

Ag-Cu based catalysts for the selective ammonia oxidation into nitrogen and water vapour

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Abstract

XRD, BET, H₂-TPR, UV-vis-DRS, XPS and XAFS were used to characterize a series of Ag and/or Cu – Ag (1-5%), Cu (10-15%) or Ag-Cu (1-1, 1-10, 1.5-10, 5-5% of metal) – supported on γ -Al₂O₃. The correlation between physicochemical properties, catalytic activity and selectivity in NH₃-SCO was thoroughly investigated. The Ag/Al₂O₃ catalysts characterization indicated that silver species mainly in the form of Ag₂O led to enhanced activity together with drop in N₂ selectivity with increasing silver loading. The activity of all Ag-containing materials was superior to Cu-containing ones. A mixture of CuO and CuAl₂O₄ formed on the Cu/Al₂O₃ catalysts, with bulk CuO_x and CuAl₂O₄ leading to decreased N₂ selectivity. The gap between the high conversion temperature over Cu/Al₂O₃ and low N₂ selectivity over Ag/Al₂O₃ was bridged by applying the Ag-Cu/Al₂O₃ catalysts, with the optimum loading of 1.5 and 10 wt.% for silver and copper, respectively. NH₃-TPD, NH₃-TPSR and *in situ* FTIR were used to determine the selective catalytic reduction (i-SCR) mechanism over 1.5% Ag/Al₂O₃, 10% Cu/Al₂O₃ and 1.5% Ag-10% Cu/Al₂O₃ respectively, which involved the partial oxidation of NH₃ into NO_x species, along with adsorbed NO_x species interacting with NH_x and being reduced to reaction products.

Keywords: alumina, silver oxide species, copper oxide species, selective ammonia oxidation, reaction mechanism

1. Introduction

Ag-based catalysts, including silver supported on γ -Al₂O₃, serve as one of the most active and N₂ selective materials for the selective catalytic ammonia oxidation into nitrogen and water vapour (NH₃-SCO) below 300 °C [e.g. [1–3]. Qu et al. [1] studied silver supported on γ -Al₂O₃, TiO₂, SiO₂ or NaY, and found that catalytic activity and selectivity depended strongly on the size and distribution of silver species. Highly dispersed Ag⁰ particles with a size of 5 nm were obtained on H₂-pretreated 10% Ag/Al₂O₃ and reported as the most active and N₂ selective in NH₃-SCO (full conversion and 89% of N₂ selectivity at 180 °C). Ag⁺ was the main active species responsible for the high catalytic performance above 140 °C. A significantly lower selectivity to N₂ (around 60–80% at 180 °C) over a similar catalyst – 10% Ag/Al₂O₃, was reported by Zhang et al. [2] or Gang et al. [4]. These discrepancies appeared possibly due to different preparation procedures of the catalysts. Nevertheless, above 300 °C, selectivity to N₂ decreased significantly over Ag/Al₂O₃ due to formation of NO over Ag₂O [5]. On the other hand, copper-based catalysts possess high intrinsic activity in the oxidation of ammonia with an excellent selectivity to N₂ at high temperatures. The copper-based materials containing about 10% of Cu were recognized as one of the most efficient catalysts in NH₃-SCO [6]. Thus, the proper mixing of silver with copper leads to highly active and selective bifunctional catalytic system, in which silver species catalyse ammonia oxidation to NO_x, while copper oxide species perform the reduction of NO_x to nitrogen [5,7]. Yang et al. [5] studied Ag-Cu/Al₂O₃ with 5-5 or 10-10% of metal and indicated the material with the first composition as highly efficient catalysts with complete conversion temperature at 325 °C and 95% N₂ selectivity. Unfortunately, the authors did not present results of catalytic tests above 350 °C. Gang et al. [8] investigated 7.5% Ag-2.5% Cu/Al₂O₃ and found full conversion of ammonia at 200-300 °C with 95% N₂ selectivity. Both activity and selectivity to N₂ significantly increased compared to Ag/Al₂O₃. Nevertheless, above 300 °C significant amounts of NO and N₂O appeared over Ag-Cu/Al₂O₃. Interestingly, a mechanical mixture of 10% Ag/Al₂O₃ and 10% Cu/Al₂O₃ showed similar catalytic performance to a silver-based catalyst alone. Thus, the intimate contact between the silver species and copper species – active species dedicated for ammonia oxidation to NO_x and reduction of NO_x to nitrogen,

respectively – led to shorter diffusion length and consequently improved catalytic activity and N₂ selectivity. The authors applied XPS measurements over 5-5, 7.5-2.5% Ag-Cu/Al₂O₃, which revealed the same oxidation state as for single 10% Ag/Al₂O₃ or 10% Cu/Al₂O₃. Additionally, LEIS analysis over 10-2.5, 2.5-7.5, 5-5, 9-1% Ag- γ Cu/Al₂O₃ excluded formation of any Ag-Cu phases. Besides studies of Gang et al. [8], up to now and to the best of our knowledge no other studies devoted to the correlations between the state of silver and/or copper oxide species in Ag-Cu/Al₂O₃ on the catalytic activity and N₂ selectivity in the ammonia oxidation have been reported. The structure-activity relationship of the bimetallic Ag-Cu/Al₂O₃ catalysts with lower silver loading (1-5%) remains ambiguous. Preliminary results revealed that silver increased activity of the Ag-Cu catalysts in the low-temperature range but also significantly decreased selectivity to nitrogen. Thus, we focused on the determination of the optimal content of silver and copper, guaranteeing optimum activity together with N₂ selectivity. We deposited different amounts of Ag (1.0-5.0%), Cu (10-15%) or Ag-Cu (1-1, 1-10, 1.5-10, 5-5% of metal) on the γ -Al₂O₃ support. We focused on characterization of bimetallic Ag-Cu/Al₂O₃ in comparison to monometallic Ag/Al₂O₃ and Cu/Al₂O₃, and determination of the metal loading on the physicochemical properties obtained and their catalytic activity and selectivity in the selective ammonia oxidation into nitrogen and water vapour. We concentrated our attention on the interaction between silver and copper oxide species deposited on the surface of the Al₂O₃ support, thus, this approach enabled the comparison of the role of active components in NH₃-SCO between 50 and 350 °C.

2. Experimental part

2.1. Catalyst preparation

γ -Al₂O₃ (Merck) was doped with Ag and/or Cu by the incipient wetness impregnation using aqueous solutions of Cu(NO₃)₂·3H₂O (Sigma-Aldrich) and AgNO₃ (Sigma-Aldrich). In the bimetallic systems, after impregnation with aqueous solution of copper salt, the sample was first dried at 80 °C overnight followed by impregnation with aqueous solution of silver salt. All prepared samples were dried and subsequently calcined in static air at 600 °C for 12 h. For catalytic experiments, a sieve fraction of particles with size of 0.250-0.50 mm was used. The weight ratio of metals was measured with respect to the mass of γ -Al₂O₃.

2.2 Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were recorded in flat plate mode in Bragg-Brentano geometry using a D5000 Siemens diffractometer and a Cu K α source ($\lambda = 1.54056 \text{ \AA}$, 45 kV, 40 mA).

The specific surface area (S_{BET}) of the samples was determined by low-temperature ($-196 \text{ }^\circ\text{C}$) N $_2$ sorption using Quantachrome Quadrasorb SI. Prior to nitrogen adsorption the samples were outgassed at $250 \text{ }^\circ\text{C}$ for 12 h using a Quantachrome Flovac degasser. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) multiple point method at partial pressures from p/p_0 range from 0.05 to 0.3. The total pore volume was determined at $p/p_0 = 0.99$.

The temperature-programmed reduction (H $_2$ -TPR) experiments of samples (30 mg) were performed using a Quantachrome ChemBET Pulsar TPR/TPD instrument. H $_2$ -TPR runs were carried out starting from room temperature to $1000 \text{ }^\circ\text{C}$, with a linear heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ and in a flow (25 ml min^{-1}) of 5 vol.% H $_2$ diluted in Ar. Water vapour was removed from effluent gas by the means of a cold trap placed in an ice-water bath. The H $_2$ consumption was detected and recorded by TCD detector.

The diffuse reflectance UV-vis (UV-vis-DR) spectra of the samples were recorded using a Perkin-Elmer Lambda 7 UV-vis spectrophotometer. The measurements were performed in the range of 200-900 nm with the resolution of 1 nm. The spectra were recorded under ambient conditions and the data transformed according to the Kubelka-Munk equation.

The X-ray photoelectron spectra (XPS) of selected samples were measured on a VSW spectrometer equipped with a hemispherical analyser. The photoelectron spectra were measured using a magnesium MgK α source (1253.6 eV). The base pressure in the analysis chamber during the measurements was $3 \cdot 10^{-6} \text{ Pa}$ and the spectra were calibrated on a main carbon C 1s peak at 284.6 eV. The composition and chemical surrounding of the sample surface were investigated based on the areas and binding energies of Ag 3d, Cu 2p, Al 2p, C 1s and O 1s photoelectron peaks. Mathematical analyses of the XPS spectra were carried out using the XPSpeak 4.1 computer software (RWM. Kwok, The Chinese University of Hong Kong).

The X-ray absorption spectra (XAS) of selected samples were performed at room temperature on station B18 at the ESRF at the Diamond Light Source national synchrotron facility. The station is equipped with a Si(111)/Si(311) double crystal monochromator, and ion chambers for measuring incident and transmitted beam

intensities for recording X-ray absorption spectra. The measurements were carried out using a Si(111) monochromator at the Ag K-edge or Cu K-edge with the respective Ag or Cu monometallic foil (10 μm) used as an energy calibrant for the monochromator. Measurements were performed in quick scanning mode; the time taken for each scan was ca. 5 min (a step size of 0.5 eV and counting time of 1/6 s/point was used for collection of data around the edge). To improve the signal-to-noise ratio, multiple scans were taken. Samples were pressed into 13 mm pellets using an appropriate amount of cellulose as binder and submitted to ex-situ XAFS experiments. All data were subjected to background correction using Athena (i.e. IFFEFFIT software package for pre and post edge background subtraction and data normalization [9,10]). XAFS spectra were normalized from 30 to 150 eV above the edge energy, while the EXAFS were normalized from 150 eV to the last data point using the Autobk algorithm. Normalization was performed between $\mu(E)$ and $\mu_0(E)$ via a line regression through the data in the region below the edge and subtracted from the data. A quadratic polynomial is then regressed to the data above the edge and extrapolated back to E_0 . The extrapolated value of the post edge polynomial at E_0 is used as the normalisation constant. This threshold energy (E_0) was determined using the maximum in the 1st derivative. A calibration curve derived from the references was used to determine oxidation states from the edge position obtained from the maximum in the first derivative of the measured XANES spectra of the selected samples. The normalized isolated EXAFS data were k^3 -weighed and a least squares fitting analysis was performed over a k -range of 3 - 8 \AA^{-1} (Ag) otherwise 3 - 11 \AA^{-1} (Cu). The FT of the k^3 -weighed data were phase corrected and fit (using single scattering paths) to the proposed theoretical model using the DL-EXCURV program. An amplitude reduction factor (S_o^2) value of 0.95 was used for all data sets. Errors in the determination of the parameters derived from the fitting of the EXAFS data were estimated to be 10 % of the coordination number and Debye-Waller factor and $\sim 0.02 \text{\AA}$ for bond distance

2.3 Catalytic tests

The catalytic experiments of selective ammonia oxidation ($\text{NH}_3\text{-SCO}$) were performed under atmospheric pressure in a fixed-bed flow microreactor (i.d., 6 mm; l., 320 mm). The reactant concentrations were continuously monitored using a QMS MKS Cirrus 2 detector directly connected to the reactor outlet using a heated capillary. Prior to the test the sample of catalyst (100 mg) was outgassed at 500 $^\circ\text{C}$ for 1 h in a flow of pure argon (20 ml

min⁻¹). The composition of the gas mixture at the reactor inlet consisted of 0.5 vol.% NH₃, 2.5 vol.% O₂ diluted in Ar. The individual flow rates were controlled by Bronkhorst mass flow controllers. The total flow rate of the reaction mixture was 40 ml min⁻¹, while the weight hourly space velocity (WHSV) was about 24,000 ml h⁻¹ g⁻¹. The studies were performed in the temperature range of 100-500 °C with the linear heating rate of 5 °C min⁻¹. For selected sample additional catalytic tests: (i) polythermal in the presence of water vapour and (ii) isothermal NH₃-SCO were carried out with the following composition of the gas mixture of 0.5 vol.% NH₃, 2.5 vol.% O₂, ([H₂O] = 3.2 vol.%) diluted in Ar. The signal of the argon line served as the internal standard to compensate small fluctuations of the operating pressure. The sensitivity factors of the analysed lines were calibrated using commercial mixtures of the gases.

2.4 Temperature-programmed desorption (NH₃-TPD) and temperature-programmed surface reaction (NH₃-TPSR)

The NH₃-TPD and NH₃-TPSR were performed in a fixed-bed flow microreactor (i.d., 6 mm; l., 320 mm) equipped with a QMS MKS Cirrus 2 detector. Prior to the ammonia sorption the sample (100 mg) was outgassed in a flow of pure argon (20 ml min⁻¹) at 500 °C for 1 h. Subsequently, the microreactor was cooled down to 70 °C and the sample was saturated with 1 vol.% of NH₃ diluted in Ar (2 h, 20 ml min⁻¹). Afterwards, the sample was purged in a flow of Ar until a constant baseline level was reached (2 h, 20 ml min⁻¹). For desorption step the temperature of the microreactor was raised from 70 up to 500 °C with a linear heating rate of 5 °C min⁻¹ in a flow of pure argon (NH₃-TPD) or in a flow of 5 vol.% of O₂ diluted in Ar (NH₃-TPSR). The total flow rate in both measurements was 20 ml min⁻¹.

2.5 Fourier transform infrared spectroscopy

The *in situ* DRIFT spectra were recorded with a Vertex 70-FTIR Bruker spectrometer equipped with a MCT detector. Prior to the FTIR study the sample was pretreated *in situ* at 400 °C in a flow of pure N₂ for 1 h and then cooled to 50 °C. The sample was saturated in a flow (5 ml min⁻¹) of gas mixture containing 1.0 vol.% of NH₃ diluted in Ar for about 0.5 h. Subsequently, the physisorbed molecules were removed in 15 min evacuation. Next, the sample contacted with NH₃ was heated in a flow of: (i) pure N₂ or (ii) 5.0 vol.% O₂ diluted in Ar up to 100-

350 °C, kept at particular temperature for 10 min and cooled down to 50 °C, while the spectrum was collected. All spectra were recorded at a resolution of 4 cm⁻¹ with 128 accumulated scans. The background spectrum was subtracted from the sample spectrum.

3. Results and discussion

The XRD analysis allowed the identifications of the crystalline phases present in the Ag-Cu-based materials. The characteristic XRD diffraction peaks corresponding to the reflections of γ -Al₂O₃ were located at about 20, 33, 38, 40, 46, 61 and 67 °2 θ [11]. The Ag⁺ species exist on low silver loadings (< 2%), while metallic silver particles were present on high silver loading catalysts (\geq 5%) [e.g. [12–14]]. As shown in Figure 1A, no changes in the structure of oxide support appeared after impregnation with Ag below 5%. However, for sample with 5% of silver, Ag₂O appeared at 2 θ of 34 and 39° [15], besides the peaks assigned to the support. Figure 1B presents the XRD diffraction pattern of Cu/Al₂O₃ with different copper loadings. The diffraction lines for CuO at (2 θ angle of 35, 38, 48, 53, 58, 62, 66 and 68 ° [16]) arose when the copper in the samples increased to 10-15%. Besides the diffraction peaks ascribed to CuO, the XRD peak attributable to CuAl₂O₄ at 37° 2 θ is also present [17]. The reflections characteristic for Ag₂O, CuO and CuAl₂O₄ appeared also in Ag-Cu bimetallic systems, as depicted in Figure 1C. The formation of bulk CuO and/or Ag₂O related to agglomeration of transition metal oxide species, presumably due to saturation of the Al₂O₃ support.

Fig. 1.

The BET analysis provided specific surface area (S_{BET}) and total pore volume (V_{p}) evolution of the Ag-Cu-based materials. As presented in Table 1, Al₂O₃ revealed S_{BET} and total pore volume of about 135 m² g⁻¹ and 0.2393 ml g⁻¹, respectively. The deposition of transition metal oxides within the pore system of the γ -Al₂O₃ support resulted in the decrease of S_{BET} and V_{p} , especially for metal loading higher than 5%. The total pore volume dropped with increasing amount of transition metals until 0.2097 ml g⁻¹ and 0.1981 ml g⁻¹ for 5% of Ag and 15% of Cu, respectively. Also, the Ag-Cu bimetallic systems showed S_{BET} and V_{p} lower compared to the Al₂O₃ support. As

a result of differences between silver and copper oxides, the specific surface area and total pore volume varied appreciably in the bimetallic Ag-Cu materials.

Table 1. Specific surface area (S_{BET}) and total pore volume (V_p) of the Ag/Al₂O₃, Cu/Al₂O₃, Ag-Cu/Al₂O₃.

Sample codes	S_{BET} [m ² g ⁻¹]	V_p [ml g ⁻¹]
Al ₂ O ₃	135	0.2393
1% Ag/Al ₂ O ₃	127	0.2228
1.5% Ag/Al ₂ O ₃	125	0.2184
2% Ag/Al ₂ O ₃	124	0.2177
5% Ag/Al ₂ O ₃	118	0.2097
1% Cu/Al ₂ O ₃	126	0.2465
5% Cu/Al ₂ O ₃	117	0.2099
10% Cu/Al ₂ O ₃	114	0.1986
15% Cu/Al ₂ O ₃	111	0.1981
1% Ag-1% Cu/Al ₂ O ₃	128	0.2301
1% Ag-10% Cu/Al ₂ O ₃	112	0.1999
1.5% Ag-10% Cu/Al ₂ O ₃	105	0.1803
5% Ag-5% Cu/Al ₂ O ₃	101	0.2060

The H₂-TPR analysis provided insight into redox properties of silver and/or copper species in the Ag-Cu-based materials. Figure 2A,C shows the H₂-TPR profiles of Ag-based catalysts. The low-temperature peak appeared in the H₂-TPR profiles of Ag-modified samples, indicating reduction of highly dispersed Ag₂O [18,19]. The maximum of the reduction shifted to higher temperatures (from 113 to 125 °C for 1 to 5% of Ag, respectively) with the increasing loading of silver, indicating partial aggregation of silver oxide species. Jabłońska et al. [20] showed two peaks (at 110 and 385 °C) in the H₂-TPR of analogues Ag/Al₂O₃ samples with 1% of silver loading. Thus, the sample contained highly dispersed, as well as Ag₂O clusters. These discrepancies appeared possibly

due to different conditions of H₂-TPR measurements. For the sample with 5% of Ag, additional peak appeared at about 565 °C due to reduction of Ag₂O clusters [19]. As shown in Figure 2B,C H₂-TPR profiles changed also with different copper loading, suggesting formation of different copper oxide species. The reduction of Cu/Al₂O₃ with 1% of copper, consisted of a three reduction peaks appeared at about 350, 615 and 775 °C, which is consistent with earlier results of Jabłońska et al. [21]. The first peak appeared due to the reduction of highly dispersed CuO_x. The peaks located in the higher temperatures were related to the reduction of bulk CuO_x and defective spinel-type surface CuAl₂O₄, respectively. CuAl₂O₄ – with most Cu²⁺ ions in a distorted octahedral geometry – was formed between CuO and Al₂O₃ as a result of its interaction at 600 °C [22,23]. For higher copper loading (5%), the reduction peak appeared due to the reduction of the highly dispersed CuO_x on the Al₂O₃ surface. This peak spread into two peaks with increasing amount of copper. The H₂-TPR profiles for the samples with of 10 and 15% of Cu showed low and high temperatures reduction peaks at about 261-273 °C and 303-315 °C, respectively. The peaks centered at 303 and 315 °C appeared due to reduction of bulk CuO_x and CuAl₂O₄ on the catalysts surface [23]. As confirmed from XRD analysis, the intensity of bulk CuO_x and CuAl₂O₄ increased in line with the copper loading on the Al₂O₃ support. The reducing temperatures of the highly dispersed CuO_x for Cu/Al₂O₃ with 10% of copper appeared at lower temperatures than for materials with other copper loadings, indicating that a redox cycle would occur easier.

The coexistence of silver and copper oxide species in the Ag-Cu bimetallic systems resulted in a shift of the H₂-TPR maximum peaks to lower temperatures. As shown in Figure 2C, the H₂-TPR profile for sample with 1% of both Ag and Cu consisted of main broad peak centered at about 227 °C. Even more significant shift to lower temperatures appeared for sample with 5% of both metals, as presented in Figure 2 D. The materials with 1-1.5% of Ag and 10% of Cu showed similar H₂-TPR profiles, however, the sample with higher silver loading (1.5% Ag-10% Cu/Al₂O₃) revealed lower reduction temperature of the easily reducible CuO_x at about 213 °C. The peak represented bulk copper oxides species (CuO and CuAl₂O₄) shifted to 292-295 °C for both samples, so temperatures lower by about 8-11 °C compared to Cu/Al₂O₃ (303 °C). Moreover, in the H₂-TPR profiles of such Ag-Cu bimetallic systems appeared small peaks cantered at around 247-248 °C, which represented a partial reduction of bulk copper oxide species.

UV-vis-DRS analysis resulted in information regarding the type of transition metal species and their aggregation in the Ag-Cu-based materials. In figure 3A, a band centered at 204-205 nm for Ag-containing samples ($\leq 2\%$) are attributed to the highly dispersed Ag^+ [24,25]. This band grew stronger and shifted to higher wavelength (218 nm) for samples with 5% of Ag, indicating decrease in the dispersion of Ag_2O particles. A shoulder at about 334-336 nm appeared due to the oxidized silver clusters $\text{Ag}_n^{\delta+}$ [26,27]. Again, for catalyst containing 5% of silver, the maximum of this peak shifted to higher wavelength. Nevertheless, for all Ag-modified samples, Ag^+ stayed the major Ag species on the Al_2O_3 surface. Figure 3B shows the UV-vis DR spectra for Cu-containing samples, with two main forms of copper oxide species on the support surface. The peak centered at 227-247 nm related to the isolated Cu^{2+} , while the absorption in 400-650 nm and above 650 nm arose due to presence of bulk CuO_x and CuAl_2O_4 , respectively [17, 21]. Again, higher concentration of copper led to stronger band corresponding to bulk copper oxide species, which correlated with XRD and H_2 -TPR results. Furthermore, the spectra recorded for Ag-Cu bimetallic systems, due to low loading of Ag revealed mainly bands related to the copper oxide species, as shown in figure 3C.

XPS measurements were carried out to further examine the oxidation state of transition metal species in the Ag-Cu-based materials. Figure 4A-K presents the Ag and Cu XPS spectra, while Table 2 gathers the position of binding energies, full width at half-maximum (FWHM), and molar ratio of the selected Ag-Cu-based materials. The Ag $3d_{5/2}$ binding energies for metallic Ag, Ag_2O and AgO are approximately 368.0-368.3, 367.6-367.8 and 367.3-367.4 eV, respectively [e.g. [28–30]]. The Ag $3d_{5/2}$ binding energies values of the Ag/ Al_2O_3 materials range from 368.8 to 367.8 eV for 1 and 5% of Ag, respectively. However, the samples characterization by XRD, UV-vis-DRS and H_2 -TPR analyses revealed that silver species deposited on the Al_2O_3 surface existed mainly in the form of Ag^+ . Furthermore, the binding energy of the highly dispersed silver oxide species was higher than of the Ag_2O clusters (368.8 and 367.8 eV for 1 and 5% of Ag, respectively). Also, in those spectra additional shoulder possibly related to the oxidized silver clusters $\text{Ag}_n^{\delta+}$ appeared at 365.1 and 364.7 eV for 1.5 and 5% of silver, respectively. Degrees of the support coverage, which are proportional to the metal dispersion were calculated using the relative areas of the XPS peaks and normalized by the metal loadings. The results in Table 2 indicated that with the silver loading from 1 to 1.5%, metal dispersion increased from 0.25 and 0.33, and then subsequently decreased to 0.20 for 5% Ag/ Al_2O_3 . Figure 4 D-G contains XPS spectra for the Ag 3d states in the

selected Ag-Cu bimetallic systems. The binding energy changed with the Ag/Cu ratios in the bimetallic materials, indicating the interaction between silver and copper oxide species. For the bimetallic system with 1% of silver and copper, the binding energy for Ag 3d_{5/2} shifted to lower value (368.8 → 368.1 eV), and become slightly broader with a full width at half maximum (FWHM) from 3.4 to 3.5 eV. Additionally, the Cu 2p peak appeared at 932.5 eV, as reported for Cu⁺. Thus, the presence of Cu⁺ species on the surface of 1% Cu/Al₂O₃ indicated the reduction of highly dispersed copper oxide species under vacuum. The copper oxide species (CuO_x and CuAl₂O₄) were characterized by the appearance of characteristic satellite peaks [29, 30]. While other tested bimetallic catalysts, with higher copper loading, showed Cu²⁺, as indicated by the shift of peaks to higher binding energies and the appearance of characteristic satellite peaks at 963-962 and 943-942 eV. While the comparison between 1% Ag - 10% Cu/Al₂O₃ and 1.5% Ag - 10% Cu/Al₂O₃ revealed that the addition of silver improved the metal dispersion from 0.37 to 0.40, respectively.

Table 2. Position of binding energies, full width at half-maximum (FWHM) and molar ratio of Ag/Al₂O₃ and Ag-Cu/Al₂O₃.

Sample code	Peak Position/FWHM			Molar ratio ^a
		[eV]		Ag 3d/Al 2p*
	Ag 3d	O 1s	Cu 2p	(Ag 3d + Cu 2p)/Al 2p**
1% Ag/Al ₂ O ₃	368.8/3.4	532.5/2.1		0.25*
		531.1/2.1		
		529.8/2.3		
1.5% Ag/Al ₂ O ₃	368.1/2.8	532.5/2.4		0.33*
	365.1/2.1	530.9/2.5		
		528.9/2.6		
5% Ag/Al ₂ O ₃	367.8/2.8	532.7/2.0		0.20*
	364.7/1.6	530.9/2.4		
		529.3/2.4		
1% Ag-1% Cu/Al ₂ O ₃	368.1/3.5	532.1/2.5	932.5/5.0	0.61**

		530.7/2.2		
		529.3/2.4		
1% Ag-10% Cu/Al ₂ O ₃	368.4/2.8	532.5/2.3	962.9/5.3	0.37**
		530.9/2.5	956.8/5.1	
		529.3/2.4	941.9/8.2	
			932.9/3.5	
1.5% Ag-10% Cu/Al ₂ O ₃	368.1/2.6	532.4/2.6	962.2/4.0	0.40**
		530.9/2.6	958.2/6.5	
		529.3/2.5	942.2/5.7	
			932.7/3.6	
5% Ag-5% Cu/Al ₂ O ₃	368.1/2.6	532.5/2.1	962.3/2.5	0.43**
	365.5/2.2	530.9/2.5	958.4/3.9	
		529.4/2.4	942.9/4.6	
			932.8/3.9	

^aEstimated from the integrated areas of the respective XPS peaks and normalized by metal loading.

XAFS analyses were carried out to further examine the oxidation state of transition metal species and the near-neighbor atomic environment of the silver and copper atoms in those selected Ag-Cu-based materials. Figure 5A presents XANES around Ag K-edge of the selected Ag-Cu-based materials together with those of Ag foil and Ag₂O. XANES spectra of 1% Ag- 1% Cu/Al₂O₃ and 1.5% Ag-10% Cu/Al₂O₃ exhibited similar edge position (at 50 % of the height of the rising absorption edge) to that to Ag₂O, which suggested that Ag⁺ were the main silver species in bimetallic materials. Furthermore, Figures 5C,D and 5E,F show raw $k^3\chi(k)$ EXAFS data and Fourier transform of k^3 -weighted EXAFS spectra of both Ag-Cu/Al₂O₃, while Table 3 presents the results of the curve-fitting analysis for the first coordination shell. Although the spectra are noisy, it is possible to derive a reasonable first shell fit to the data. Both bimetallic materials were similar to each other with the Ag-O and Ag-Ag bond length of 0.226 and 0.276 nm, respectively, consistent with the presence of small silver clusters thought to be up to ~ 4 silver atoms [31, 32]. The slightly larger Ag-O and Ag-Ag coordination numbers seen in the 1.5% Ag-10%

Cu/Al₂O₃ sample than those seen in 1% Ag-1% Cu/Al₂O₃ suggested slightly larger silver clusters in the former sample. Furthermore, figure 5B shows XANES around Cu K-edge of the selected Ag-Cu-based materials and CuO as reference. The comparison between the edge position of CuO and for both Ag-Cu/Al₂O₃ samples revealed that the investigated materials contained essentially Cu²⁺. The differences in the rising adsorption edge and XANES region (~ 50 eV above E₀) are suggestive of slight differences in the Cu environment. Based on previous XANES studies of Cu²⁺ the first coordination sphere of the Cu²⁺ environment in 1% Ag-1% Cu/Al₂O₃ and CuO are broadly similar but the second coordination number/sphere is greater in CuO. The XANES spectrum for the 1.5% Ag-10% Cu/Al₂O₃ sample in contrast is suggestive of a very different Cu²⁺ environment. A plot of the fourier transformed *k*³-weighted EXAFS spectra (Fig. 5G) and accompanying EXAFS analysis results shown in Table 3 confirmed the presence of comparatively isolated Cu²⁺ species in the 1% Ag-1% Cu/Al₂O₃ sample. (see [ref 10.1016/j.apcatb.2014.02.037](https://doi.org/10.1016/j.apcatb.2014.02.037)) Analysis of the XANES derivative plots in Fig. 5H suggests the major Cu containing phase in the 1.5% Ag-10% Cu/Al₂O₃ sample to be CuAl₂O₄ [33].

However, XRD, H₂-TPR, UV-vis-DRS and XPS analyses revealed the mixture of CuO and CuAl₂O₄ formed on Cu-containing catalysts.

Table 3. Coordination number (CN), bond distance between adsorbed and backscatter atoms (R), inner potential correction to account for the difference in the inner potential between the sample and the reference compound (E), Debye-Waller factor ($2\sigma^2$), and residual factor (R) of 1% Ag-1% Cu/Al₂O₃ and 1.5 %Ag-10%Cu/Al₂O₃.

Sample code	Shell	CN	R [nm]	E [eV]	$2\sigma^2$	R [%]
1% Ag-1% Cu/Al ₂ O ₃	Ag-O	1.9	0.226	-0.47	0.027	32
	Ag-Ag	2.7	0.276		0.062	
	Cu-O	4	0.195	-0.55	0.018	31
	Cu-Cu	2.7	0.305		0.04	
1.5% Ag-10% Cu/Al ₂ O ₃	Ag-O	2	0.226	-2.3	0.027	30.3
	Ag-Ag	2.9	0.276		0.062	

The catalytic tests results of the selective ammonia oxidation into nitrogen and water vapour (NH₃-SCO) provided insight into activity and selectivity of silver and/or copper species in the Ag-Cu-based materials. The γ -Al₂O₃ support was almost inactive in the investigated temperature range [21]. Figure 6 shows the results of NH₃-SCO of Ag-Cu-based catalysts, while Table 4 gathers temperatures for which full conversions (T₁₀₀) were achieved for tested catalysts together with selectivity to particular products at these temperatures. The catalytic activity increased gradually with increasing silver loading (Fig. 6A-D). Ag/Al₂O₃ doped with 1% of silver reached full conversion at temperature as high as 500 °C. Significantly higher activity and selectivity were obtained over the 1.5-2% Ag/Al₂O₃ catalysts with full ammonia conversion from reaction mixture at 300-325 °C and 84% N₂ selectivity. Even higher activity was achieved over catalysts containing 5% of silver. However, the selectivity to N₂ decreased to unsatisfactory level of 57% at 400 °C, and then started to increase possibly due to increasing role of Ag₂O clusters with lower reducibility (Fig. 2A). Moreover, significant amounts of by-products produced in the presence of 5% Ag/Al₂O₃ excluded such catalysts from the application in NH₃-SCO. The above results clearly showed that silver-containing catalysts were active for the ammonia oxidation, and superior to the Cu-modified Al₂O₃. In particular, for material containing 1% of copper, the full conversion of ammonia from the reaction mixture was not reached up to 500 °C. Similarly to the Ag/Al₂O₃ catalysts, the activity of Cu-doped materials significantly increased with increasing amount of transition metal. Though further variation of the copper loading from 5-15% did not result in a significant different activity. For catalysts with 10-15% of copper, full ammonia conversion was reached at 425 °C. While the selectivity to N₂ decreased with increasing amount of copper, possibly due to increasing amount of bulk CuO_x and CuAl₂O₄ on the catalysts surface (Fig. 2B). With further catalysts improvement, Al₂O₃ was modified simultaneously with silver and copper, as shown on Fig. 6I-L. Among all tested combinations – 1-1, 1-10, 1.5-10, 5-5% of silver and copper, respectively, – 1.5% Ag-10% Cu/Al₂O₃ reached optimum ammonia conversion at 375 °C and 94% N₂ selectivity at this temperature. Noteworthy, the activity of this catalyst did not change significantly in NH₃-SCO under wet conditions (3.2% of water vapour). The activity of this sample tested in the wet conditions shifted to the temperature higher by about 50 °C, while selectivities to all products remained nearly constant. The stability tests for 1.5% Ag-10% Cu/Al₂O₃ (Fig. 6P) was carried out at 325 °C over feed containing besides NH₃ and O₂, also water vapour, and revealed

conversion of 76% with N₂ selectivity of 97%, after 500 min of the test. The Ag-Cu-modified Al₂O₃ (Ag-Cu: 7.5-2.5, 5-5, 10-10%) were studied before but only in the range of 350-400 °C by Gang et al. [8] and Yang et al. [5]. Among tested catalysts, 7.5% Ag-2.5 % Cu/Al₂O₃ facilitated complete ammonia conversion at 300 °C with 95% N₂ selectivity. Above 300 °C appeared more by-products. An increase in silver loading resulted in activation of the catalyst, but caused also an increasing NO_x and N₂O formation [8]. Thus, the activity and selectivity of NH₃-SCO over the Ag-Cu/Al₂O₃ catalysts strongly depends on the transition metals loadings. Our results showed that the activity and selectivity to N₂ can be steered into the desired direction by a co-impregnation of proper amount of silver and copper on the Al₂O₃ support. Accordingly, selectivity to by-products were nearly eliminated.

Table 4. Comparison of the results of catalytic tests (T₁₀₀ temperature needed for 100% of NH₃ conversion).

Sample codes	T ₁₀₀ [°C]	N ₂ selectivity	NO selectivity	N ₂ O selectivity
1% Ag/Al ₂ O ₃	500	74	13	13
1.5% Ag/Al ₂ O ₃	325	84	3	13
2% Ag/Al ₂ O ₃	300	84	2	14
5% Ag/Al ₂ O ₃	275	83	1	16
1% Cu/Al ₂ O ₃	-	-	-	-
5% Cu/Al ₂ O ₃	450	81	7	12
10% Cu/Al ₂ O ₃	425	85	5	10
15% Cu/Al ₂ O ₃	425	83	7	10
1% Ag-1% Cu/Al ₂ O ₃	425	87	10	3
1% Ag-10%Cu/Al ₂ O ₃	375	92	2	6
1.5% Ag-10% Cu/Al ₂ O ₃ *	375	94	2	4
*with 3.2% H ₂ O	375	95	2	3
5% Ag-5% Cu/Al ₂ O ₃	275	79	2	19

The temperature programmed desorption (NH₃-TPD) and temperature programmed surface reaction (TPSR) were carried out to investigate the ammonia adsorption and the surface reaction between adsorbed ammonia and oxygen. Figure 7A presents NH₃ temperature programmed desorption profiles for 1.5% Ag/Al₂O₃. NH₃ desorbed over this catalyst at broad range of temperatures at 70 to 450 °C. Apart from ammonia, reaction products – N₂, NO and N₂O – were detected at temperatures from 70 to 500 °C. N₂O as the first reaction product appeared around 250 °C. N₂ appeared at higher temperatures (>400 °C), while NO was not detected during experiment. Thus, NH₃ could be oxidized over lattice oxygen of Ag_xO to a limited extent, and N₂O was the main product around 250-450 °C. Furthermore, figure 7B shows NH₃ temperature programmed surface reaction profiles over Ag/Al₂O₃. NH₃ desorbed mainly at low temperatures (<250 °C), indicating that high NH₃ oxidation efficiency of Ag/Al₂O₃. N₂ was the main reaction product in the range of 70-250 °C, while N₂O appeared in two broad stages: 70-250 and 250-500 °C. Minor amount of NO was detected over Ag/Al₂O₃ above 350 °C during NH₃-TPSR. Thus, the adsorbed NH₃ reacted mainly with the gas phase O₂ over Ag/Al₂O₃ yielding reactions products – N₂, N₂O and NO. Figure 7C presents the NH₃-TPD profile of Cu/Al₂O₃. NH₃ was desorbed over such catalysts up to 350 °C, with N₂ as the main reaction product in the range of 200-400 °C. Besides N₂, by-products were also detected: N₂O above 150 °C and NO above 375 °C, respectively. Thus, NH₃ was partially oxidized by lattice oxygen of copper oxide species under these conditions. During the NH₃-TPSR performed for ammonia desorption in the presence of O₂, N₂ appeared in the range of 200-350 °C. While significant amounts of N₂O and NO was detected above 150 and 350 °C, respectively, as presented in figure 7D. Furthermore, figures 7E and 7F presents NH₃-TPD and NH₃-TPSR for 1.5% Ag-10% Cu/Al₂O₃. As a result of differences between silver and copper oxide species, the profiles of NH₃ desorption and reaction products evolution varied appreciably during both experiments over the bimetallic sample. In particular, during NH₃-TPD experiment over Ag-Cu/Al₂O₃, the lattice oxygen of copper oxide species partially oxidised adsorbed ammonia, yielding N₂ as the main reaction product in the range of 200-400 °C. N₂O was the minor product above 150 °C with the maximum in the range of 150-300 °C. While NO was not detected over Ag-Cu/Al₂O₃. During NH₃-TPSR, a significant amount of NO appeared in the high temperature range (above 350 °C). Thus, the interaction between silver and copper oxide species played an important role in NH₃ activation and its oxidation. The silver oxide species enhanced low temperature activity

of NH₃ oxidation mainly into N₂. However, at high temperatures increased the selectivity to by-products. While the copper oxide species facilitated the formation of N₂ at higher temperature range up to 350 °C.

In situ DRIFTS studies were carried out to investigate the role of silver and/or copper oxide species for the adsorption of NH₃ on the Ag-Cu-based catalysts. Table 5 summarizes the assignments of the FTIR bands observed upon adsorption of NH₃. In figure 8A, the bands at 1687, 1475 and 1396 cm⁻¹ appeared due to the deformation modes of NH₄⁺ formed by the interaction of NH₃ with Brönsted acid sites on 1.5% Ag/Al₂O₃ [34-37]. The bands at 1622 and 1235 cm⁻¹ raised from the asymmetric and symmetric deformation modes, respectively, of NH₃ molecules coordinated on Lewis acid sites of the Al₂O₃ support [34-37]. The two bands – at 1449 cm⁻¹ ascribed to the imide (–NH) deformation modes, and at 1350 cm⁻¹ ascribed to the amide (–NH₂) wagging [38, 39] – appeared at 50 °C. Both bands together with the bands from NH₃ coordinated on Brönsted and Lewis acid sites decreased gradually with increasing temperature. The band at 1449 cm⁻¹ remained stable until 300 °C, while the band at 1350 cm⁻¹ disappeared above 50 °C. At about 300 °C, the peak related to the amide (–NH₂) scissoring gradually increased at 1580 cm⁻¹. Thus, NH₃ adsorbed on Ag/Al₂O₃ was activated to form –NH_x (–NH₂ and –NH) intermediates, which desorbed from the surface of the catalyst. Nevertheless, the band located at 1580 cm⁻¹ could arise due to bidentate nitrates [34], however, in the NH₃-TPD profile for Ag/Al₂O₃ (Fig. 7A), we did not observe NO_x produced in the studied temperature range of 70-500 °C. The bands in the N-H stretching region occurred at a broad band in the range of 3350-3100 cm⁻¹ [38, 39]. Furthermore, the NH₃-SCO mechanism was studied with respect to the behavior of adsorbed NH₃ species interacting with O₂ on the surface of Ag/Al₂O₃. Figure 8B presents the *in situ* FTIR spectra of Ag/Al₂O₃ at various temperatures (50-350 °C). The bands of NH₃ coordinated on Brönsted acid sites appeared at 1691, 1475 and 1393 cm⁻¹, while the bands coordinated on Lewis acid sites existed at 1622 and 1243 cm⁻¹. The band of –NH and –NH₂ appeared at 50 °C at 1449 and 1350 cm⁻¹, respectively, and their intensity slightly increased with the increasing temperature. Above 100 °C, the band of –NH₂ appeared at 1580 cm⁻¹ and strongly increased up to 350 °C. The band at 1580 cm⁻¹ could be attributed to bidentate nitrate, because NO was formed above 350 °C over Ag/Al₂O₃ in the presence of gaseous O₂ as indicated NH₃-TPSR results (Fig. 7B). Additionally, new bands at 1652 cm⁻¹ (at about 250 °C), at 1463 cm⁻¹ (at about 150 °C) and at 1330 cm⁻¹ (at about 350 °C), appeared also due to bridging nitrate, chelating nitro and free NO₂⁻ ion [35], respectively. Thus, the adsorbed NH_x was mainly oxidized by the gas phase O₂, and

adsorbed as nitrites/nitrates on the Ag/Al₂O₃ catalyst in the presence of O₂. While the reaction between NO and excessive hydrogen abstraction of NH₃, i.e. NH_x species, yielded N₂ and N₂O (Fig. 7B). The FTIR bands observed upon adsorption of NH₃ on Ag/Al₂O₃ after successive purging in N₂ appeared also in the spectra of Cu/Al₂O₃ (NH₃ coordinated on (i) Brönsted acid sites: 1684, 1475 and 1396 cm⁻¹; (ii) Lewis acid sites: 1629 and 1255 cm⁻¹; Fig. 8C) and Ag-Cu/Al₂O₃ (i): 1690, 1481 and 1396 cm⁻¹; (ii): 1622 and 1258 cm⁻¹; Fig. 8E). NH₃ adsorbed mainly on Brönsted and Lewis acid sites, however, these bands showed different intensity on the M-Al₂O₃ (M = Ag, Cu, or Ag-Cu) catalysts. Cu/Al₂O₃ revealed relatively low intensity of the bands corresponding to NH₃ coordinated on Brönsted acid sites. Additionally, small bands appeared above 150 °C for Cu/Al₂O₃ at 1558 and 1540 cm⁻¹, while for Ag-Cu/Al₂O₃, at 1553 cm⁻¹, which were assigned to the bidentate (1558-1553 cm⁻¹) and monodentate nitrates (1540 cm⁻¹) [36]. Thus, in the absence of O₂, adsorbed ammonia was oxidised by lattice oxygen (O₂⁻) of copper oxide species with formation of NO_x ad-species. Such *in situ* formed NO_x ad-species possibly reacted with adsorbed NH₃ yielding N₂ and N₂O (Fig. 7C and 7E). The interaction of adsorbed NH₃ with gaseous O₂ revealed the bands of NH₃ assigned to (i) Brönsted acid sites: 1652, 1475 and 1396 cm⁻¹; (ii) Lewis acid sites: 1622 and 1261 cm⁻¹ over Cu/Al₂O₃; Fig. 8D), and (i): 1690 and 1481 cm⁻¹; (ii): 1619 and 1249 cm⁻¹ over Ag-Cu/Al₂O₃; Fig. 8F). Analogously, other bands attributed to the bidentate and monodentate nitrates at 1557 and 1539 cm⁻¹, respectively, appeared in the spectrum of Cu/Al₂O₃ after successive purging in O₂. While the bands assigned to bridging nitrate (1651 cm⁻¹), chelating nitro (1403 cm⁻¹) and free NO₂⁻ ion (1326 cm⁻¹) appeared in the spectrum of Ag-Cu/Al₂O₃. The formation of these three species over Ag-Cu/Al₂O₃ was strongly enhanced by the presence of gas phase O₂. Moreover, the spectrum of Ag-Cu/Al₂O₃ contained bands detected also for Ag/Al₂O₃ (-NH at 1450 cm⁻¹, -NH₂ scissoring or bidentate nitrates at 1583 cm⁻¹) and for Cu/Al₂O₃ (bidentate nitrates at 1553 cm⁻¹) species. Thus, the presence of silver oxide species enhanced dehydrogenation of chemisorbed NH₃ molecules much faster than copper oxide species, and therefore the significant population of NH_{3-x} (x = 1,2) species appeared on the Ag/Al₂O₃ and Ag-Cu/Al₂O₃ surfaces.

Based on the above *in situ* FTIR results, adsorbed NH₃ was activated through the hydrogen abstraction over Ag/Al₂O₃, and further partially oxidized by gas phase O₂ to bridging nitrate, chelating nitro and free NO₂⁻ ion, finally yielding N₂ and N₂O. Moreover, adsorbed NH₃ – as protonated NH₄⁺ on Brönsted acid sites and coordinated NH₃ on Lewis acid sites – was oxidized to bidentate and monodentate nitrates over lattice oxygen of

copper oxide species of Cu/Al₂O₃. In the presence of gas phase O₂, the evolution of NO was observed only in the high temperature range (Fig. 7B,D,F), in which there was no chemisorbed ammonia able to convert *in situ* formed NO_x ad-species to N₂ and N₂O. Therefore, we concluded that NH₃-SCO on the Ag/Al₂O₃, Cu/Al₂O₃ and Ag-Cu/Al₂O₃ followed an *in situ* selective catalytic reduction (i-SCR) mechanism, which involved the partial oxidation of NH₃ into NO_x species, along with adsorbed NO_x species interacting with NH_x and being reduced to reaction products. Thus, *in situ* formed NO_x were the intermediates of this mechanism. We could not excluded that interaction between the NH₃ and *in situ* formed NO_x ad-species led to formation of NH₂NO, NH₂NO₂ or NH₂NO₃ intermediate species with low thermal stability, which easily decomposed into N₂ with N₂O as a by-product [34,35,36]. Noteworthy, the results of NH₃-TPD or NH₃-TPSR did not reveal the evolution NO₂, indicating NO as the main reaction intermediate. Nevertheless, further studies are underway over such systems applying *in situ* DRIFTS coupled with transient techniques (TAP, SSITKA) in order to provide information on the surface coverage of active and inactive (spectators) species under reaction conditions.

Table 5. Assignments of the FTIR bands.

Wavenumber [cm ⁻¹]	Surface species	Ref.
1691-1684	NH ₄ ⁺	[40]
1481-1475		[41]
1403-1396		[40, 41]
1629-1619	NH ₃ L	[38, 41]
1261-1235		[39, 40]
1450-1449	-NH	[42, 43]
1350	-NH ₂ wagging	
1583-1580	-NH ₂ scissoring	
	bidentate nitrates	[34]
1652-1651	bridging nitrate	[36]
1558-1553	bidentate nitrate	

1540-1539	monodentate nitrate
1463	chelating nitro
1330-1326	free NO ₂ ⁻ ion

4. Conclusion

We investigated the different loading of Ag and/or Cu – Ag (1-5%), Cu (10-15%) or Ag-Cu (1-1, 1-10, 1.5-10, 5-5% of metal) on the physicochemical properties, catalytic activity and selectivity in NH₃-SCO. XRD, H₂-TPR, UV-vis-DRS, XPS and EXAFS analyses revealed that silver species existed mainly in the form of Ag₂O, while copper oxide species coexisted as CuO and CuAl₂O₄ on Ag/Al₂O₃, Cu/Al₂O₃ and Ag-Cu/Al₂O₃ surfaces, respectively. Silver species significantly decreased temperature of the ammonia oxidation but also decreased the selectivity to N₂ with increasing silver loading up to 5%. Copper oxide species were significantly less active in the ammonia oxidation, but more selective to N₂. Easily reducible highly dispersed CuO_x promoted the activity of 5-15% Cu/Al₂O₃ catalysts, while bulk CuO_x and CuAl₂O₄ decreased N₂ selectivity. Thus, the activity and selectivity were optimized by tuning the loading of silver and copper in the Ag-Cu/Al₂O₃ catalysts. We selected 1.5% Ag-10% Cu/Al₂O₃ as promising catalyst for NH₃-SCO, which operated at relatively low temperature with high selectivity to N₂ (full NH₃ conversion at 375 °C with 94% N₂ selectivity). NH₃-TPD, NH₃-TPSR and *in situ* FTIR measurements confirmed the *in situ* selective catalytic reduction (i-SCR) mechanism over 1.5% Ag/Al₂O₃, 10% Cu/Al₂O₃ and 1.5% Ag-10% Cu/Al₂O₃. However, copper oxide species were less active in ammonia oxidation than silver oxide species. Thus, the high activity and N₂ selectivity of Ag-Cu/Al₂O₃ catalyst were assigned to the enhanced activity of silver species in ammonia oxidation to NO_x and activity of copper oxide species in NO_x reduction with unreacted ammonia to N₂ and N₂O.

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