Preparation of Ag–Cu/Al₂O₃ Composite Catalyst for Ammonia Decomposition

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Received May 7, 2014, Accepted October 2, 2014, Published online January 5, 2015

A catalyst of Ag with alumina has been widely used for the decomposition of odorous ammonia. In order to meet cost effectiveness, copper was added with five different doping ratios of Ag/Cu in this work, and NH₃ decomposition was examined at 150–400 °C. Experimental results show that the catalyst doped with only Cu shows very weak potential to oxidize NH₃ despite its excellent selectivity for nitrogen molecules than NO or N₂O at temperatures over 300 °C. Analysis by X-ray photoelectron spectroscopy indicates that Ag⁰ is the major chemical functionality that determines the decomposition rate of NH₃ at low temperature, e.g., 200 °C, while Ag⁺ and Ag²⁺ are efficient at higher temperatures. Among the five segregated copper functionalities, only Cu 2p_{a/2} appeared to be favorable for the activity of Ag particles. It was found from the experimental results that Ag/Cu = 1:9 could provide a cost-effective combination for the low temperature regime.

Keywords: Selective catalytic oxidation, NH₃ decomposition, Ag-Cu/Al₂O₃ catalyst, Cost evaluation

Introduction

One of the growing air pollution concerns in fast-growing major cities around the world, such as Seoul, is the menace of odor pollution.¹ One of the main pollutants is ammonia, usually released from the decomposition of protein-based wastes and other biochemical processes.² The need to curb the incessant surge in the release of this gas has gained some attention, thanks to the public outcry against the atmospheric discomfort they are subjected to, especially by those living near incineration or chemical process plants. This has led to stringent control through appropriate regulations and the need for efficient control technologies.

The most conventional method for NH₃ odor control has been thermolysis at significantly high temperatures to NO_x and N₂. But, because of the inherent high cost associated with this method, the use of many efficient catalysts has been researched and proposed.³ However, with the aid of an appropriate technique, selective catalytic oxidation (SCO) of NH₃ to N₂, which is the most environmentally benign process, has been studied in the last couple of decades.^{4–6} A number of catalysts, including γ -Al₂O₃-supported Ni, Fe, Mn, Cu, and Ag, have been reportedly utilized for this purpose.^{5,6} Also, at low temperature, SCO of ammonia with oxygen to nitrogen and water is potentially an efficient method to abate ammonia pollution.^{7–9} The use of metal oxide catalysts such as Co_3O_4 , MnO₂, CuO, Fe₂O₃, V₂O₅, and MoO₃ have also been studied in this regard.^{10–15} From the literature review, ammonia conversion levels are found to be unimpressive when carried out at relatively low temperatures. The inclusion of Ag-based catalysts to enhance the process has been studied and reported by some researchers.^{16–20} In earlier works by Il'chenko *et al.*, it was reported that the specific catalytic activity of Ag metal at 300 °C is lower than that of the other precious metals Pt and Pd.^{17,18} Recently, it was reported that alumina-supported Ag (Ag/Al₂O₃) catalysts are extremely active for NH₃ oxidation at low temperature, and the performance of these catalysts is even superior to that of noble metal catalysts.^{16,19} However, because of the high cost of Ag metal, some researchers have sought means to considerably lower the cost of its use in this respect without jeopardizing the integrity of the primary aim of NH₃ control.

In this light, we attempted the use of low-cost Cu doping of alumina-supported Ag (Cu–Ag/Al₂O₃) catalysts in the thermal conversion of NH₃ at low temperature.

Experimental

Sample Preparation. The starting materials consisted of 99% AgNO₃ and 99.8% Cu(NO₃)₂ for the preparation of the catalyst composites, while the granular γ -type alumina support (particle diameter, dp = 2-3 mm) used was procured from Parteck Corp. (Seoul, Korea). The pristine support has a specific surface area of 149.8 m²/g. The different Ag/Cu loading ratios on alumina were derived by using the expression $Ag_{(10)}$ $-x^{-x}$ -Cu_x, with $0 \le x \le 10$, from which eight composites were prepared by wet impregnation. The sample nomenclatures are summarized in Table 1. The surface coating was homogeneously distributed on the support by stirring during a 24-h impregnation period, after which the excess water was removed by filtration followed by drying at 100 °C for 6 h. The samples were calcined at 500 °C in pure N2 atmosphere with a continuous flow rate of 50 mL/min for a period of 3 h. After this preparation period, the samples were pelletized Sample ID

а

b

с

d

e

f

g

(particle size, dp = 2-3 mm), named according to the mixing ratio (Table 1), and consequently used for NH₃ conversion test.

 NH_3 Decomposition. The schematic diagram depicted in Figure 1 shows the lab-scale setup for the catalytic oxidation of NH_3 by the test samples.

NH₃ solution (28–30% of NH₃) mixed with high-purity air (99.99% pure) by bubbling was used as the test gas feed. Compressed air was mixed constantly with the aid of a Line Mixer (sus 304, 15A, 20L; Duckchi Inc., Hwaseong-si, Korea). The mixture was injected into a round-bottom flask, sealed with a Pyrex stopper. A mass flow controller was used for adjusting the concentration of the supplied gas. A specially designed ceramic heater (max. temp. 500 °C; Duckchi Inc., Hwaseong-si, Korea), which was connected to a temperature controller (TZN-4H; Autonics, Busan, Korea), was installed on the entire outer wall of the reactor for temperature control and monitoring. Thermal insulation was improved by the inclusion of a heat conservation insulation cover (ceramic fiber wool), which was evenly wrapped around the outside

Ag (wt %)

12.50

11.25

8.75

6.25

3.75

1.25

0

Cu (wt %)

0

1.25

3.75

6.25

8.75

11.25

12.50

Table 1. Description of test samples in this study.

Ag/Cu ratio

10:0

9:1

7:3

5:5

3:7

1:9

0:10

of heater in order to minimize heat loss. The change in NH_3 concentration around the catalytic decomposition setup was measured with the aid of gas detection tubes (GASTEC, Japan, 8-8-6 Fukayanaka, Ayase-City, Kanagawa 252-1195, Japan). The experimental conditions used in this work are summarized in Table 2.

Catalyst Characterization. Textural examination was carried out by measuring the specific surface area and mesopore size distribution, obtained from Bruner–Emmett–Teller (BET) and Barrett–Joiner–Halenda (BJH) plots, respectively. Chemical characterization was made through powder X-ray diffraction (XRD) with Cu K α radiation from an X-ray tube operating at 40 kV and 40 mA (Rigaku D/Max-RB X-ray Diffractometer, D8 advance, Bruker, Japan). The surface chemical structure of the active species on the catalysts was characterized by X-ray photoelectron spectroscopy (XPS), using Al K α radiation with h ν = 1486.7 eV (XPS, PHI Quantera Spectrometer, ULVAC-PHI, Inc., Kanagawa, Japan).

Results and Discussion

It is expected that the fed NH_3 could be activated by the catalyst ultimately to form the intermediates $-NH_2$ and -NH through abstraction of hydrogen, as expressed in Eqs. (1) and (2):

Table 2. Operation condition of NH₃ decomposition test.

Application
N ₂
$10000\mathrm{h^{-1}}$
600 ppm NH ₃ (balance gas: N ₂)
150–400 °C



Figure 1. Schematic diagram of the catalytic reactor for NH₃ oxidation.

$$NH_3 \rightarrow NH_2 + H \tag{1}$$

$$NH_2 \rightarrow NH + H$$
 (2)

The primary process of NH₃ oxidation on hydrogenpretreated Ag/Cu/Al₂O₃ is believed to involve the reaction with elemental oxygen. The subsequent conversion process follows the reactions $(3)-(5)^{21}$:

 \rightarrow NH₂ \pm H

NLL

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

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

$$HNO + HNO \rightarrow N_2O + H_2O$$
(5)

Structural Examination. Textural analysis using N2 adsorption at 77 K showed that all samples are nonporous in nature as they exhibit type II adsorption isotherm profiles composed mainly of mesopores, as shown in Figure 2. Their mesopores within the size range approved by the IUPAC (i.e., 2-50 nm) are plotted and compared in Figure 3. Both figures indicate no significant change on the porosity and S_{BET} , which varied from 130 to $140 \text{ m}^2/\text{g}$ depending on the binary metal



Figure 2. N_2 adsorption at 77 K of test samples for estimating S_{BET} .



Figure 3. BJH plots for estimating the mesopore regime.

combination. In general, the metal coating might block the tiny pores of catalyst surface as well as provide additional active sites. Nevertheless, one could envisage that the structural properties of the modified samples would have no relevance to their potential catalytic behavior. Thus, the dominating functionalities could be reviewed with similar textural basis of test sample catalysts.

Chemical Analysis and NH₃ Decomposition. Table 3 provides the information for deconvolution of the Ag 3d and Cu 2p spectra. The estimation of the elemental compositions in percentages of test samples based on the XPS analysis is provided in Table 4.

It was found, as expected, that the Ag content decreased with the increase in Cu level. This tendency was accompanied by a haphazard distribution in chemical quantities of oxygen and aluminum species of the samples. However, classification of catalyst particles depending on their chemical structure and oxygen states was pertinent to identify which particular specie(s) is/are responsible for NH₃ decomposition at the target temperature of 200 °C. In addition, the mixture of Ag with Cu could affect the ammonia decomposition. Peak deconvolution was carried out in order to correlate the amount of Ag and Cu species with the decomposition efficiency.

Figure 4 shows the NH₃ decomposition efficiency of the test catalysts thermally treated at 500 °C for 3 h. In the reaction at 200 °C, the catalyst doped only with Ag showed the highest decomposition. The addition of Cu (Ag-Cu/Al₂O₃ composite catalyst) reduced the decomposition rate of gaseous ammonia. The highest efficiency with Cu was found with the ratio of 50% in the Ag-Cu/Al₂O₃ composites. The poorest effect was

Table 3. Binding energy allocation of Ag and Cu species present on test samples.

Ag								
Peak I	Peak II		Peak III					
368.1 ± 0.1	367.7 ± 0.2		367.4 ± 0.2					
Cu								
Peak I	Peak II	Peak III	Peak IV	Peak V				
932.5	934.6	940.3	943.1	952.7				

Table 4. Results of percentage elemental composition obtained from XPS analysis.

Sample	Ag 3d5 (at. %)	Al 2p (at. %)	C 1s (at. %)	Cu 2p3 (at. %)	O 1s (at. %)
a	1.49	34.32	15.21	ND	48.98
b	1.29	32.61	15.10	0.43	50.57
c	0.91	30.88	19.64	0.70	47.86
d	0.80	33.50	16.22	0.78	48.70
e	0.22	34.38	15.46	0.77	49.17
f	0.05	36.50	13.92	1.27	48.26
g	ND	35.30	14.81	1.50	48.39

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obtained at pure Cu catalyst (g). With increasing temperature, a progressive convergence trend of efficiency was observed, indicating the performance enhancement of the catalysts at elevated temperature. The decomposition rate rose dramatically above 300 °C. On reaching 400 °C, all samples exhibited almost complete conversion, irrespective of the doping ratio.

Figure 5 depicts the XPS deconvolution of Ag spectra, and quantitation of three identified species is graphically presented in Figure 6. All three kinds of Ag species were present in samples a–d, while elemental silver (Ag^0) seemed to have completely oxidized, as only peaks II and III were found in samples e and f. As expected, obvious phase transition could occur without remaining silver elements after the reaction.

The quantified Ag species of the sample a, with respect to their oxidation states, tends to be evenly present on the coated alumina support. According to Zhang *et al.*,²² Ag⁰ is the main active species at low temperature. At temperatures higher than 140 °C, ionic silver (Ag⁺ and Ag²⁺) could also be complementary functionalities for the activation of NH₃ prior to reacting with the oxygen molecules. This correlation is depicted in

100 $\rm NH_{a}$ decomposition efficiency [%] 80 (a) x = 060 (b) x = 1(c) x = 340 -(d) x = 5-(e) x = 720 -(f) x = 9-(g) x = 100 200 300 350 150 250 400 Temperature [°C]

Figure 4. NH₃ decomposition efficiency of test catalysts in terms of the combination ratio of Cu to Ag.



Figure 5. Deconvolution of the Ag 3d spectra into Ag⁰, Ag⁺, and Ag² ⁺, respectively, as peaks I, II, and III.

Figure 7. Ground-state elemental silver (Ag^0) is seen here to be the antagonistic species in the NH₃ conversion to N₂ or NO_x at 200 °C, as a positive correlation trend is evident between the Ag⁺ and Ag²⁺ species and the efficiency of the Cu-doped catalysts.²³

With regard to Ag–Cu/Al₂O₃ composites, it is noteworthy that the efficiency of pure Ag catalyst decreased by the presence of Cu. In this view, it could be thought that Cu is an inhibitor and does not contribute to enhancing the efficacy of the Ag catalyst. However, an investigation into the species of Cu by XPS analysis revealed some species that are responsible for such drawback. Figures 8 and 9 provide the peak deconvolution and quantification of Cu XPS 2p spectra into two major spectra, with one bearing three satellites.

It was observed that the magnitude of peak I decreases gradually with increasing Cu content from samples a–d, while an unusual twist of increasing amount ensued from samples e–g (Figure 9). Also, a correlation between these Cu functionalities and conversion efficiency was carried out, which is shown in Figure 10.



Figure 6. Quantitative estimation of Ag species from XPS analysis in Figure 5.



Figure 7. Correlation of Ag species oxidation state with NH₃ conversion efficiency.

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At a glance, it could be observed that peak I seems to show an opposite trend with the conversion efficiency, while peaks III and IV show relative relevance. Although no species showed any excellent correlation as earlier confirmed, the two terminal satellites of peak I proved to be poorer inhibitors for the activity of Ag than others.

Article

XRD analysis was carried out to complement the chemical structure carried out with XPS. The obtained XRD patterns for test samples (samples a–g) and γ -type alumina support (sample h) are displayed in Figure 11. The γ -type alumina showed the dominant peaks in the XRD pattern throughout the test samples. Only Al₂O₃ peak pattern appeared on the samples that were dominated by Cu rather than Ag (samples f and g). The XRD examination clearly showed the amount of variation of Ag in the catalyst. It also implies efficient combination of Cu with Ag; at the same time, it can be guessed that elemental copper doped well on the alumina support. It therefore is believed that the precursors of the catalysts were well dispersed in the aqueous solution. On the other hand, crystal-line Cu compounds usually cannot be detected by XRD.²⁰ The



Figure 8. Deconvolution of the Cu 2p spectra into Cu $2p_{3/2}$ and its satellites (peaks I–IV) and Cu $2p_{1/2}$.



Figure 9. Quantitative estimation of Cu catalyst species from XPS analysis in Figure 6.

peaks attributed to crystalline Ag₂O were overlapped with those of Al₂O₃ around the angle 38°, as seen in samples a–c.¹⁶ **Cost Evaluation.** Price information from the reagent supplier showed that the cost of 99.8% and 99% AgNO₃ and Cu(NO₃)₂ in USD/g is approximately 1700 and 25, respectively. The relative cost, therefore, is Ag/Cu = 68:1. The obvious difference in the prices was the motivation to carry out this work focusing on the optimum combination of two catalytic agents. Ammonia decomposition at possibly low temperature of 200 °C could be achieved at 93.8%. The extrapolation of cost and efficiency is displayed in Figure 12.

Sample f containing 90% copper with 10% silver showed the most cost-effective recipe. However, the conversion efficiency reduction from 93.8% at sample d to about 61.2% with corresponding decrease in cost ratio of 27.2 tends to bring about confusion in terms of the relevance of efficiency and cost. With this observation, it is proposed that, depending on the trade-off between the two, one could easily employ



Figure 10. Correlation of Cu functionalities' state with NH₃ conversion efficiency.



Figure 11. XRD patterns of the prepared catalyst samples.



Figure 12. Correlation of NH_3 decomposition efficiency with cost evaluation.

the information in Figure 12 to evaluate the doping ratio of Cu/ Ag for environmental clean-up of NH₃.

Conclusions

The present study leads to the following conclusions:

- 1. Despite reduction in the catalytic decomposition of ammonia, the addition of copper must be effective based on the cost and benefit, particularly at low-temperature reactions.
- 2. Ground-state elemental Ag is the major chemical functionality that determines the removal of NH₃ at low temperatures (200 °C), while Ag⁺ and Ag²⁺ could be complementary when present and more efficient at higher temperature.
- 3. The presence of the Cu 2p_{3/2} peak is favorable for the activity of Ag species.
- 4. The use of a small amount of the precious metal Ag would only be beneficial for cost reduction, while equal proportion with Cu diluent seems to favor consideration of both efficiency and cost.

Acknowledgment. This research was financially supported by the Ministry of Environment (MOE), Republic of Korea (Project no. 401-112-015).

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