Relationship between oxidation states of copper supported on alumina and activities for catalytic combustion of NH_3

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The relationship between the oxidation state of Cu supported on an alumina catalyst (Cu/Al_2O_3) and the activity for combustion of NH_3 was investigated. Combustion of NH_3 on the catalyst treated in hydrogen at 800 °C occurred at lower temperature than on the catalyst treated in air. It was also much better than Pt and Rh catalysts for the conversion of NH_3 to N_2. Characteristics of the catalyst were investigated by XRD, XPS, and the N_2O pulse injection method to understand the reason of its high catalytic activity. The reason of the high activity of the catalyst treated in hydrogen at the high temperature was attributed to the lower oxidation state of Cu in the catalyst.

Keywords: copper catalyst, combustion of NH_3, oxidation state of copper, high-temperature treatment

1. Introduction

Removal of odors in living environments such as houses, trains, and factories is paid greater attention with progress of living level. Many kinds of catalysts have been already used for deodorization [1,2] in refrigerators, space heaters, purification of exhaust gas from factories [3], etc. Catalytic removal of offensive odors such as amine, mercaptan, and valeric acid was studied scarcely [4–9], and details of the reaction characteristics have not been studied extensively.

A group of nitrogen-containing compounds (N-compounds), such as trimethylamine (TMA) and NH_3, is one of the typical odors. Harmful NO_x and N_2O are often formed in the catalytic combustion of N-compounds [8,9].

Compared with studies on activities of platinum group metals catalysts for combustion of NH_3 to N_2 [10–12], studies on copper catalysts for the combustion are very few. A reaction mechanism for the NH_3 combustion on Cu-ion-exchanged Na-Y zeolite was proposed [13], where a Cu^{2+} ammonia complex was formed at first, and it transformed to Cu^{+} complex which led to N_2 by its decomposition. In a study on an alumina-supported CuO catalyst for the combustion [14], adsorption of NH_3 is essential for formation of the N≡N bond of N_2 or N_2O. The presence of water interferes with adsorption of NH_3, causing low conversion of NH_3 to N_2 and N_2O. Concentration of O_2 in a reactant gas affected activities of Cu_2O catalyst for NH_3 combustion [15]. Low concentration of O_2 led to increase of N_2 formation, but high concentration led to increase of N_2O. In these studies, the relationship between the oxidation state of copper and the activity for combustion of NH_3 to N_2 was not discussed. On the other hand, the relationship between the oxidation state of copper and the activity for combustion of CO has been reported as follows. In case of alumina-supported copper catalysts [16,17], the high activities of copper in lower oxidation state, such as Cu_2O and Cu, than CuO were observed for the combustion. The pretreatment conditions affected redox properties of the copper catalyst [16]. A Langmuir–Hinshelwood mechanism surface reaction between adsorbed CO molecules and O atoms was supported [17]. The activities of alumina-supported copper catalysts for CO combustion were similar to those for NH_3 combustion.

This study was conducted to elucidate the relationship between the oxidation state of copper in various alumina-supported copper catalysts (Cu/Al_2O_3), which were pretreated under different conditions, and the activity for combustion of NH_3.

2. Experimental

2.1. Catalyst preparation

An alumina (JRC-ALO4) supplied by Catalysis Society of Japan was calcined at 1060 °C for 30 min in air [18] and used as the catalyst support. Copper catalysts supported on alumina (Cu/Al_2O_3) and Pt-group metals (Pt/Al_2O_3 and Rh/Al_2O_3) were prepared by classical impregnation. Metal salts of $Cu(NO_3)_2 \cdot 3H_2O$, $Pt(NO)_2(NH_3)_4$ and $Rh(NO_3)_3$ were used for the impregnation. The Al_2O_3 impregnated with the aqueous solution was dried at 60 °C overnight, and calcined at 350 °C for 1 h. It was pretreated in air or in 10% H_2 diluted in He at various temperatures before the

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Table 1
Catalysts prepared by different methods.

Catalyst			Procedure of pretreatment[a]		Copper		
No.	Metal	Metal content (wt%)	Atmosphere	Temperature (°C)	Surface area (m^2/g-cat.)	Particle size (nm)	Dispersion (%)
1	Cu	7.3	Air	350	6.6	7.4	14
2	Cu	7.3	Air	650	6.7	7.3	14
3	Cu	7.3	Air	800	5.8	8.4	12
4	Cu	7.3	H_2	350	6.6	7.4	14
5	Cu	7.3	H_2	500	4.8	10	10
6	Cu	7.3	H_2	650	3.0	17	6.3
7	Cu	7.3	H_2	800	1.9	26	4.1
8	Cu	3.7	H_2	800	1.0	24	4.3
9	Cu	11.1	H_2	800	1.2	64	1.6
10	Cu	14.7	H_2	800	1.6	63	1.7
11	Pt	1.0	H_2	800			
12	Rh	1.0	H_2	800			

[a] Pretreatment 30 min in 10% H_2 diluted in He.

combustion test. Conditions of the pretreatments and the physical properties of the catalysts are presented in table 1.

2.2. Characterization

Surface area of the reduced Cu part in the catalysts was measured by the N_2O pulse method [18,19]. The N_2O pulse method is based on the decomposition of a nitrous oxide molecule on a copper surface which is accompanied by liberation of one nitrogen molecule corresponding to the following equation:

$$N_2O + 2Cu \rightarrow N_2 + Cu_2O \tag{1}$$

It was confirmed in previous reports [18,19] that only surface Cu was oxidized by N_2O to Cu_2O below 100 °C, and bulk Cu was oxidized above this temperature. The most adequate temperature range for the method is between 70 and 100 °C [19]. Surface area and average spherical particle size are calculated by the amount of consumed N_2O in the method. A 200 mg of a catalyst was introduced into a tubular quartz reactor, where the powder is maintained in between two glass wool plugs. The catalyst sample was reduced in 10% H_2 diluted by He at 350 °C for 30 min. 100 μl pulses of N_2O were injected at 90 °C until no more uptake of N_2O was detected. Structure change of copper catalysts during the reaction test were followed by using XRD using a Shimadzu XD-D1 analyzer.

X-ray photoelectron spectroscopy (XPS) was used to investigate the state of Cu in the Cu catalysts. We used a ULVAC-PHI model 5500 ESCA/MC/SIMS using Mg Kα X-ray at 1253.6 eV as the excitation source. The anode operated at 15 kV and 400 W. Sputter for depth profiling was performed with 3 kV Xe^+ ions.

2.3. Reaction test

Catalytic combustion of NH_3 was studied using a tubular quartz reactor with an inner diameter of 8 mm. 1.0 g of a catalyst was packed into the reactor. The catalysts, in powder form, were first pelletized, crushed and sieved to 6–10 mesh. Before reaction, the catalysts were pretreated (table 1) *in situ* in flowing air or H_2 (60 ml/min). The reaction gas mixture was composed of 800 ppm NH_3, 21% O_2 and He balanced. The gas-hourly-space velocity (GHSV) was 12,000 h^{-1}. The reaction temperature was varied from 120 to 320 °C stepwisely while flowing the reaction gas. The temperatures were maintained at 120, 150, 175, 200, 225, 250, 275, 300 and 320 °C, and the increase from one temperature to the next occurred at a rate of 2 °C/min. Before sampling the reaction mixture, the catalyst was preconditioned at each reaction temperature for 10 min in the reaction gas. The sampling was repeated every 15 min until the composition of the products became almost constant.

The effluent gases were analyzed by chemiluminescence (Shimadzu analyzer, NOA-7000) for NO_x detection. A Shimadzu GC-14A gas chromatograph, equipped with a thermal conductivity detector (TCD) and using a 2 m long MS-5A glass column was used to separate O_2, N_2 and CO. Another 2 m long Porapak Q column was used to separate CO_2 and N_2O. Finally, a second gas chromatograph GC-14A, equipped with a TCD and using a glass column of Chromosolb 103, was used to determine the amount of unreacted NH_3 left after the combustion of NH_3.

3. Results and discussion

3.1. Effect of the calcination temperature on the combustion of NH_3

In figure 1, the effect of the calcination temperature on the combustion of NH_3 is shown. The effect of the calcination is minor. Whatever the calcination temperature, NH_3 combustion to N_2 began at ca. 175 °C, even if the activity decreased slightly with an increase of the calcination temperature. Cu particle size increased slightly after calcination at 800 °C, indicating a slight sintering of Cu resulting in a minor decrease in the activity.

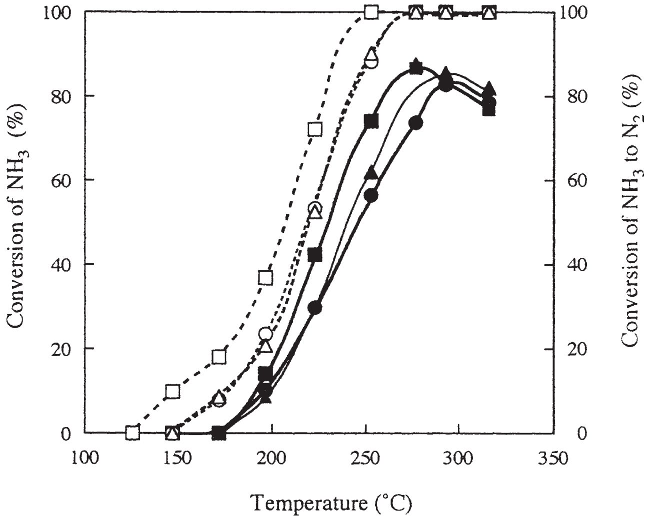

Figure 1. Effect of the calcination temperature of the copper catalyst on the conversion of NH_3. Calcination temperature: (□, ■) catalyst 1, 350 °C; (△, ▲) catalyst 2, 650 °C; (○, ●) catalyst 3, 800 °C. Open symbols: conversion of NH_3, closed symbols: conversion of NH_3 to N_2. Reactants: NH_3 850 ppm, O_2 21%, He balanced. SV: 12,000 h^{-1}.

3.2. Effect of thermal treatment of the catalyst in H_2 on combustion of NH_3

Figure 2 shows the change in catalytic activity of the catalysts treated at different temperatures in a stream of H_2 balanced with He. The activity of the catalyst before the pretreatment in H_2 (catalyst 1) is shown in the same figure for comparison. The reaction temperature for 100% conversion of NH_3 was lowered after the pretreatment (figure 2(a)), and the conversion of NH_3 to N_2 also occurred at ca. 25 °C lower temperature after the pretreatment than on catalyst 1 (figure 2(b)). However, the conversion of NH_3 to N_2 on catalyst 4 pretreated at 350 °C under 10% H_2 in He decreased at higher temperatures above 220 °C. The pretreatment at 500 °C did not improve the activity, but after the pretreatment at higher temperatures above 500 °C, the conversion of NH_3 to N_2 above 220 °C increased gradually with increase of pretreatment temperature. The effect of the pretreatment became more clear at 800 °C. The conversion of NH_3 to N_2 on catalyst 7 pretreated at 800 °C decreased above 280 °C. Since the combustion of NH_3 to NO_x on alumina support alone was observed above 270 °C, the decrease is supposed to be caused by combustion on the alumina support. As shown in table 1, the pretreatment decreases surface area and increases average particle size of Cu. These results show that reduction of copper supported on alumina is markedly enhanced at temperatures above ca. 650 °C. Cu particles of about 26 nm in diameter are required to maintain the selectivity to N_2 at a high level even at high reaction temperature. The reason is considered that Cu particles, having a proper size around 26–30 nm, stay in a more reduced state even under the oxygen excess conditions [20,21].

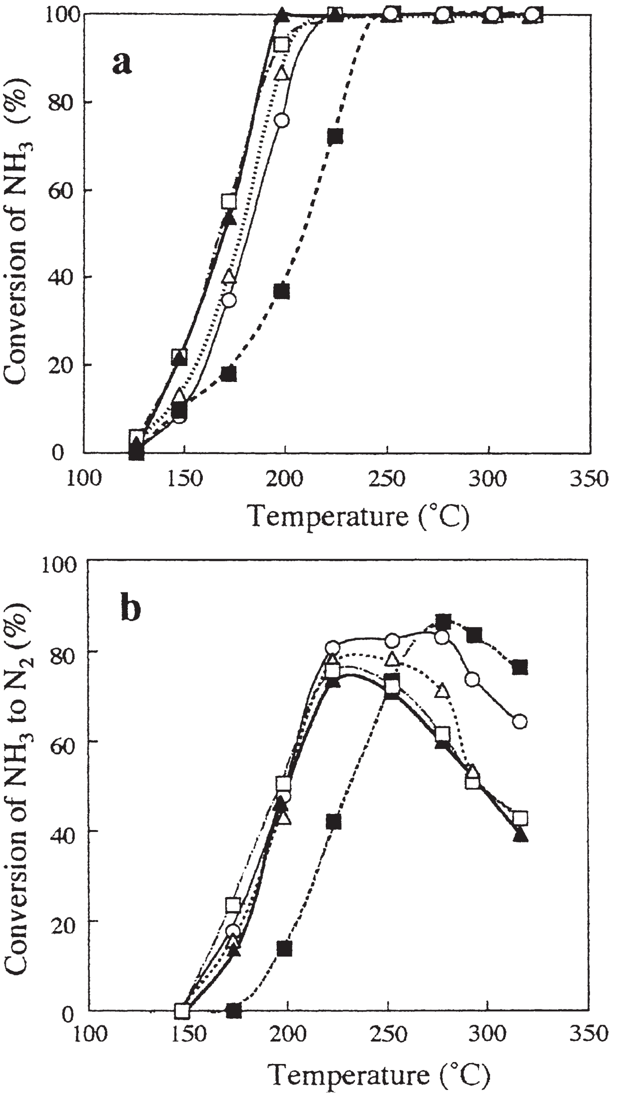

Figure 2. Effect of the temperature of the thermal treatment of the catalyst in H_2 on combustion of NH_3. (a) Conversion of NH_3, (b) conversion of NH_3 to N_2. (■) Catalyst 1, 350 °C (in air); (□) catalyst 4, 350 °C, (▲) catalyst 5, 500 °C; (△) catalyst 6, 650 °C; (○) catalyst 7, 800 °C. Reactants: NH_3 850 ppm, O_2 21%, He balanced. SV: 12,000 h^{-1}.

3.3. Effect of Cu loading on the activity

Copper loading was varied from 3.7 to 14.7 wt%. Those catalysts were subsequently treated in a stream of 10% H_2 in He at 800 °C for 30 min. The results are shown in figure 3. The activities of catalysts 8, 9 and 10 were the same in the lower temperature range, but catalyst 8 showed a lower activity at higher temperatures. As a result, catalyst 7, which had a medium loading, 7.3 wt%, gave the best results at both low and high temperature. With higher Cu loading, catalysts 9 and 10 consist of large particles and exhibit a lower efficiency in NH_3 oxidation. The effect of Cu loading on both the activity for NH_3 combustion and the surface area of copper shown in table 1 is much lower than the effect of the pretreatment temperature. These results suggest that the surface property of copper after the pretreatment is concerned in the activity for NH_3 combustion.

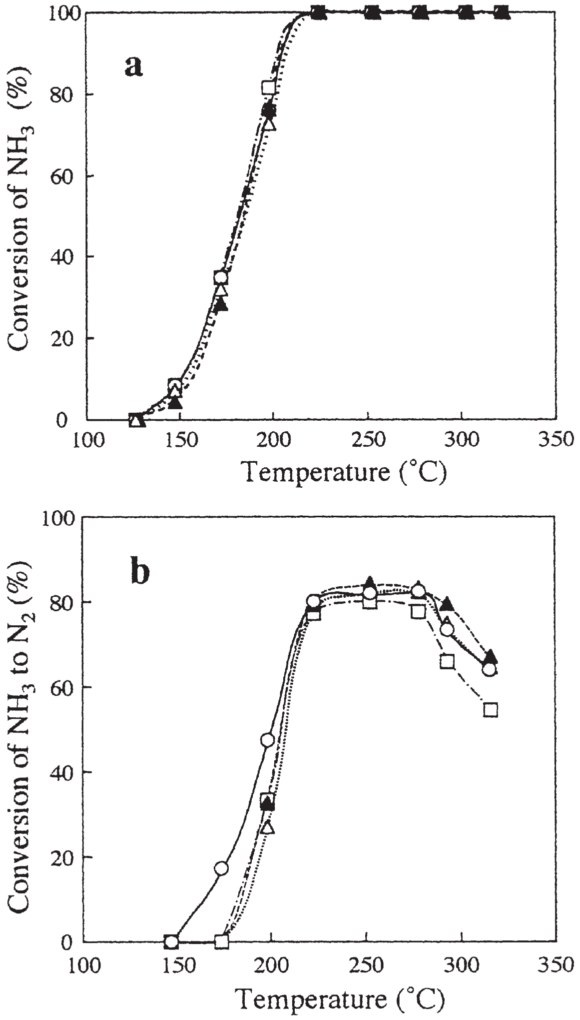

Figure 3. Effect of Cu loading on the combustion of NH_3. Pretreatment at 800 °C under 10% H_2 diluted in He. (a) Conversion of NH_3, (b) conversion of NH_3 to N_2. (□) Catalyst 8, 3.7 wt%; (○) catalyst 7, 7.3 wt%; (△) catalyst 9, 11.1 wt%; (▲) catalyst 10, 14.7 wt%. Reactants: NH_3 850 ppm, O_2 21%, He balanced. SV: 12,000 h^{-1}.

3.4. Comparison of Cu, Pt and Rh catalysts for the combustion of NH_3

In figure 4, the catalytic activities in the combustion of NH_3 of catalyst 7 and platinum group metal catalysts (catalysts 11 and 12) are shown. The combustion of NH_3 to N_2 on catalyst 11 (Pt/Al_2O_3) starts 30 °C lower than what was measured on catalyst 7. Furthermore, much more N_2O was formed while the conversion of NH_3 to N_2 was lower. The selectivity to N_2 became constant at about 50% above 170 °C. In the case of catalyst 12 (Rh/Al_2O_3), the selectivity to N_2 increased to 76% rapidly with increase of the reaction temperature, but it decreased above 235 °C. The selectivity to N_2 on catalyst 7 was higher than those on catalysts 11 and 12.

3.5. Effect of the reaction temperature on the activity

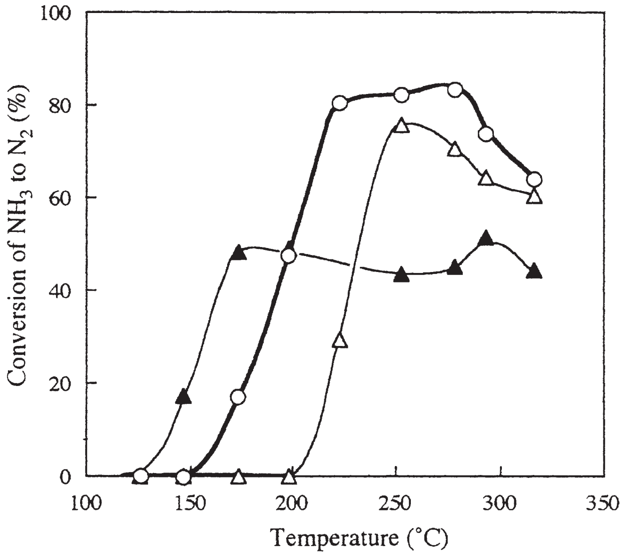

Figure 4. Comparison of Cu, Pt and Rh catalysts for the combustion of NH_3. (○) Catalyst 7, Cu; (▲) catalyst 11, Pt; (△) catalyst 12, Rh. Reactants: NH_3 850 ppm, O_2 21%, He balanced. SV: 12,000 h^{-1}.

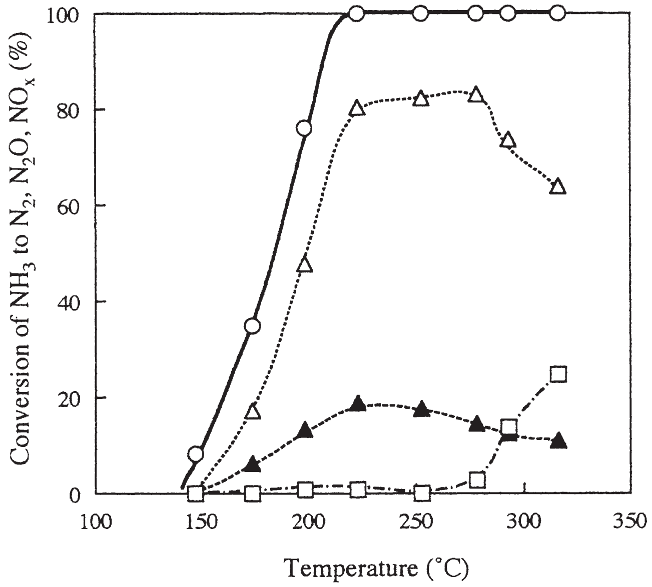

Figure 5. Effect of temperature on the conversion of NH_3 to N_2, N_2O, and NO_x on Cu/Al_2O_3 pretreated at 800 °C under 10% H_2 in He (catalyst 7). (○) NH_3, (△) N_2, (▲) N_2O, (□) NOx. Reactants: NH_3 850 ppm, O_2 21%, He balanced. SV: 12,000 h^{-1}.

Details of the activity of catalyst 7 in the combustion of NH_3 are shown in figure 5. The combustion of NH_3 starts at about 140 °C, and combustion rate increased as the reaction temperature increased. Above 220 °C, NH_3 was completely combusted. Products including nitrogen were N_2, N_2O, and NO_x. At low temperature, the conversion of NH_3 to N_2 also increased with the increase of the temperature, but then it decreased as NO_x formation increased above 280 °C.

3.6. Durability of the catalyst (catalyst 7)

The durability of catalyst 7 for the combustion of NH_3 was tested at 253 °C for 9 h. The activity on catalyst 7 was maintained throughout the reaction test, indicating the good stability of the catalyst even in oxidative reaction conditions.

3.7. Oxidation state of copper during the combustion of NH_3

In figure 6, XRD spectra for catalyst 7 before and after pretreatment at 800 °C in 10% H_2 and the patterns after reaction are shown. Cupric oxide was observed before the pretreatments, but it is reduced completely to metallic Cu after pretreatment. Reduced Cu in catalyst 7 after pretreatment is re-oxidized to CuO. After the combustion of NH_3, diffraction lines for CuO were broad, compared to the sharp lines for CuO observed for catalyst 2 calcined in air at 650 °C. Similar broadening of Cu_2O lines was reported in the past [16], and the authors suggested the formation of disordered Cu^+ and Cu^0 phases and the possible creation of active sites in one or both of these phases. In this study, it is supposed that the CuO phase formed after the combustion of NH_3 includes Cu species in a lower oxidation state than Cu^{2+}.

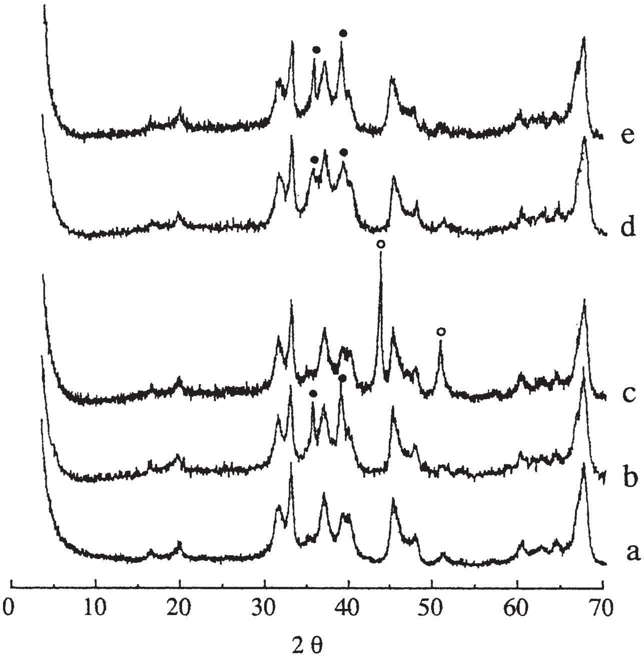

Figure 6. XRD spectra of catalysts. (a) Alumina support, (b) catalyst 1 (fresh), (c) catalyst 7 (synthesized), (d) catalyst 7 (after reaction), (e) catalyst 2 (after reaction). (○) Cu, (●) CuO.

Figure 7 presents Cu 2p and Cu Auger XPS spectra of different catalysts after reaction. In figure 7(a), XPS profiles of Cu 2p for both catalyst 7, pretreated in 10% H_2 at 800 °C, and catalyst 2, calcined in air at 650 °C, showed lower intensity of the shake-up satellite peaks at 940.0–949.0 and 960.0–967.0 eV than in pure CuO (provided by Wako Pure Chemical Industries). Furthermore, the intensity of the satellite peaks for catalyst 2 was stronger than for catalyst 7. An electron in an inner shell of Cu is released by irradiation of the X-ray beam, and it is observed as an XPS spectroscopy. The release also activates an electron in an outer shell, and the activated electron in the outer shell sometimes is excited to other empty orbitals. The excitation is observed as shake-up satellite peaks in the XPS spectra. In case of Cu, it is well known that the satellite peaks are observed only for Cu^{2+} which has empty 3d orbital, and not for both of Cu^0 and Cu^+, where the 3d orbital is fulfilled by electrons. Consequently, these results suggest that both Cu^{2+} and Cu^+ and/or Cu^0 species exist on the surface after the reaction [22], and that Cu^{2+} species in catalyst 2 are in

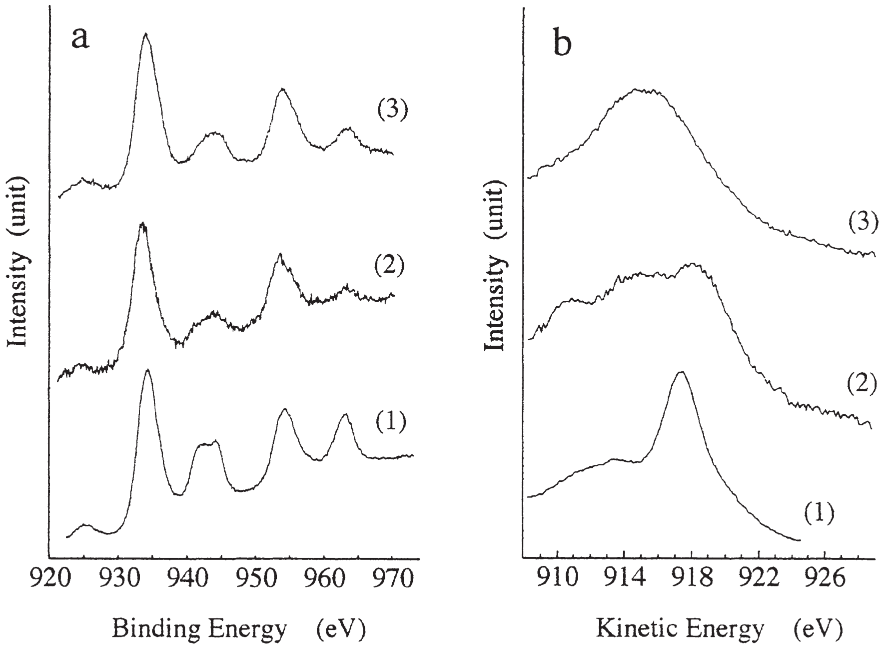

Figure 7. After reaction XPS spectra of Cu/Al_2O_3 catalysts treated in different conditions. (1) CuO (fresh pure agent), (2) pretreated at 800 °C under 10% H_2 in He (catalyst 7), (3) calcined at 650 °C in air. (a) Cu 2p, (b) Cu LMM.

greater number than in catalyst 7. Cu Auger XPS spectra for catalyst 7 in figure 7(b) showed a high-kinetic-energy peak at 918.2 eV. A calculated Auger parameter, which is conventionally defined as the sum of the binding energy of Cu $2p_{3/2}$ and the kinetic energy of Cu Auger transition (LMM) [23] and is used to distinguish between different oxidation states of copper [24–26], was 1851.6 eV, which could be assigned to Cu^0 species [24,27]. The high-kinetic-energy peak was not observed on catalyst 2, suggesting that the Cu^0 species are stable on the surface of catalyst 7 even under reaction conditions in the presence of large excess of O_2.

The XPS spectra of catalysts 4–7 after reaction, which were pretreated at different temperatures in 10% H_2, were measured. No difference in the Cu 2p XPS peaks among catalysts 5–7 was observed. Nevertheless, the intensity of the Cu 2p satellite peaks for catalyst 4 were larger than those for catalysts 5–7. The amount of Cu^+ and Cu^0 in catalysts 4–7, roughly estimated from the ratio of the Cu 2p satellite peak in a range of 940–949 eV to that of Cu $2p_{3/2}$ at 935.6 eV [22,27], correspond respectively to 26, 60, 58 and 58% of the total amount of Cu at the surface. This result suggests that reduced copper in catalyst 4, pretreated in H_2 at 350 °C, can be oxidized more easily than catalysts 5–7 reduced at higher temperature. The Cu LMM peak at 918 eV increased with the increase of the pretreatment temperature under 10% H_2 in He. The intensity of the Cu LMM peak varies in the same way as the activity of the catalysts, as shown in figure 2. This result strongly suggests that stable Cu^0 species are produced by the treatment in 10% H_2 at high temperature which play a significant role in the combustion of NH_3 to N_2.

The XPS spectra for the spent catalysts of 8–11, which include different Cu loadings, are measured. The high-kinetic-energy peak at 918.2 eV observed on catalyst 7, which could be assigned to Cu^0 species, was observed in every XPS Auger spectrum of the catalysts. These results suggest that a little difference among the activities of catalysts 7–11 is caused by existence of the Cu^0 species.

The Cu depth profile of catalyst 7 after reaction, obtained after sequential sputtering with Xe^+ ions, was measured. Little difference in the Cu 2p peak was observed. However, the Cu LMM peak at 918 eV was characteristic of the outer surface of the catalyst particles. This result indicates that the Cu^0 species at the surface affects the activity of the catalyst in the combustion of NH_3 significantly.

The results of this study can be understood if the reaction mechanism involves a microscopic redox cycle [25,28]. NH_3 adsorbed on the copper surface combusts with consumption of the oxygen atom coming from the oxidized copper. It generates isolated reduced Cu active sites. On the reduced site, the combustion of NH_3 to N_2 progresses until the active site is reoxidized by oxygen from the gas phase. During this period, the surface of the copper particles consists of a mixture of Cu^{2+}, Cu^+ and Cu^0. Before complete re-oxidation, other Cu sites on the surface are reduced by the combustion and create new active sites. The combustion of NH_3 to N_2 occurs then in a cyclic way. Observation of these microscopic changes is usually difficult, because reoxidation of the surface proceeds rapidly and easily. However, Cu^0 species observed in this study suggests that the Cu reduced by the pretreatment under 10% H_2 in He is relatively stable against oxidation during a reaction under oxidative conditions. The large particle size of copper may yield Cu^0 species, because large particles were more hardly reoxidized than smaller ones. However, the Cu depth profile indicates that this consideration is incorrect. Reoxidation of reduced copper particles should start from the surface of Cu to inside, but the Cu^0 species was observed only at the surface. It is reported that alumina-supported CuO became a mixture of Cu_2O and a small amount of Cu after a cyclic redox pretreatment, where a catalyst was heated at 250 °C, exposed to pure CO for 15 min, then exposed to air for 15 min cyclically. This mixture was stable against oxidation to CuO even under air at 135 °C [16]. In the report, broad XRD diffraction patterns for Cu and Cu_2O were observed after the cyclic pretreatment. High activity for CO oxidation was observed on CuO after the pretreatment. It was suggested that the cyclic treatments formed disordered Cu_2O and Cu phases and created active sites for CO oxidation. In this study, similar broadening of CuO XRD lines in the catalyst pretreated under 10% H_2 in He at 800 °C was observed after combustion of NH_3, suggesting a formation of disordered CuO phase. The disordered phase makes the Cu^0 species stable against reoxidation. When the catalyst surface exhibited an “oxygen-deficient stoichiometry”, high activity for the production of nitrogen in NH_3 combustion was observed on Cu_2O catalyst [15]. It is also supposed that the disordered phase enhances adsorption of NH_3 on copper, in the same way as adsorption of CO in CO oxidation on an alumina-supported copper catalyst [17].

4. Conclusion

Activity of Cu catalysts in the combustion of NH_3 to N_2 strongly depended on the oxidation state of Cu in the catalyst. Most active sites for combustion are created by pretreatment of the catalyst at 800 °C under 10% H_2 in He. Those sites, described as Cu^0 species, are located on the outer surface of the Cu particles. The Cu^0 species are stable against re-oxidation and give rise to the high activity of the catalyst in the combustion of NH_3 to N_2. Broadening of CuO XRD lines in the catalyst pretreated under 10% H_2 in He at 800 °C suggested formation of a disordered CuO phase. The disordered phase makes the Cu^0 species stable against re-oxidation.

References

[1] Y. Ono, K. Kimura, H. Wakita, Y. Yamade and H. Nishida, US Patent 5,278,113.
[2] Y. Ono, A. Nishino and H. Numoto, US Patent 5,195,165.
[3] E. Michalko, US Patent 3,259,454.
[4] C.W. Nutt and S. Kapur, Nature 220 (1968) 697.

[5] J.L. Grand and G.C. Woodard, J. Catal. 61 (1980) 543.
[6] S. Ramesh, S.S. Manoharan, M.S. Hegde and K.C. Patil, J. Catal. 157 (1995) 749.
[7] N. Watanabe, A. Kato, H. Yamashita, H. Miyadera and S. Tominaga, in: *Proc. Int. Workshop Catal. Combust.*, Tokyo, 1990, p. 120.
[8] M. Haruta, Catal. Today 36 (1996) 153.
[9] H. Kuwabara, T. Okuhara and M. Misono, Chem. Lett. (1992) 947.
[10] J.J. Ostermaier, J.R. Katzer and W.H. Manogue, J. Catal. 33 (1974) 457.
[11] T. Pignet and L.P. Schmidt, J. Catal. 40 (1975) 212.
[12] C.W. Nut and S. Kapur, Nature 224 (1969) 169.
[13] W. Burton, D.R. Flentge and J.H. Lunsford, J. Catal. 37 (1975) 258.
[14] H.S. Gandhi and M. Shelef, J. Catal. 40 (1975) 312.
[15] L.L. Holbrook and H. Wise, J. Catal. 27 (1972) 322.
[16] E.D. Pierron, J.A. Rashkin and J.F. Roth, J. Catal. 9 (1967) 38.
[17] K.I. Choi and M.A. Vannice, J. Catal. 131 (1991) 22.
[18] J.J.F. Scholten and J.A. Konvalinka, Trans. Faraday Soc. 65 (1969) 2465.
[19] K. Narita, N. Takezawa, H. Kobayashi and I. Toyoshima, React. Kinet. Catal. Lett. 19 (1982) 91.
[20] Y. Ono, M. Shibata and T. Inui, J. Catal., submitted.
[21] T. Inui, T. Takeguchi, A. Kohama and K. Kitagawa, Stud. Surf. Sci. Catal. 75 (1993) 1453.
[22] S. Poulston, P.M. Parlett, P. Stone and M. Bowker, Surf. Interface Anal. 24 (1996) 811.
[23] C.D. Wagner and A. Joshi, J. Electron Spectrosc. Rel. Phenom. 47 (1988) 283.
[24] G. Moretti, Zeolites 14 (1994) 473.
[25] G.G. Jernigan and G.A. Somorjai, J. Catal. 147 (1994) 567.
[26] M.A. Kohler, H.E. Curry-Hyde, A.E. Hughes, B.A. Sexton and N.W. Cant, J. Catal. 108 (1987) 323.
[27] E.S. Shpiro, R.W. Joyner, W. Grünert, N.W. Hayes, M.R.H. Siddiqui and G.N. Baeva, Stud. Surf. Sci. Catal. 84 (1994) 1483.
[28] T. Inui, S. Iwamoto, S. Kojo, S. Shimizu and T. Hirabayashi, Catal. Today 22 (1994) 41.