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Ammonia Combustion Properties of Copper Oxides-based Honeycomb and Granular Catalysts

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Although NH3 has been recently regarded as a renewable and/or carbon-free energy source, the use of NH3 fuel is hindered by its high ignition temperature and N2O/NO production. To overcome these problems, catalytic NH3 combustion systems and novel powder (granule) catalysts that showed high activity and low N2O/NO selectivity were previously developed. In this study, we extended our research to investigate the NH3 combustion properties of copper oxides (CuOx)-based honeycomb catalysts (CuOx/Al2O3, CuOx/10Al2O3·2B2O3, CuOx.Ag/Al2O3, CuOx/Pt/Al2O3, and so on) for practical applications. Therefore, several monolithic honeycomb catalysts were prepared and their reaction properties were evaluated and compared with those of granular catalysts. The spatial distribution in coated honeycombs before and after thermal aging was examined by the X-ray line analysis technique, which suggested that supported catalysts (thickness of the layers: ca. 100 μm) had homogeneously dispersed CuO and/or Pt in each catalyst. NH3 combustion properties (activities and selectivities) for honeycomb catalysts were similar to those of the granular catalysts, indicating that their properties were typically independent from the shape of the catalysts. Spectra from X-ray photoelectron spectroscopy were obtained to estimate the fraction of Cu0/Cu+ for the honeycomb catalysts of CuOx/10Al2O3·2B2O3. By density functional theory computations, it was suggested that highly dispersed Ag nanoparticles show a high activity.

Keywords
Ammonia, Catalytic combustion, Honeycomb, Granule

1. Introduction

In recent years, NH3 is being considered as a potential carbon-free energy source for micro-gas turbines and industrial furnaces1),2). However, compared with fossil fuels, NH3 shows several disadvantages: (1) a high ignition temperature and (2) N2O/NO production from combustion. Therefore, to overcome these disadvantages, the development of a new NH3 combustion system is required. Previously, we had developed a catalytic NH3 combustion system using novel catalysts showing high activity, N2 selectivity and thermal stability3)−6). We showed that copper oxides (CuOx) supported on Al2O3-based composite oxides (such as 10Al2O3·2B2O3 and 3Al2O3·2SiO2) exhibited high N2 selectivity and thermal stability3),5). In addition, we found that binary CuOx and silver (Ag) and/or platinum (Pt) catalysts supported on Al2O3 also exhibited high activity and N2 selectivity4),6). However, these studies only reported the NH3 combustion properties of granular-shaped catalysts, which are far from the reality of honeycomb-shaped catalysts that are used in practice.

However, for NH3 oxidation, several studies on the reaction properties of honeycomb-shaped catalysts have been reported7)−13). Isupova et al. prepared honeycomb-shaped perovskite LaMeO3 (Me = Mn, Co, Fe, Ni, Cu) catalysts to test the performance of NH3 oxidation7). Qu et al. reported the selective catalytic NH3 oxidation properties for a novel wire-mesh honeycomb comprising Ag, Cu, and so on and concluded that Ag acted as
an active site for the oxidation of NH₃ and Cu improved the N₂ selectivity.

More recently, bi-functional mixed and dual-layered Cu-SSZ-13 and Pt/Al₂O₃ were prepared by Shrestha et al., who studied their activity and selectivity for NH₃ oxidation. However, these published studies regarded NH₃ as air pollution; therefore, their NH₃ oxidation tests were evaluated at low NH₃ concentrations under moderate reaction temperatures.

According to the fundamental results for granular catalysts, we have extended our research to NH₃ combustion properties of honeycomb catalysts for practical applications. In this study, we have prepared several monolithic honeycomb catalysts and evaluated their reaction properties, so that their reactions properties could be compared with those of granular catalysts, which were previously developed.

2. Experimental

2.1. Catalyst Preparation

Support materials: To support a high performance for NH₃ combustion, aluminium oxide borate (Al₂B₂O₆, 10Al₂O₃·2B₂O₃: 10A2B) was prepared by a reverse coprecipitation method. An aqueous solution containing Al(NO₃)₃ and H₃BO₃ (Wako Pure Chem. Ind., Ltd.) with a molar ratio of Al : B was diluted to 50 mg of powder catalysts and an inorganic binder. The precipitate obtained was used as a model cluster because of its high symmetric property and the instrumental morphology for coordinatively unsaturated sites. Geometry optimisations were conducted until there were no imaginary frequencies. The adsorption energy of NH₃ onto Ag₂O was estimated to be Eads = Etot(NH₃) + Etot(Ag₂O) − Eads(NH₃·Ag₂O), where Etot is the total energy.

2.3. Catalytic NH₃ Combustion Tests

Catalytic NH₃ combustion tests for the granular and/or honeycomb catalysts were performed in a flow reactor at atmospheric pressure. The granular (10-20 mesh, < 0.3 mm thickness, 50 mg) and/or honeycomb (600 cpsi) catalysts were fixed in a quartz tube (o.d., 8 mm; i.d., 6 mm) and/or (o.d., 8 mm; i.d., 6 mm), respectively, using quartz wool at both ends of the catalyst bed. The temperature dependence of the catalytic activity was evaluated by heating the catalyst bed from room temperature to 600 °C at a constant rate of 10 °C min⁻¹ in a gas mixture containing (A) 8 % NH₃ and 92 % air (18.6 % O₂) and/or (B) 1.0 % NH₃, 1.5 % O₂ and a He balance supplied at 100 cm³ min⁻¹ (W/F = 5.0 × 10⁻³ g min cm⁻³). The dependence of the NH₃ combustion activity and product selectivities on the O₂-excess ratio were also studied. The O₂-excess ratio of NH₃ combustion was expressed as λ = (pO₂/pNH₃)exp. (pO₂/pNH₃)achim., with (A) λ = 3.1 and (B) λ = 2.0. The concentrations of NH₃/NO/NO gas were analysed using a nondispersive infrared (NDIR) gas analyser (VA-3011, HORIBA, Ltd.).
3. Results and Discussion

3.1. Structure and Morphology of Catalysts before and after Thermal Aging

The XRD patterns of the powder catalysts are shown in Supporting Information (Fig. S1), and the diffraction peaks for metal, oxide and composite oxide materials were observed. The peaks for CuOx/Al2O3(900 °C), CuOx/10A2B(900 °C), CuOx/Ag/Al2O3(800 °C), Pt/Al2O3(900 °C) and CuOx/Pt/Al2O3(900 °C) could be assigned to CuAl2O4, metallic Ag and metallic Pt3,4,6). In the case of Al2O3-supported catalysts after thermal aging at temperatures higher than 800 °C, the Al2O3 phase for the binary catalysts was transformed from γ to α3). On the other hand, the peaks for the as-prepared CuOx/Ag/Al2O3 could also be assigned to AgAlO2 that existed at the Ag-Al2O3 interface, thereby inducing highly dispersed Ag nanoparticles anchored by the formation as well as by the Ag-O-Al interaction4). Figures 1-3 show the back scattered electron (BSE) and wavelength-dispersive X-ray spectrometry (WDX)-mapping images obtained by the X-ray line analysis technique for the monolithic honeycomb catalysts. The color of the mapping displays the detected relative counts of fluorescence lines, as well as the red and blue colors indicate high and low, respectively, as shown in Fig. 1. For all the honeycomb catalysts, the layers of the powder catalysts (thickness: ca. 100 μm) are in intimate contact with the surface of the cordierite honeycomb substrate. For the Cu-K fluorescence lines, Al2O3-supported catalysts showed the homogeneously dispersed CuOx in each catalyst, while 10A2B-supported catalyst exhibited the heterogeneously dispersed CuOx. These behaviours are consistent with our previous reports which indicate that manifold CuOx particles with size of more than 20 nm were found in CuOx/10A2B(900 °C) in comparison with CuOx/Al2O3(900 °C)3). For the Ag-L fluorescence lines, CuOx/Ag/Al2O3 showed highly dispersed Ag, while CuOx/Ag/Al2O3(800 °C) exhibited the sintering of Ag nanoparticles at the surface of the catalyst layer. Therefore, their sintering was possibly induced by the thermal aging at 800 °C. On the other hand, for the Pt-M fluorescence lines, binary CuOx/Pt/Al2O3(900 °C) showed highly dispersed Pt, while single Pt/Al2O3(900 °C) exhibited the sintering of Pt nanoparticles.

By contrast, the multimodal crack and void for the catalyst layer are also observed for all the catalysts (Figs. 1-3), and those for CuOx/Pt/Al2O3(900 °C) are signature (Fig. 3, left). The crack and void were supposedly induced by the several decrease for Brunauer-Emmett-Teller (BET) surface area (SBET) of the catalysts before and after thermal aging as well as the phase transition from γ- to α-Al2O3. SBET of granular catalysts as well as their phases before (as-prepared, the calcination at 600 °C) and after thermal aging are summarised in Supporting Information (Table S1).
Despite the same thermal aging at 900 °C, a significant decrease in $S_{\text{BET}}$ was especially observed for CuO$_x$/Pt/Al$_2$O$_3$(900 °C) ($139 \rightarrow 14 \, \text{m}^2\,\text{g}^{-1}$) in comparison with the other catalysts, which is consistent with the phase transition from $\gamma$- to $\alpha$-Al$_2$O$_3$ obtained from XRD patterns (Fig. S1, Supporting Information). Therefore, it is considered that the significant $S_{\text{BET}}$ decrease can be attributed to the phase transition from $\gamma$- to $\alpha$-Al$_2$O$_3$. For $\gamma$-Al$_2$O$_3$ without any additives, the phase transition to $\alpha$-Al$_2$O$_3$ was observed at approximately 1200 °C$^{20}$. On the other hand, the effects of divalent cation additives on the phase transition of Al$_2$O$_3$ were previously reported, and the coexistence of Cu$^{2+}$ of CuO, prompted the transition from $\gamma$- to $\alpha$-Al$_2$O$_3$, which could be attributed to the formation of CuAl$_2$O$_4$ at lower than 1200 °C$^{21}$. In addition, it is suggested that the coexistence of Pt also prompted the formation of CuAl$_2$O$_4$ and the transition of $\gamma \rightarrow \alpha$-Al$_2$O$_3$ as well as the decrease in $S_{\text{BET}}$. A similar behavior was also found for Cu-Al-O and Cu-Pt-Al-O system catalysts after thermal aging at 1000 °C$^{22}$. For the catalyst layer of CuO$_x$/Pt/Al$_2$O$_3$ (900 °C) in honeycomb catalysts, the significant crack and void between cordierite would also be formed because of the decrease in $S_{\text{BET}}$ and the phase transition from $\gamma$- to $\alpha$-Al$_2$O$_3$ (i.e., the crystallization) presumably induced by thermal aging.

3.2. NH$_3$ Combustion Properties for Catalysts before and after Thermal Aging

Figures 4-6 compare the temperature dependence of the NH$_3$, N$_2$O and NO concentration ratios for NH$_3$ combustion reaction over granular and/or honeycomb catalysts. In addition, Table 1 summarises the catalytic properties. The activity is expressed in terms of the light-off temperature at which 10 % conversion of NH$_3$ is reached ($T_{10}$), and the product selectivities are evaluated at the reaction temperature at which NH$_3$ conversion is 90 % ($T_{90}$). For the granular catalysts, CuO$_x$/Al$_2$O$_3$(900 °C) showed higher catalytic NH$_3$ combustion activity ($T_{10}$, Table 1) and lower N$_2$O/NO selectivity at $T_{90}$ than CuO$_x$/10A2B(900 °C).
In addition, the honeycomb catalyst of CuOx/Al2O3(900 °C) also exhibited higher activity (lower \( T_{10} \)) and lower N2O/NO selectivity at \( T_{90} \) than that of CuOx/10A2B(900 °C). Although there are the differences in value for \( T_{10} \), N2O and NO selectivity at \( T_{90} \) between honeycomb and granular catalysts (Table 1), it is suggested that the trends of combustion properties for the honeycomb catalysts were almost similar with those granular catalysts.

To study the surface oxidation states of the honeycomb catalysts for different positions in the reactor, XPS spectra for the spent catalysts were obtained. Figure 7 shows the Cu2p XPS spectra of the CuOx/10A2B (900 °C) honeycomb catalysts for NH3 combustion at the inlet, middle and outlet position in the reactor. For all the spectra, the deconvolution of the observed peaks revealed doublet feature due to spin-orbit coupling effect assigned to Cu+\(^{\text{2+}}\), Cu+\(^{\text{2+}}\) and three satellite peaks assigned to Cu+\(^{\text{2+}}\) with the 3d\(^{\text{0}}\) electronic configuration. The deconvolution as well as curve fitting analysis revealed that the fraction of Cu+\(^{\text{2+}}\) increased in the following order: inlet position (Cu+\(^{\text{2+}}\): 60 %, Cu+\(^{\text{2+}}\): 40 %) < middle position (Cu+\(^{\text{2+}}\): 39 %, Cu+\(^{\text{2+}}\): 61 %) < outlet position (Cu+\(^{\text{2+}}\): 28 %, Cu+\(^{\text{2+}}\): 72 %) of the CuOx/10A2B (900 °C) honeycomb catalysts. These results suggest that the catalysts for the downstream side in NH3 combustion possibly contain a higher fraction of Cu+\(^{\text{2+}}\). Similar behaviour was reported by Doronkin et al. who

![Fig. 4](image)

**Table 1** Properties of the Catalysts before and after Thermal Aging

| Catalyst | Shape | Phase\(^{\text{a)}}\) | \( T_{10}^{\text{b)}} [\degree\text{C}] \) | \( T_{90}^{\text{b)}} [\degree\text{C}] \) | Selectivity at \( T_{90}^{\text{b)}} [%] \) |
|----------|------|----------------|-----------------|-----------------|-----------------|
| CuOx/Al2O3 (900 °C) | honeycomb | - | 302 | 423 | 8 | 1 |
| CuOx/10A2B (900 °C) | honeycomb | CuAl2O4/\( \alpha \), \( \gamma \)-Al2O3 | 302 | 471 | 13 | 2 |
| CuOx/Ag/Al2O3 | granule | CuAl2O4/10A2B | 369 | 594 | 4 | 1 |
| CuOx/Ag/Al2O3 (800 °C) | honeycomb | CuAl2O4/Ag/\( \gamma \)-Al2O3 | 354 | 583 | 5 | 1 |
| CuOx/Pt/Al2O3 (900 °C) | honeycomb | CuAl2O4/Ag/\( \gamma \)-Al2O3 | 222 | 368 | 4 | 1 |
| CuOx/Pt/Al2O3 (800 °C) | granule | CuAl2O4/Pt/\( \alpha \)-Al2O3 | 295 | 416 | 6 | 1 |
| CuOx/Pt/Al2O3 (900 °C) | honeycomb | CuAl2O4/Pt/\( \alpha \)-Al2O3 | 284 | 320 | 5 | 1 |
| Pt/Al2O3 (900 °C) | honeycomb | CuAl2O4/Pt/\( \alpha \)-Al2O3 | 181 | 286 | 12 | <1 |
| Pt/Al2O3 (900 °C) | granule | CuAl2O4/Pt/\( \alpha \)-Al2O3 | 220 | 339 | 13 | 1 |
| Pt/Al2O3 (900 °C) | honeycomb | CuAl2O4/Pt/\( \alpha \)-Al2O3 | 262 | 315 | 13 | 1 |
| Pt/Al2O3 (900 °C) | granule | CuAl2O4/Pt/\( \alpha \)-Al2O3 | 213 | 266 | 12 | <1 |

\(^{\text{a)}}\) Determined from our previous literature\(^{\text{b)}}\).

\(^{\text{b)}}\) Temperature at which NH3 conversion reached 10 % and 90 %.

![Fig. 6](image)

**Fig. 6** NH3, N2O and NO Concentration Ratios for the Catalytic NH3 Combustion over Granular and/or Honeycomb Catalysts of CuOx/Pt/Al2O3 and Pt/Al2O3 after Thermal Aging at 900 °C for 100 h in Air

![Fig. 7](image)

**Fig. 7** Cu2p XPS Spectra for CuOx/10A2B(900 °C) Honeycomb Catalysts for NH3 Combustion at the Inlet, Middle and Outlet Position in the Reactor.
measured spatially-resolved Cu K-edge XANES spectra for Cu-SAPO-34 catalysts in a microreactor for NH₃ oxidation (0.1 % NH₃, 10 % O₂)⁶. The reason of the lower fraction of Cu²⁺ for upstream side is under investigation. However, we previously demonstrated that the catalytic NH₃ combustion proceeds via the Mars-van Krevelen mechanism, which implies that NH₃ reacts with the lattice oxygen of CuO⁷. For the Mars-van Krevelen mechanism, it is generally considered that the adsorption of gaseous O₂ onto a vacancy in the anionic lattice is rapid. However, there is the report that the re-oxidation of Cu⁺ to Cu²⁺ is difficult at high reaction temperature because of the presence of NH₃⁸. We also revealed that the Cu²⁺ fractions of supported CuO, after NH₃ combustion reaction decreased due to the reduction of CuO, which were obtained by XPS analysis⁹,¹⁰. Because the NH₃ concentration for upstream side is higher than that for downstream side, the CuO lattice oxygen for upstream side might be consumed by NH₃ in higher amount than that for downstream side. Thus, the catalysts for the downstream side would show a higher fraction of Cu²⁺.

For both CuOₓ/Ag/Al₂O₃ and CuOₓ/Ag/Al₂O₃(800 °C) (Fig. 5), the properties exhibited by the honeycomb catalysts were almost the same as those exhibited by the granular catalysts. Therefore, the reproducibility of high concentration NH₃ combustion properties of honeycomb catalysts was confirmed. CuOₓ/Ag/Al₂O₃ had a tendency to exhibit higher activity than CuOₓ/Ag/Al₂O₃(800 °C). Previously, we considered that the deactivation of CuOₓ/Ag/Al₂O₃ after thermal aging at 800 °C was due to the sintering of Ag nanoparticles supported on Al₂O₃. According to previous literature⁵, highly dispersed Ag nanoparticles showed a high activity for a NH₃ combustion reaction and as expected, the sintering of Ag nanoparticles was observed (Fig. 2). Because the honeycomb catalysts of CuOₓ/Ag/Al₂O₃ and CuOₓ/Ag/Al₂O₃(800 °C) showed the high performance, the NH₃ combustion tests with gas mixture containing NH₃ and air supplied at 125 cm³ min⁻¹ (W/F = 4.0 × 10⁴ g min cm⁻³) were also evaluated in comparison with granular catalysts (Fig. S2, Supporting Information). Table S2 (Supporting Information) also summarises the catalytic properties. N₂O and NO selectivity profiles for both honeycomb and granular catalysts showed similar, and the light-off curves of NH₃, T₁₀ and T₉₀ shifted to higher temperatures in comparison with results for 100 cm³ min⁻¹ (Fig. 5 and Table 1). However, light-off curves of NH₃ and T₉₀ for the honeycomb catalysts before and after aging were slightly lower temperatures than those of the granular catalysts.

To confirm the correlation between Ag nanoparticles (clusters) and the activities, the adsorption energy (E_ads) of NH₃ to an Ag₂₀ cluster with four (111) faces with an Ag–N bond was estimated by DFT calculations with different configurations, as shown in Fig. 8 and summarised in Table 2. The Ag–N E_ads of three types of initial geometries has a tendency to increase in the following order: atop < edge < vertex that possibly indicates that NH₃ adsorbs onto coordinatively unsaturated Ag sites in the clusters and is activated. In addition, the bond lengths of N–H in NH₃ adsorbed on vertex was longer than atop and/or edge. Therefore, based on these results, it was suggested that highly dispersed Ag nanoparticles also show a high activity for the N–H bond dissociation.

On the other hand, for CuOₓ/Pt/Al₂O₃(900 °C) and Pt/Al₂O₃(900 °C) (Fig. 6), the NO selectivities at a relatively high reaction temperature for the honeycomb catalysts were higher than those for the granular catalysts. For the catalytic oxidation and combustion of NH₃ to N₂, these reaction mechanisms were considered to have proceeded through internal selective catalytic NO reduction by NH₃ (i-SCR)³¹,⁴¹–⁴³. The reaction mechanism comprises two steps: (1) NH₃ oxidised to N₂ and/or NOx; (2) NOx reduced by unreacted NH₃ to N₂ and/or N₂O. Compared with the granular catalysts, the honeycomb catalysts showed lower superficial contact between the reactants and the catalyst possibly because of the honeycomb morphology and dead space. As expected, even in the case of the granular catalysts, the NO selectivity tends to increase with decreasing W/F.

![The solid and dashed lines represent E_ads and three N–H bond lengths, respectively, for the atop, edge, and vertex configurations of NH₃–Ag₂₀, where insets show the geometric structures. See also Table 2 for the values.](image)
(i.e. the superficial contact)\(^3\), indicating that the reaction rate of (2) was decreased. Therefore, the NO selectivities for the honeycomb catalysts were considered to be higher than those of the granular catalysts.

4. Conclusions

In this study, monolithic honeycomb catalysts were prepared and their NH\(_3\) combustion properties were evaluated to compare with those of granular catalysts (CuO/10A2B, CuO/Ag/Al\(_2\)O\(_3\), CuO/Pt/Al\(_2\)O\(_3\) and so on). From BSE and WDX-mapping images and analysis, the layers of the powder catalysts were considered to be in intimate contact with the surface of the cordierite honeycomb substrate. In the case of CuO/Al\(_2\)O\(_3\)(900 °C) and CuO/10A2B(900 °C), the combustion properties for the honeycomb catalysts were almost the same as those for the granular catalysts. Additionally, for the surface oxidation state, the fraction of Cu\(^{2+}\) increased in the following order: inlet < middle < outlet position of the CuO/10A2B(900 °C) honeycomb catalysts. Moreover, the properties of the honeycomb catalysts for CuO/Ag/Al\(_2\)O\(_3\) and CuO/Ag/Al\(_2\)O\(_3\)(800 °C) were almost similar to those of the granular catalysts. However, CuO/Ag/Al\(_2\)O\(_3\)(800 °C) exhibited a lower activity than the as-prepared CuO/Ag/Al\(_2\)O\(_3\) possibly because of the sintering of Ag nanoparticles and this consideration is consistent with the DFT calculations. On the other hand, for both CuO/Pt/Al\(_2\)O\(_3\)(900 °C) and Pt/Al\(_2\)O\(_3\)(900 °C), the NO selectivities at a high reaction temperature for the honeycomb catalysts were higher than those for the granular catalysts.

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Supporting Information

Supplementary data associated with this article can be found, in the online version, at https://jstage.jst.go.jp/browse/jpi/-char/en (DOI: doi.org/10.1627/jpi.63.274).

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要旨

酸化銅系ハニカム触媒と粒状触媒のアンモニア燃焼特性

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NH3燃焼特性に高活性・低N2O/NO選択性を示すCuO/Al2O3, CuO/10Al2O3・2B2O3, CuO/Ag/Al2O3, CuO/Pt/Al2O3等の粉末状の酸化銅系触媒をコーディライトハニカムにウォッシュコートした担持触媒を調製し、粒状触媒との触媒性能を比較検討した。調製したハニカム触媒のWDX-mapping観察より、触媒層厚の厚みは約100μmで、Agは熱処理により凝聚が確認されたが、CuOおよびPtは比較的高分散状態を維持していった。ハニカム触媒と粒状触媒のNH3燃焼特性を比較すると、いずれの組み合わせもNH3燃焼活性ならびにN2O/NO選択性が類似することから、NH3燃焼特性は触媒の形状より、むしろ触媒の材料特性に依存すると推定された。XPSより、CuO/10Al2O3・2B2O3ハニカム触媒のCu2+とCu+の割合が見積もられた。DFT計算より、配位不飽和（高分散）なAgがNH3を活性化すると推察された。

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