Supported binary CuOₓ–Pt catalysts with high activity and thermal stability for the combustion of NH₃ as a carbon-free energy source†

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Recently, NH₃ has been thought to be a renewable and carbon-free energy source. The use of NH₃ fuel, however, is hindered by its high ignition temperature and N₂O/NO production. To overcome these issues, in this study, the combustion of NH₃ over copper oxide (CuOₓ) and platinum (Pt) catalysts supported on aluminium silicates (3Al₂O₃-2SiO₂), aluminium oxides (Al₂O₃), and silicon oxides (SiO₂) were compared. To achieve high catalytic activity for the combustion of NH₃ and high selectivity for N₂ (or low selectively for N₂O/NO), conditions for the preparation of impregnated binary catalysts were optimised. With respect to the binary catalysts, sequentially impregnated CuOₓ/Pt/Al₂O₃ exhibited relatively higher activity, N₂ selectivity, and thermal stability. From XRD and XAFS analyses, CuOₓ and Pt in CuOₓ/Pt/Al₂O₃ were present as CuAl₂O₄ and metallic Pt, respectively. Given that the combustion activity was closely associated with the Pt nanoparticle size, which was estimated from the Scherrer equation and the pulsed CO technique, highly dispersed Pt nanoparticles were crucial for the low-temperature light-off of NH₃. For single and binary catalysts, although NH₃ (imide) deformation modes as a key species for N₂O production were detected by in situ FTIR spectral analysis, the band intensity of CuOₓ/Pt/Al₂O₃ was less than those of CuOₓ/Al₂O₃ and Pt/Al₂O₃. Therefore, CuOₓ/Pt/Al₂O₃ exhibits high selectivity for N₂ in NH₃ combustion.

Introduction

Recent studies have reportedly considered NH₃ to serve not only as a H₂ carrier material but also as a renewable, carbon-free energy source because of its high energy density (3160 W h L⁻¹) and negligible thermal NOₓ emission.¹ Currently, NH₃ is industrially produced at a high pressure using N₂ (produced from air) and H₂ (produced from natural gas) by employing the Haber–Bosch process, which consumes a large amount of energy. However, the energy and costs associated with H₂ production and natural gas is 70–90% of that required for NH₃ production.³ Therefore, the low energy and costs that are associated with H₂ production along with the fact that it is a renewable energy source should be emphasised to ensure that the society utilises H₂ along with NH₃. As a proof-of-concept for using NH₃ as a fuel, an NH₃-fuelled micro-gas turbine has been employed to demonstrate the potential of NH₃-fired power plants at the Fukushima Renewable Energy Institute in Japan, as well as an NH₃-fuelled industrial furnace.² Compared to fossil fuels, however, NH₃ exhibits disadvantages of a high ignition temperature, low combustion rate, and N₂O/NOₓ production. Therefore, to overcome these issues, it is imperative to develop a novel NH₃ combustion system. First, a catalytic NH₃ combustion system, which decreases the ignition temperature and N₂O/NOₓ emissions, was developed. Previously, our group has successfully developed a catalytic NH₃ combustion system and novel catalysts exhibiting high activity, N₂ selectivity, and thermal stability.⁴ For example, copper oxides (CuOₓ) supported on Al₂O₃-based composite oxide materials (such as 10Al₂O₃·2B₂O₃ and 3Al₂O₃·2SiO₂) exhibit high N₂ selectivity and thermal stability, whereas binary CuOₓ and silver (Ag) supported on Al₂O₃ exhibit high activity and N₂ selectivity.³ However, the former catalyst exhibits a low activity (ignition temperature at ~300 °C), while the latter catalyst exhibits low thermal stability (deactivation temperature at ~900 °C likely because of the low melting point of Ag).⁴ Therefore, it is imperative to develop catalysts to exhibit high activities and thermal stabilities for NH₃ combustion.

†Electronic supplementary information (ESI) available: Calculation formulae, calculated thermodynamic Pt-PtO phase equilibrium, XRD patterns, HAADF-STEM/EDX mapping images, product selectivities for the NH₃–O₂ and NH₃–NO–O₂ reactions, relationship between NH₃ combustion activity and Pt particle size, NH₃- and NO-TPD profiles. See DOI: 10.1039/c8ra07969b
On the other hand, binary systems comprising supported CuO–Ag, CuO–Pt, CuO–Au, CuO–CeO, and Li2O catalysts exhibiting a high performance for the selective catalytic oxidation of NH3 (NH3–SCO) have been previously reported. In particular, CuO–Pt systems are expected to exhibit high thermal stability because of the high melting point of Pt (∼1770 °C). Recently, Sun et al. have synthesised impregnated CuO–Pt/TEOS catalysts and reported that CuO on Pt species can lead to higher NH3–SCO performance compared to single catalysts. On the other hand, Jablonska has synthesised Al2O3–TiO2–ZrO2-supported CuO catalysts and found that Pt–CuO mixed catalysts exhibit high activity and N2 selectivity for NH3–SCO. However, in these studies, NH3 is considered to cause air pollution; therefore, the thermal stability is investigated at temperatures of less than 900 °C.

In this study, supported binary CuO–Pt catalysts were synthesised, and their catalytic properties for the combustion of NH3 (as an energy source) at high reaction temperatures were examined. To achieve high catalytic activity for the combustion of NH3, N2 (low N2O/NO) selectivity and thermal stability, preparation conditions for impregnated binary catalysts were optimised. Moreover, the relationship between the local structure and catalytic properties for the combustion of NH3 over supported CuO–Pt catalysts was discussed.

**Experimental**

**Catalyst preparation**

3Al2O3–2SiO2 (3AS2) of the catalyst support material was prepared by using an alkoxide method. According to previous studies, SiO2 (TEOS, Wako Pure Chemicals) was first dissolved in C2H5OH (Wako Pure Chemicals) at a concentration of 1 M at room temperature (RT). Second, after the addition of H2O and HCl (Wako Pure Chemicals), the solution was stirred at 70 °C for 5 h, and a Si solution was prepared. Third, the alcohol was dehydrated. The H2O and HCl concentrations were H2O/TEOS = 2 (mol mol⁻¹) and HCl/TEOS = 0.1 (mol mol⁻¹), respectively. Next, Al[OCH(CH3)2]3 (AIP, Sigma-Aldrich) was subjected to reflux conditions and dissolved in (CH3)2CHCH2OH (Nacalai Tesque) to prepare an Al solution. The precursor solution was prepared by mixing the Al and Si solutions in a volume ratio of 3 : 2 at RT. H2O was added, and the solution was stirred for 1 h to prepare the precursor solution. The precursor sols were dried at 110 °C for 48 h, affording xerogel precursor powders. These powders were pulsed and calcined at 600 °C for 3 h and finally at 1200 °C for 5 h in air. In addition, CuO (Wako Pure Chemicals), γ-Al2O3 (JRC-ALO-8, Catalysis Society of Japan), SiO2 (JRC-SI0-10, Catalysis Society of Japan), and CuO (Wako Pure Chemicals) were used as support materials.

Single and binary supported CuO2 (CuO loading of 6 wt%) and Pt (Pt loading of 2 wt%) catalysts were prepared by the co-impregnation (CuO2–Pt) of an aqueous solution of Cu(NO3)2 (Wako Pure Chemicals) and [Pt(NH3)2(NO3)2] (Tanaka Kikinzoku Kogyo), followed by drying and calcination at 600 °C for 3 h in air. In addition, the sequentially impregnated binary catalysts, i.e. Pt and subsequent CuO2 (CuO2/Pt) and/or CuO2 and subsequent Pt (Pt/CuO2), were synthesised in a similar fashion.

As CuO2/Pt/Al2O3 exhibited a high catalytic activity for the combustion of NH3, physically mixed catalysts (CuO + Pt/Al2O3, CuAl2O4 + Pt/Al2O3, and CuO/Al2O3 + Pt/Al2O3) with the same composition ratios were also prepared. To evaluate their thermal stabilities and catalytic properties, the as-prepared catalysts were subjected to thermal aging at 900 °C for 100 h in air and/or at 1000 °C for 5 h in air.

**Characterisation**

Powder X-ray diffraction (XRD) patterns were recorded using monochromatic Cu Kα radiation (30 kV, 20 mA, Multiflex, Rigaku). The average size of the Pt particles was calculated by the XRD line broadening method by using the Scherrer equation. The chemical composition was determined by X-ray fluorescence (XRF; EDXL-300, Rigaku) measurements. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping images were recorded on a JEM-ARM200CF (JEOL) system. Brunauer–Emmett–Teller (BET) surface area (SBAER) values were calculated from the N2 adsorption isotherms, which were recorded at −196 °C (Belsorp, Bel Japan, Inc.). Pt dispersion and particle size were determined by the pulsed CO technique (BELCAT-B, BEL Japan, Inc.) at 50 °C after O2 oxidation and subsequent H2 reduction at 400 °C according to previous studies. Pt dispersion and particle size were calculated by assuming hemispherical particles with the stoichiometric adsorption of CO on Pt at a CO : Pt ratio of 1 : 1. Cu K-edge and Pt L1-edge X-ray absorption fine structure (XAFS) spectral analyses were carried out at BL9A of PF and BL01B1 of SPring-8. XAFS spectra were recorded in the transmission mode at RT using an ionisation chamber filled with N2 for the incident beam, another chamber filled with 75% N2/Ar for the Cu K-edge and 50% N2/Ar for Pt L1-edge for the transmitted beam, and a Si(111) double-crystal monochromator. Reference samples (e.g. Cu2O, CuO, CuAl2O4, and PtO2) were mixed with boron nitride (BN) powder to achieve an appropriate absorbance at the edge energy, whereas the catalysts were used without mixing with BN. XAFS data were processed using the IFEFFIT software package (Athena and Artemis).

**Catalytic NH3 combustion tests**

The catalytic combustion of NH3 was performed in a flow reactor at atmospheric pressure. Catalysts (10–20 mesh, <0.3 mm thickness, 50 mg) were fixed in a quartz tube (OD: 6 mm, ID: 4 mm) with quartz wool at both ends of the catalyst bed. The temperature dependence of the catalytic activity was evaluated by heating the catalyst bed from RT to 900 °C at a constant rate of 10 °C min⁻¹ while a gas mixture containing 1.0% NH3, 1.5% O2 and He balance at 100 cm³ min⁻¹ (W/F = 5.0 × 10⁻⁴ g min cm⁻³) was supplied. The O2 excess ratio for NH3 combustion was expressed as λ = (pO2/pNH3)exp./(pO2/pNH3)stoich., where p denotes pressure. The NH3/N2O/NO, N2 and NO2 gas concentrations were analysed using a nondispersive infrared gas analyser (VA-3011, Horiba), chromatography (GC-8A, Shimadzu) and chemiluminescence (NOA-7000, Shimadzu).
Shimadzu) measurements. The ESI† provides the calculation formulae used to determine the concentration ratios.

In situ Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer using a diffuse-reflectance reaction cell with a BaF2 window connected to a gas supply and a heating system to enable measurements at atmospheric pressure. First, the catalysts were preheated in situ in flowing He at 400 °C for 30 min prior to each experiment. After pre-treatment, the temperature of the catalyzed was decreased to 200 °C, followed by the subsequent purging of the cell with He and then filling with 0.3% NH3/He mixed gas. Finally, FTIR spectra were recorded while the catalysts were maintained under a stream of NH3/He.

Computational details
Spin-restricted density functional theory (DFT) computations were carried out for NH3/Pt◦ (x = 13 and/or 20) at the M06 level using the def-SV(P) basis sets, with the 60-electron relativistic effective core potential for Pt, as implemented in TURBOMOLE under the resolution of the identity approximation.24 The model clusters of Pt13 with I3 symmetry and Pt20 with Td symmetry having four (111) faces were locally optimised until imaginary frequencies were removed. One atop geometry for NH3–Pt13, and three initial geometries for NH3–Pt20 were considered, i.e. atop the (111) face; bridge-to-edge site; and atop the vertex site, respectively. These geometries were optimised until no imaginary frequencies were observed. The adsorption energy of NH3 on Pt◦ was estimated as 

\[ E_{\text{ads}} = E(\text{NH}_3) + E(\text{Pt}) - E(\text{NH}_3 - \text{Pt}) \]

where \( E(A) \) denotes the electronic energy of species \( A \).

Results & discussion
Local structures of supported CuOx and Pt catalysts
Fig. 1 shows the XRD patterns of sequentially impregnated binary (CuOx/Pt) catalysts, because CuOx/Pt/Al2O3 exhibited higher activity, \( N_2 \) (lower \( N_2O/NO \)) selectivity, and thermal stability for the combustion of \( NH_3 \) compared to all binary catalysts before and after thermal ageing at 900 °C (Table 1). ESI† shows the XRD patterns of the other catalysts. The XRD patterns of as-prepared CuOx/Pt/3A2S and CuOx/Pt/SiO2 before and after aging revealed peaks corresponding to CuO, whereas peaks corresponding to CuAl2O4 were observed for CuOx/Pt/3A2S and CuOx/Pt/Al2O3 (900 °C), possibly related to the solid-state reaction between γ-Al2O3 and CuOx. Diffraction peaks for Cu species were not observed for as-prepared CuOx/Pt/Al2O3, possibly related to the high dispersion of CuOx. The Al2O3 phase of the binary catalysts was transformed from \( \gamma \) to \( \alpha \), and the diffraction peaks for Pt became sharper after thermal aging at temperatures of higher than 900 °C. Therefore, the growth of particles and sintering of Al2O3 and Pt are induced by thermal aging. Indeed, the Pt particle sizes calculated by the Scherrer equation increased with the aging temperature (Table 1). On the other hand, as peaks corresponding to CuOx were observed for the binary catalysts prepared using \( \alpha \)-Al2O3, CuOx/Pt/\( \alpha \)-Al2O3 before and after aging, it was possibly difficult to form CuAl2O4 from the solid-state reaction between \( \alpha \)-Al2O3 and CuOx (ESI†).

Fig. 2 shows the normalised Cu K-edge X-ray absorption near-edge structure (XANES) spectra and k-space extended X-ray absorption fine structure (EXAFS) oscillations of the catalysts and the three reference compounds (CuOx, CuO and CuAl2O4, respectively). Cu K-edge XANES spectra and k-space EXAFS oscillations of CuOx/Pt/3A2S (900 °C) and CuOx/Pt/Al2O3 before and after thermal aging at 900 °C were similar to those of CuAl2O4, whereas those of CuOx/Pt/3A2S and CuOx/Pt/SiO2 before and after thermal aging at 900 °C were similar to those of CuOx. In the XANES spectra of CuOx/Pt/3A2S and CuOx/Pt/SiO2 before and after aging, the pre-edge (at ~8985 eV, corresponding to Cu\(^{2+}\) 1s \( \rightarrow \) 4p + ligand and Cu\(^{2+}\) 1s \( \rightarrow \) Cu\(^{2+}\) charge-transfer excitation)\(^{11} \) for CuO was observed. XAFS analyses were consistent with the XRD patterns of the catalysts. The Pt L\(_3\)-edge XAFS profiles of the catalysts and two references (i.e. Pt foil and PtO\(_2\), respectively) are also depicted in Fig. 3. For as-prepared CuOx/Pt/Al2O3, the XANES profile was slightly similar to that observed for PtO\(_2\). According to the calculated thermodynamic Pt–PtO\(_2\) phase equilibrium (ESI†), PtO\(_2\) and metallic Pt exhibited thermodynamic stability at RT and 600 °C, respectively. Therefore, Pt nanoparticles (especially, their surfaces) in CuOx/Pt/Al2O3 are thought to be oxidised during the cooling process of calcination. By contrast, the XANES profiles of the other catalysts were similar to that of Pt foil (metallic Pt) as against the calculated phase equilibrium. This disagreement is supposedly caused by the calcination and/or thermal aging-induced sintering of metallic Pt nanoparticles in these catalysts; hence, the bulk metallic Pt particles are stable at RT.

Next, HAADF-STEM and EDS mapping images of sequentially impregnated CuOx/Pt/Al2O3 (900 °C) were recorded (Fig. 4). From the HAADF-STEM image, dispersed nanoparticles with a bright contrast supported on Al2O3 particles (blue for Al) were observed, and the EDS mapping images revealed the presence of Pt (red). On the other hand, for the CuOx species of CuOx/Pt/Al2O3 (900 °C), the EDS mapping images revealed the presence of CuOx aggregates (green). However, because the
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catalysts before and a
90%. In contrast, the selectivity of N2O over the catalysts
would result in a slightly higher N2O selectivity.

Temperature at which NH3 conversion reached 10% and 90%. $b$ Calculated from XRD line broadening method. $c$ Calculated from pulsed CO chemisorption. $d$ Estimated by NH3 and NO-TPD ranging from 50 °C to 500 °C. $e$ The amount of CO chemisorption was not detected (n. d.).

Table 1 Catalytic properties of supported catalysts before and after thermal aging at 900 °C for 100 h in air

| Catalyst                                      | Phase               | $T_{10}$ $^a$/°C | $T_{90}$ $^a$/°C | N2        | N2O       | NO          | $S_{BET}$ /m$^2$ g$^{-1}$ | Pt particle size/nm | Desorbed gas $^b$/μmol m$^{-2}$ | NH3 | NO   |
|-----------------------------------------------|---------------------|-------------------|-------------------|-----------|-----------|-------------|--------------------------|---------------------|-----------------------------------|-----|------|
| CuO/Pt/3A2S                                   | CuO/Pt/3A2S        | 210               | 356               | 90        | 8         | 2           | 32                      | 18                  | 1.3                               | 0.050 |       |
| CuO/Pt/3A2S (900 °C)                          | CuAl2O3/Pt/3A2S    | 203               | 344               | 89        | 10        | 1           | 27                      | 50                  | 0.4                               | 0.063 |       |
| CuO/Al2O3                                     | CuAl2O3/γ-Al2O3    | 303               | 476               | 92        | 6         | 2           | 149                     |                    | 11                               | 11   | 0.051 |
| CuO/Al2O3 (900 °C)                            | CuAl2O3/γ-Al2O3    | 295               | 450               | 91        | 8         | 1           | 102                     |                    | 31                               | 2.0  | 0.140 |
| Pt/Al2O3                                      | Pt/γ-Al2O3         | 188               | 289               | 81        | 19        | <1          | 156                     | 11                  | 5                                | 1.6  | 0.064 |
| Pt/Al2O3 (900 °C)                             | Pt/γ, Al2O3        | 266               | 12                | 99        |           |             |                          | 139                 | 13                               | 1.5  | 0.444 |
| CuO/Al2O3 (900 °C)                            | CuAl2O3/γ-Al2O3    | 189               | 278               | 86        | 13        | <1          | 139                     | 15                  | 13                               | 13   | 1.3   |
| CuO/Al2O3 (900 °C)                            | CuAl2O3/γ-Al2O3    | 220               | 339               | 14        |           |             |                          | 317                 | 176                              | 1.5  | 0.444 |
| CuO/Pt/SiO2                                   | Cu/Pt/SiO2         | 234               | 316               | 93        | 7         | <1          | 182                     | 13                  | 13                               | 13   | 1.3   |
| CuO/Pt/SiO2 (900 °C)                          | Cu/Pt/SiO2         | 301               | 456               | 96        | <1        | 3           | 81                      | 24                  | 24                               | 24   | 1.2   |

a Temperature at which NH3 conversion reached 10% and 90%. b Calculated from XRD line broadening method. c Calculated from pulsed CO chemisorption. d Estimated by NH3 and NO-TPD ranging from 50 °C to 500 °C. e The amount of CO chemisorption was not detected (n. d.).

Combustion properties of supported CuO2 and Pt catalysts
Fig. 5 shows the comparison of the temperature dependence on the selectivities of products obtained over supported CuO2/Pt, CuO2/Al2O3 and Pt/Al2O3 before and after thermal aging at 900 °C under O2 excess conditions (λ = 2). ESIF shows those of the other catalysts. With respect to the supported CuO2/Pt catalysts before and after aging, CuO2/Pt/Al2O3 exhibited a comparatively higher catalytic NH3 combustion activity and N2 (lower N2O/NO) selectivity. For CuO2/Pt/Al2O3 and Pt/Al2O3 before and after aging, the light-off curves for NH3 were obtained at ~200 °C, whereas CuO2/Al2O3 exhibited lower catalytic activity ($T_{10}$: ~300 °C). On the other hand, before and after aging, CuO2/Pt/Al2O3 and CuO2/Al2O3 exhibited lower NO selectivity compared to Pt/Al2O3 although NO selectivities for all catalysts were observed after the NH3 conversion reached ~90%. In contrast, the selectivity of N2O over the catalysts before and after aging increased in the order of CuO2/Al2O3 < CuO2/Pt/Al2O3 < Pt/Al2O3. Finally, CuO2/Pt/Al2O3 exhibited higher N2 selectivity.

Table 1 summarises the catalytic properties of supported CuO2 and/or Pt before and after aging at 900 °C, and ESIF shows those of the other catalysts. Catalytic activity was expressed in terms of the light-off temperature at which 10% conversion of NH3 was achieved ($T_{10}$), and the product selectivities were evaluated at the reaction temperature at which 90% NH3 conversion was achieved ($T_{90}$). ESIF shows the temperature dependence of the product selectivities for the combustion of NH3 over the catalysts. For single catalysts supported on each material (i.e. 3A2S, Al2O3 and SiO2), supported...
CuO exhibited low activity and N₂O/NO selectivities, whereas supported Pt exhibited high activity and N₂O/NO selectivity (ESI†). On the other hand, binary supported catalysts exhibited the same high activity as the single supported Pt, albeit a slightly lower N₂O/NO selectivity. As the combustion activity was closely associated with the Pt particle size, which was calculated by the Scherrer equation (plot shown in the ESI†), highly dispersed Pt nanoparticles supposedly played a key role in the low-temperature light-off of NH₃. In this study, for pulsed CO chemisorption, it is expected that CO is adsorbed not only on Pt but also on CuO in case of binary system catalysts. Therefore, the correlation between the NH₃ combustion activity \( T_{10} \) and the Pt particle size can be estimated using the XRD line broadening method by employing the Scherrer equation.

To elucidate the correlation between the activity and size of Pt nanoparticles, the adsorption energy \( E_{\text{ads}} \) between NH₃ and Pt₁₃ and/or Pt₂₀ clusters (Pt–N) were estimated by DFT computations (Fig. 7). Compared with the Pt–N \( E_{\text{ads}} \) of the vertex for the Pt₂₀ (larger) cluster, that of the vertex for the Pt₁₃ (smaller) cluster was higher, indicating that NH₃ preferentially adsorbs on highly dispersed Pt nanoparticles as well as coordinatively unsaturated (cus) Pt atoms. Indeed, for the Pt₂₀ cluster, the Pt–N \( E_{\text{ads}} \) of three initial geometries (see inset in Fig. 7) increased in the order of atop < edge < vertex. Moreover, the bond distance of N–H in NH₃ adsorbed on Pt₁₃ was longer than that on Pt₂₀, suggesting that cus Pt exhibits high activity for the dissociation of the N–H bond in adsorbed NH₃. Compared with the activity of binary CuO–Pt catalysts prepared by co-impregnation, those of the sequentially impregnated CuOₓ/Pt catalysts were higher.
probably because Pt nanoparticles can be highly dispersed onto each support material without inhibition from the presence of CuOx.

Among the CuOx/Pt catalysts supported on various support materials, CuOx/Pt/Al2O3 exhibited a relatively higher activity, N2 selectivity, and thermal stability (Table 1). However, a significant decrease in S BET was observed for CuOx/Pt/Al2O3 (900 °C) (139 → 14 m2 g−1) in comparison with that observed for CuOx/Al2O3 (900 °C) and Pt/Al2O3 (900 °C). For this reason, first, it is considered that the significant decrease in specific surface area can be attributed to the phase transition of (γ → α) Al2O3 as well as thermal aging at 900 °C. However, in case of only γ-Al2O3, the phase transformation to α-Al2O3 was observed at approximately 1200 °C.17 Next, however, according to a previous report related to the effects of divalent cation additives on the phase transition of (γ → α) Al2O3, the additive Cu2+ species that coexist with γ-Al2O3 accelerates its phase transition to α-Al2O3 at a low temperature of 1200 °C, which can be attributed to the fact that CuAl2O4 is formed at a temperature of lower than 1200 °C.18 Indeed, in this study, α-Al2O3 was observed in CuOx/Al2O3 after thermal aging at 900 °C (Table 1). Finally, it is probable that the additive and co-existing Pt also accelerates the formation of CuAl2O4 as well as the phase transition to α-Al2O3. Although no concrete data are available, a similar significant decrease of the specific surface area could be observed in both Cu–Al–O and Cu–Pt–Al–O system catalysts after thermal aging occurred at 1000 °C.19 Notably, the high performance for CuOx/Pt/Al2O3 was maintained after thermal aging at 1000 °C despite the phase transition (γ → α) and decrease in the surface area. On the other hand, CuOx/Pt supported on α-Al2O3 exhibited slightly higher N2O/NO selectivities compared to CuOx/Pt/Al2O3 (using γ-Al2O3), the results of which can be explained from the difference in the CuOx phase of CuO in CuOx/Pt/α-Al2O3 and CuAl2O4 in CuOx/Pt/γ-Al2O3. Previously, our group has reported that supported CuAl2O4 exhibits a higher NH3–NO–O2 reaction activity to N2 compared to supported CuO because supported CuAl2O4 exhibits a higher fraction of the Cu2+ active species for the reaction.4 Therefore, the trend for N2O/NO selectivities over CuOx/Pt/α-Al2O3 and CuOx/Pt/Al2O3 can be explained in a similar manner. Moreover, physically mixed catalysts (CuO + Pt/Al2O3, CuAl2O4 + Pt/Al2O3 and CuOx/Al2O3 + Pt/Al2O3) exhibited lower N2 selectivity at high reaction temperatures (ca. > 600 °C) compared to binary catalysts (ESI†), indicating that highly dispersed Pt and proximate CuOx particles
are required to achieve high N₂ selectivity for catalytic NH₃ combustion. On the other hand, Pt/CuO exhibited high N₂ selectivity, albeit low catalytic activity (ESI†), probably because of low Pt dispersion. To examine the acid and base properties of these catalysts, the amount of desorbed gas per surface area of the catalyst was estimated using NH₃- and NO-temperature-programmed desorption (TPD) over a range of 50–500 °C (ESI†). Table 1 summarises this data. For all catalysts after aging, the amount of desorbed NO increased noticeably, likely because of decreased surface area. However, before and after aging, CuOₓ/Al₂O₃ exhibited relatively higher NH₃ and NO adsorption properties compared to CuOₓ/Al₂O₃ and Pt/Al₂O₃. These results indicated that CuOₓ/Al₂O₃ exhibits higher acidity and basicity compared to single supported catalysts; therefore, the reactivity of NHO₂/NO to N₂ is enhanced on the CuOₓ/Al₂O₃ surface.

Finally, the effects of CuO, Cu₂O and metallic Cu on the catalytic NH₃ combustion properties are discussed. ESI† denotes the comparison of the temperature dependence on the selectivities of the products that were obtained when compared to those of the commercially available CuO, Cu₂O and metallic Cu. The metallic Cu was prepared from CuO that was reduced at 400 °C for 30 min in 5% H₂/He because CuO can be reduced to metallic Cu at an approximate temperature of 300 °C, as demonstrated from the H₂-TPR measurement. For observing the NH₃ combustion activity, the light-off curve for CuO was obtained at approximately 300 °C; further, Cu₂O and metallic Cu exhibited lower activity when compared to that exhibited by CuO. Therefore, it can be considered that CuO (Cu²⁺ oxidation state) acts as an active site during the reaction. However, while considering the selectivities of the products, Cu₂O and metallic Cu exhibited low N₂O/NO selectivities because their activities (NH₃ conversions) were observed to be low. In the O₂-excess condition for NH₃ combustion (λ = 2.0), it can be considered that the combustion over CuOₓ catalysts proceeds because of redox cycling between CuO and Cu₂O. Further, the XRD patterns of CuO and Cu₂O before and after aging (λ = 2.0) also indicate redox cycling because the patterns of Cu₂O after the reaction revealed diffraction peaks corresponding to those of CuO (ESI†). In addition, based on our previous studies related to operando XAFS, similar redox behaviours could be observed in the supported CuO catalysts (CuOₓ/SiO₂). Therefore, it can be assumed that the effect of metallic Cu on combustion is negligible.

Conclusions

In this study, binary CuOₓ and Pt catalysts supported on 3A2S, Al₂O₃ and SiO₂ suppressed the production of N₂O/NOₓ via the catalytic combustion of NH₃ as a carbon-free energy source. Among the binary supported CuOₓ and Pt catalysts, sequentially impregnated CuOₓ/Pt catalysts tended to exhibit higher activity because Pt nanoparticles were highly dispersed onto each support material without inhibition due to the presence of CuO. Compared to sequentially impregnated CuOₓ/Pt3A2S and CuOₓ/Pt/SiO₂, CuOₓ/Pt/Al₂O₃ exhibited high NH₃ combustion activity, N₂ selectivity, and thermal stability. Before and after aging, CuOₓ/Pt/Al₂O₃ was characterised as proximate CuAl₂O₄ and dispersed metallic Pt particles. As the combustion activity was closely associated with the Pt particle size, highly dispersed Pt nanoparticles were thought to play a key role in the low-temperature light-off of NH₃. For selectivity, the proximate CuAl₂O₄ in CuOₓ/Pt/Al₂O₃ enhanced the NH₃–NO to N₂ reaction, and the catalyst prevented the dissociative adsorption of NH₃ to N₂, which was regarded as an intermediate species obtained during the N₂O production. Therefore, CuOₓ/Pt/Al₂O₃ exhibits high N₂ selectivity.

Conflicts of interest

There are no conflicts to declare.

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Fig. 6 In situ FTIR spectra of NH₃ adsorbed on supports and catalysts before and after thermal aging in air at 900 °C for 100 h. The spectra were recorded at 200 °C in gas feeds of 0.3% NH₃ with He balance.

Fig. 7 Adsorption energy (E_ads) between NH₃ and Pt₁₃ and/or Pt₂₀ clusters (Pt–N) and bond distances of N–H in NH₃ adsorbed on Pt₁₃ and/or Pt₂₀ obtained by the DFT computations.
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