ sample, while Ag⁺ is the dominant species on Ag/micro-Al₂O₃ samples are possibly due to the different interactions between Ag species and the Al₂O₃ support during the calcination. As was previously reported, Ag⁰ is the active site for the high activity of Ag/nano-Al₂O₃.

3.4. Mechanism Studies. *3.4.1. In Situ DRIFTS Study over* $Ag/micro-Al_2O_3$. The in situ DRIFTS results of NH₃ adsorption over Ag/micro-Al_2O_3 at 30 °C are shown in Figure 9A. The negative bands at 3728, 3689, and 3669 cm⁻¹⁶⁰ were due to the consumption of surface hydroxyl groups. The N–H stretching vibration bands of NH₃ appeared at 3416, 3364, 3283, 3215, and 3173 cm^{-1.29,31,61,62} In addition, bands related to Brønsted acid sites (1483 and 1445 cm⁻¹)^{61,63,64} and Lewis acid sites (1614 and 1224 cm⁻¹)^{29,31,61} were also detected.

The in situ DRIFTS of NH_3 -TPD was used to evaluate the changes in the adsorbed ammonia species on the catalysts with increasing temperature. The result for Ag/micro-Al₂O₃ is shown in Figure 9B. The bands attributed to ionic NH_4^+ and coordinated NH_3 both showed an obvious decrease in intensity with increasing temperature. Other than the changes of bands related to NH_{32} no other intermediates were observed.

The reaction between O2 and preadsorbed NH3 was next studied through in situ DRIFTS over Ag/micro-Al₂O₃. NH₃ was preadsorbed for 30 min at 220 °C and then purged with N₂ for 30 min. As can be seen in Figure 9C, after O_2 was introduced, peaks related to NH₃ species disappeared about 10 min later and nitrate bands (1544, 1450, $1\overline{286}$ cm⁻¹)^{22,65-68} appeared and grew gradually in intensity. The band at 1544 cm⁻¹ was attributed to bidentate nitrate,^{22,65} and bands at 1450 and 1286 cm⁻¹ were ascribed to monodentate nitrate.⁶⁵⁻⁶⁸ When NH₃ was reintroduced into the system, the monodentate nitrate quickly disappeared, while the bidentate nitrate remained, indicating that monodentate nitrate is more active than bidentate nitrate for the reaction with NH₃. Similar findings have also been reported in the studies about the NH_3 -SCR reaction.^{60,65,69} No other intermediate products were observed over Ag/micro-Al2O3. This process was consistent with the mechanism proposed before by many researchers which was called the i-SCR mechanism. $^{15,33-35}$

3.4.2. In Situ DRIFTS Study over Ag/nano-Al₂O₃. The in situ DRIFTS spectra of NH₃ adsorption over Ag/nano-Al₂O₃ at 30 °C are shown in Figure 10A. The N–H stretching vibration bands of NH₃ appeared at 3407, 3355, 3264, 3209, and 3144 cm^{-1.29,31,61,62} Bands corresponding to Brønsted acid sites (1680 and 1456 cm⁻¹)^{61,63,64} and Lewis acid sites (1614 and 1218 cm⁻¹)^{29,31,61} were detected. The two bands at 1523 and 1341 cm⁻¹ were ascribed to $-NH_2$ stretching and wagging vibration modes, ^{34,63,70,71} respectively. However, these two peaks were not observed on Ag/micro-Al₂O₃, possibly because NH₃ could not dissociate on its surface.

The in situ DRIFTS spectra of NH_3 -TPD over Ag/nano-Al₂O₃ are shown in Figure 10B. With an increase in temperature, the intensity of $-NH_2$ bands at 1523 and 1339 cm⁻¹ gradually decreased, while an -NH peak at 1453



Figure 9. In situ DRIFTS results over Ag/micro-Al₂O₃: (A) NH₃ adsorption at 30 °C for 30 min and N₂ purging for 30 min; (B) NH₃ desorption at various temperatures after N₂ purging at 30 °C; (C)

Figure 9. continued

reaction between O_2 and preadsorbed NH_3 species at 220 °C and further reaction between NH_3 and in situ formed nitrate. Reaction conditions: $[NH_3] = 500$ ppm, O_2 10%, and N_2 balance.

 $\rm cm^{-1}\,^{29,30}$ and a new band at 2160 $\rm cm^{-1}$ appeared. No exact assignment can be found in the literature for the new band at 2160 cm⁻¹. The possible intermediates mainly include HNO species, nitrate species, and N₂O for the NH₃-SCO reaction. HNO is a key intermediate in the imide mechanism, and its IR peak appears at 1480 cm⁻¹. Bidentate nitrate (1544 cm⁻¹), monodentate nitrate (1450 and 1286 cm⁻¹), and bridging nitrate (1625 and 1269 cm⁻¹) are the three main forms of surface nitrate species, and their peaks are also located far from 2160 cm⁻¹. We also investigated the possibility of N₂O adsorption by using in situ DRIFTS (Figure S5). It was shown that the N₂O appeared with two peaks at 2210 and 2234 cm⁻¹. The adsorbed N₂O was not stable and would quickly desorb from the catalyst surface with the N₂ purge. Therefore, all of the above possible species could be excluded. Since previous studies have reported that the band location of the N2⁻ species is very close to 2160 cm^{-1,31,62} the band at 2160 cm⁻¹ was tentatively ascribed to N_2^{-} . In order to confirm the assignments of the band at 2160 cm⁻¹, DFT calculation of N_2^{-} adsorbed on a Ag₇ cluster was performed. The calculated model of N_2^- on the Ag₇ cluster and the labeling of atoms are shown in Figure 10B (inset). The calculated vibrational frequency is 2171 cm^{-1} , in excellent agreement with the peak observed in the experiment (2160 cm^{-1}). Therefore, the peak at 2160 cm^{-1} can be assigned to $\nu(N \equiv N)$ on the basis of the experimental and calculated results.

As shown in Figure 10B, with a decrease in the intensity of the $-NH_2$ peak, the peak intensities of -NH and N_2^- gradually increased, indicating that $-NH_2$ further dissociated into -NH (1453 cm⁻¹) and N_2^- (2160 cm⁻¹), which were the intermediates during NH_3 oxidation over Ag/nano-Al₂O₃. The N_2^- species appeared at 80 °C and grew in intensity as the temperature increased to 160 °C, showing that this species is relatively stable in the absence of O₂. When the temperature was raised to 220 °C, the band at 2160 cm⁻¹ disappeared, which might be due to the desorption of N_2^- to form gaseous N_2 .

As shown in Figure 10C, the reaction between O_2 and preadsorbed NH₃ was studied through in situ DRIFTS over Ag/nano-Al₂O₃ at 120 °C. NH₃ was preadsorbed for 30 min at 120 °C and then purged with N₂ for 30 min. After adsorption and purging at 120 °C, the N₂⁻ species (2160 cm⁻¹) was formed. When O₂ was introduced, all peaks related to NH₃ species and the peak of N₂⁻ (2160 cm⁻¹) decreased rapidly. The corresponding process was also conducted in a fixed-bed flow reactor, and the result is shown in Figure 10C (inset). Without O₂ in the reactant flow, the N₂ selectivity was almost 100%. When O₂ was introduced into the reactant flow, the generation of N₂O increased sharply. Thus, we infer that N₂O was a byproduct generated from the reaction between N₂⁻ and O₂/O.

3.5. Kinetic Studies. To further confirm the difference in the NH₃ oxidation pathways between Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃ catalysts, we carried out kinetic tests over both samples. Figure 11 shows Arrhenius-type plots for the rates of NH₃ oxidation over the Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃ catalysts in the temperature ranges of 80-120 and 140-180



Figure 10. In situ DRIFTS results over Ag/nano-Al₂O₃: (A) NH₃ adsorption at 30 °C for 30 min and N₂ purging for 30 min; (B) NH₃ desorption at various temperatures after N₂ purging at 30 °C (inset:

Figure 10. continued

the optimized model of N_2^- on Ag₇ cluster); (C) reaction between O_2 and preadsorbed NH₃ species at 120 °C (inset: relationship between N_2O generation and O_2 addition). Reaction conditions: $[\rm NH_3]$ = 500 ppm, O_2 10%, and N_2 balance.



Figure 11. Arrhenius plots of the intrinsic reaction rate constants over Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃.

°C, respectively. The apparent activation energy of the reaction on the Ag/nano-Al₂O₃ catalyst is 51.6 kJ mol⁻¹, while the apparent activation energy is about 101.8 kJ mol⁻¹ on the Ag/ micro-Al₂O₃ catalyst. These results provide further evidence that the reaction pathway is different between the two samples. The NH₃-SCO reaction over Ag/nano-Al₂O₃ is easily initiated due to its low activation energy, therefore leading to higher performance at low temperatures.

The reaction orders with respect to O_2 were next measured to investigate the influence of O_2 concentration on the NH₃-SCO reaction on both Ag/micro-Al₂O₃ and Ag/nano-Al₂O₃. As shown in Figure S6, the O_2 concentration had little influence on the NH₃-SCO activity over Ag/micro-Al₂O₃ when the concentration was above 8%; therefore, the reaction order for O_2 on Ag/micro-Al₂O₃ was zero. In contrast, the NH₃ conversion was gradually enhanced over Ag/nano-Al₂O₃ with increasing O_2 concentration, and the reaction order with respect to O_2 was calculated to be 1.24. The big difference in O_2 reaction order observed on Ag/micro-Al₂O₃ and Ag/nano-Al₂O₃ (0 and 1.24) suggests that the O_2 adsorption and activation should be the key factor in the difference in activity between Ag/nano-Al₂O₃ and Ag/micro-Al₂O₃.

4. DISCUSSION

We prepared Ag/Al₂O₃ catalysts by using nanosized and microsized Al₂O₃ as the supports. It was observed that there is a remarkable nanosize effect of Al₂O₃ in Ag/Al₂O₃ catalysts for the NH₃-SCO reaction, and Ag/nano-Al₂O₃ exhibited much higher NH₃-SCO activity ($T_{90} = 90$ °C) in comparison to Ag/ micro-Al₂O₃ ($T_{90} = 160$ °C) at low temperatures. The BET results show that small-sized internal pores comprise the majority in Ag/micro-Al₂O₃ and thus the internal surface dominates the overall surface area. However, the piled pores are dominant in Ag/nano-Al₂O₃ and the external surface area makes the major contribution to total surface area. Since the surface, especially the external surface of Al_2O_3 , plays an important role in the loading and dispersion of the active components, the very large external surface area of nano-Al₂O₃ is beneficial to the dispersion of Ag, and the gap between nanoparticles could prevent the large-scale migration and aggregation of Ag. It was demonstrated by the HRTEM results that the Ag/nano-Al₂O₃ sample presented much smaller Ag particle sizes with a more uniform distribution, with an average particle size of 3.7 nm (Figure 1B2). Due to the large external surface area and higher dispersion of Ag (Table 1), the nanosized Al₂O₃ supported catalyst was conducive to exposure of the active sites, contributing to the high activity of the Ag/ nano-Al₂O₃ catalyst. In addition, from the NH₃-TPD results, it can be seen that the Ag/nano-Al₂O₃ sample has more abundant acid sites in comparison to the Ag/micro-Al₂O₃ catalyst, which are beneficial for the adsorption and activation of NH₃. The XRD, H₂-TPR, UV-vis, and XAFS results showed that the Ag/ nano-Al₂O₃ sample possesses more abundant metallic Ag species than Ag/micro-Al₂O₃. As was previously reported, Ag is the active site for NH₃-SCO at low temperatures,⁸ and more metallic Ag species will be beneficial to the catalytic performance. The Ag⁺ species was found to be much less active for NH₃-SCO than metallic Ag species at low temperature (<120 °C), and it mainly participates in the reaction at high temperatures (>120 °C).^{8,29} On the basis of the characterization results, we concluded that Ag/nano-Al₂O₃ possesses much smaller Ag particles and more metallic Ag species and also contains abundant acid sites, therefore demonstrating much higher NH₃-SCO activity.

As we mentioned before, there have been three major NH_3 -SCO mechanisms proposed in the literature. In the imide mechanism, NH_3 conversion to N_2 , N_2O , and H_2O as final products takes place with amide $(-NH_2)$, imide (-NH), and nitrosyl (HNO) as intermediates:^{27–30}

$$\mathrm{NH}_3 \to -\mathrm{NH}_2 + \mathrm{H} \tag{1-1}$$

$$-\mathrm{NH}_2 \rightarrow -\mathrm{NH} + \mathrm{H} \tag{1-2}$$

$$-NH + O \rightarrow -HNO$$
 (1-3)

$$-NH + -HNO \rightarrow N_2 + H_2O \tag{1-4}$$

$$2 - HNO \rightarrow N_2O_{ads} + H_2O \tag{1-5}$$

HNO is the most important intermediate in the imide mechanism, and its IR peak appears at 1480 cm^{-1, 30} However, it was not observed in our in situ DRIFTS results, which indicated that the imide mechanism was not suitable for the NH₃-SCO over either Ag/micro-Al₂O₃ or Ag/nano-Al₂O₃.

The hydrazine mechanism mainly generates N_2 and H_2O , with hydrazine-type (N_2H_4) species as an intermediate:^{30,31}

$$2 - NH_2 \rightarrow N_2H_4 \tag{2-1}$$

$$N_2H_4 + 4M^{n+} \rightarrow N_2 + 4M^{(n-1)+} + 4H^+$$
 (2-2)

$$2M^{(n-1)+} + 1/2O_2 + 2H^+ \to 2M^{n+} + H_2O$$
 (2-3)

It can be seen that there is no N_2O formed in this mechanism, while N_2O was the primary byproduct formed during the NH_3 -SCO reaction on the Ag/nano-Al₂O₃ catalyst. Meanwhile, no peak related to N_2H_4 can be observed on the samples. This result indicated that the hydrazine mechanism was not appropriate in the present study.

The i-SCR (internal selective catalytic reduction) mechanism consists of ammonia oxidation to NO and $\rm NH_3$ -SCR in two main steps:^{15,33-35}

$$4\mathrm{NH}_3 + 5\mathrm{O}_2 \to 4\mathrm{NO} + 6\mathrm{H}_2\mathrm{O} \tag{3-1}$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
 (3-2)

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O$$
 (3-3)

As shown in Figure 9A, adsorbed NH₃ species (1483, 1445, 1614, and 1224 cm⁻¹) were formed on Ag/micro-Al₂O₃ after it was exposed to a flow of NH₃ (500 ppm) + N₂ for 30 min. With the addition of O₂ (without NH₃, shown in Figure 9C), bidentate $(1544 \text{ cm}^{-1})^{22,65}$ and monodentate (1450 and 1286 cm⁻¹) nitrate bands^{60,72,73} appeared. When NH₃ was reintroduced, the monodentate nitrate quickly reacted with NH₃ and disappeared after 30 min (Figure 9C), indicating that the NH₃-SCO reaction on Ag/micro-Al₂O₃ followed the i-SCR mechanism.^{15,33-35} However, no nitrate bands were observed with O₂ addition on Ag/nano-Al₂O₃, which excluded the possibility of the i-SCR mechanism. Thus, different NH₃-SCO reaction pathways existed on the two catalysts, which was also confirmed by the huge difference in apparent activation energies between the two samples.

A novel NH₃-SCO reaction pathway was then proposed on the basis of the in situ DRIFTS results of Ag/nano-Al₂O₃, which was called the N₂⁻ mechanism. The in situ DRIFTS results showed that the abundant metallic Ag_{NPs} species in Ag/ nano-Al₂O₃ facilitated the activation of O₂ molecules (Figure S6 in the Supporting Information) and then the NH₃ dissociated to amide ($-NH_2$) and imide (-NH) species with the participation of the activated oxygen species at 60 °C (Figure S7 in the Supporting Information). After that, the important intermediate N₂⁻ species were generated through the combination of two $-NH_2/NH$ species, which is considered to be the rate-determining step (Figure S8 in the Supporting Information). Finally, the N₂⁻ species was converted into N₂ or N₂O in the presence of O₂. The detailed reaction pathway might take place as follows:

$$O_2 \to 2[O] \tag{4-1}$$

$$\mathrm{NH}_3 + [\mathrm{O}] \to \mathrm{NH}_2 + \mathrm{OH} \tag{4-2}$$

$$NH + [O] \rightarrow N + OH \tag{4-3}$$

$$2OH \to H_2O + [O] \tag{4.4}$$

$$2M^{n+}N \to M^{n+}N_2^{-} + M^{(n+1)+}$$
(4.5)

$$M^{n+}N_2^- \to N_2 + M^{(n-1)+}$$
 (4-6)

$$M^{n+}N_2^- + O_2 \to N_2O + M^{n+}O^-$$
 (4-7)

Since the NH₃-SCO reaction over the Ag/nano-Al₂O₃ catalyst follows the N₂⁻ mechanism, N₂O was easily produced by the reaction between O₂ and N₂⁻. In contrast, NH₃ could not be dissociated into $-NH_2$ and then converted into N₂⁻ species on Ag/micro-Al₂O₃, and thus N₂O was hardly formed. Therefore, the Ag/nano-Al₂O₃ catalyst presented relatively low N₂ selectivity in comparison to Ag/micro-Al₂O₃.

5. CONCLUSIONS

In this study, a nanosized Al_2O_3 supported Ag/nano- Al_2O_3 catalyst exhibited much higher NH₃-SCO activity ($T_{90} = 90$

°C) in comparison to microsized Al_2O_3 supported Ag/micro- Al_2O_3 ($T_{90} = 160$ °C) at low temperatures. The better dispersion of silver and abundant acid sites in Ag/nano-Al_2O_3 are beneficial for the adsorption and activation of ammonia, and the abundant metallic Ag_{NPs} on the Ag/nano-Al_2O_3 sample can facilitate the dissociation of NH₃. Research on the NH₃-SCO mechanism showed that the reaction pathway on Ag/micro-Al_2O_3 followed the i-SCR mechanism, which was proved by the kinetics results to exhibit much higher apparent activation energy in comparison to the reaction on Ag/nano-Al_2O_3. A new reaction pathway we called the N_2^- mechanism, which exhibited much lower apparent activation energy, was proposed on Ag/nano-Al_2O_3.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b03799.

Information on nano and micro-Al₂O₃ supports, effect of GHSV, experimental details concerning the elimination of mass transport effect, test results under practical application conditions, in situ DRIFTS results of N₂O adsorption, reaction order with respect to O₂ over Ag/ (nano/micro)-Al₂O₃, role of O₂ in NH₃ dissociation, and determination of the rate-determining step for NH₃-SCO reaction over Ag/nano-Al₂O₃ (PDF)

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Notes

The authors declare no competing financial interest.

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