Catalytic NH_3 Combustion Properties of $CuO_x/3Al_2O_3·2SiO_2$

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Abstract: Although NH_3 has recently been regarded as a renewable and carbon-free energy source, NH_3 fuel has problems of high ignition temperature and the production of N_2O/NO_x. To overcome these problems, the present study demonstrates that the NH_3 combustion activity of copper oxide (CuO_x) catalysts supported on $3Al_2O_3·2SiO_2$ (3A2S) was found to be superior to CuO_x/Al_2O_3 and CuO_x/SiO_2. The high activity for CuO_x/3A2S was closely associated with the high reducibility and small particle size of CuO_x. Finally, the relation between the local structure of CuO_x/3A2S and its catalytic NH_3 combustion properties was discussed.

Keywords: Ammonia, Catalytic combustion, Copper oxides.

1. Introduction

Recently, NH_3 has been regarded as a renewable and carbon-free energy source due to its high energy density. However, in comparison with fossil fuels, NH_3 fuel has issues including high ignition temperature and N_2O/NO_x production. Previously, we proposed novel catalytic NH_3 combustion systems that enable low ignition temperatures as well as negligible N_2O/NO_x emissions[1], and demonstrated that CuO_x/Al_2O_3 and CuO_x/SiO_2 show high activity and high N_2 selectivity for catalytic NH_3 combustion, respectively. In this study, therefore, we focused on CuO_x catalysts supported on composite oxides of Al_2O_3 and SiO_2 ($3Al_2O_3·2SiO_2$: 3A2S) to investigate catalytic properties for the combustion of NH_3 as an energy source.

2. Experimental

3A2S as a catalyst support material was prepared using an alkoxide method, and finally calcined at 1200 °C for 5h. Al_2O_3 (JRC-ALO-8) and SiO_2 (JRC-SIO-10) were also used as support materials for CuO_x catalysts. Supported CuO_x (6 wt% loading as CuO) was prepared by an impregnation of an aqueous solution of $Cu(NO_3)_2$, followed by drying and calcination at 600 °C for 3 h in air. To evaluate the thermal stability, as-prepared catalysts were thermally aged at 900 °C for 100 h in air. The catalysts were characterized by XRD, *operando* XAFS, H_2-TPR, and so on. Catalytic NH_3 combustion was conducted in a flow reactor at atmospheric pressure ($10\ °C·min^{-1}$, 1.0% NH_3, 1.5% O_2, He balance, and $W/F = 5.0 \times 10^{-4}\ g·min·cm^{-3}$). The O_2-excess ratio on NH_3 combustion was expressed as $\lambda = (pO_2/pNH_3)_{exp.}/(pO_2/pNH_3)_{stoichiom.}$. The gas concentrations were analyzed using NDIR and gas chromatography.

3. Results and discussion

XRD patterns for CuO_x/3A2S, CuO_x/SiO_2, and CuO_x/SiO_2(aged) could be assigned to CuO and each support, whereas the diffraction peaks of Cu species for CuO_x/3A2S(aged) and CuO_x/Al_2O_3(aged) could be assigned to $CuAl_2O_4$. Therefore, the solid-state reaction between CuO_x and Al_2O_3 species was considered to be induced by the thermal aging at 900 °C to form $CuAl_2O_4$. By contrast, Al_2O_3 phase for CuO_x/Al_2O_3(aged) was partly transformed from γ to α by thermal aging. These structural results are summarized in Table 1.

Figure 1 shows Cu K-edge (a) XANES spectra and (b) FT-EXAFS for CuO_x/3A2S(aged) and CuO_x/SiO_2(aged) during NH_3 combustion ($\lambda = 2$) together with those for references. XANES spectra for CuO_x/3A2S(aged) and CuO_x/SiO_2(aged) at RT were similar to those for $CuAl_2O_4$ and CuO, respectively, which is consistent with the XRD patterns. However, the absorption energy of the XANES spectra for CuO_x/3A2S(aged) shifted slightly to lower energy on increasing the combustion temperature to 400 and 600 °C (see inset in Figure 1a). By contrast, the absorption energy of the spectrum for CuO_x/SiO_2(aged) at 600 °C exhibited a weak pre-edge assigned to the Cu^+ 1s → 4p transition, which was observed in the spectrum for Cu_2O. For FT-EXAFS (Figure. 1b), CuO_x/3A2S(aged) displayed an intense Cu–O peak (r ~ 1.94 Å) attributed to $CuAl_2O_4$, r of which was preserved after heating at 600 °C. These results indicate that CuO_x/3A2S(aged) also form $CuAl_2O_4$ during the NH_3 combustion. By contrast, CuO_x/SiO_2(aged) displayed an intense Cu–O peak (r ~ 1.85 Å) attributed to Cu_2O on reaching the reaction temperature of 400 °C. These results are consistent with XANES and suggest that the structure of CuO in CuO_x/SiO_2(aged) was partly changed (reduced) to that of Cu_2O during the NH_3 combustion reaction. For CuO_x/Al_2O_3 before and after aging, the *operando* XAFS profiles were similar to those for CuO_x/3A2S(aged) (not shown here).

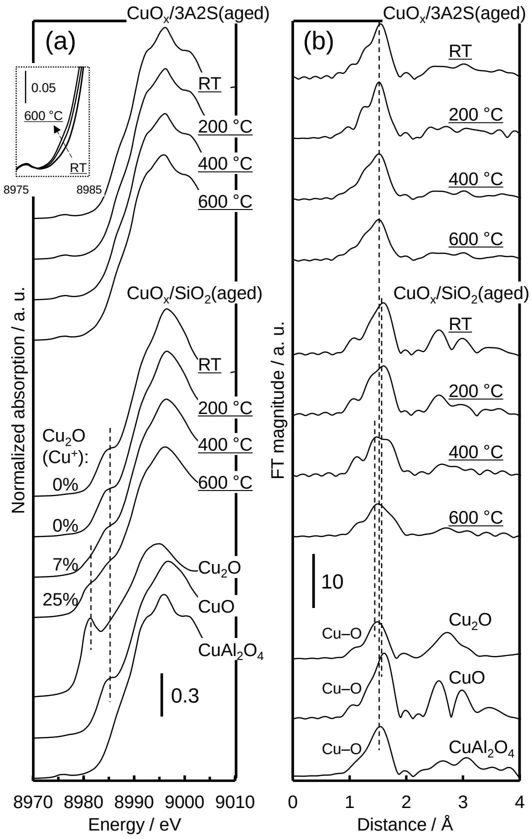

Figure 1. Cu K-edge (a) normalized XANES spectra and (b) k^3-weighted FT-EXAFS of CuO_x/3A2S(aged), CuO_x/SiO_2(aged), and these catalysts during NH_3 combustion at reaction temperatures of 200, 400, and 600 °C for 30 min.

Table 1 summarizes the catalytic properties of supported CuO_x before and after thermal aging. T_{10} increased in the following order: CuO_x/3A2S < CuO_x/Al_2O_3(aged) < CuO_x/Al_2O_3 < CuO_x/3A2S(aged) < CuO_x/SiO_2 ≈ CuO_x/SiO_2(aged). This finding is almost consistent with the order of the reduction temperatures observed in the H_2-TPR experiments, suggesting that the reduction of CuO_x is closely associated with the combustion activity. In addition, it is considered that the lattice oxygen of the CuO_x surface acts as a reactant for adsorbed NH_3, and catalytic NH_3 combustion over supported CuO_x proceeds *via* the Mars–van Krevelen mechanism. The supported CuO_x with smaller particle sizes tended to exhibit lower reduction temperatures. N_2 selectivity at T_{90} decreased in the following order: CuO_x/3A2S ≈ CuO_x/SiO_2 > CuO_x/3A2S(aged) > CuO_x/SiO_2(aged) > CuO_x/Al_2O_3 > CuO_x/Al_2O_3(aged). Therefore, it is suggested that CuO_x/3A2S before and after thermal aging exhibited improved the performance for catalytic NH_3 combustion than CuO_x/Al_2O_3 and CuO_x/SiO_2.

Table 1 Catalytic properties of supported CuO_x before and after thermal aging.

Catalyst	Phase	T_{10} ^{a} / °C	T_{90} ^{a} / °C	Selectivity at T_{90} ^{a} / %			Reduction temperature ^{b} / °C	Cu particle size ^{c} / nm
				N_2	N_2O	NO		
CuO_x/3A2S	CuO/3A2S	292	484	97	<1	3	209	3.1
CuO_x/3A2S(aged)	$CuAl_2O_4$/3A2S	326	570	94	3	3	234	43
CuO_x/Al_2O_3	$CuAl_2O_4/\gamma\text{-}Al_2O_3$	303	476	92	6	2	185	2.4
CuO_x/Al_2O_3(aged)	$CuAl_2O_4/\alpha, \gamma\text{-}Al_2O_3$	295	450	91	8	1	155	1.8
CuO_x/SiO_2	CuO/SiO_2	334	490	97	1	2	220	9.4
CuO_x/SiO_2(aged)	CuO/SiO_2	335	557	93	4	3	234	17

[a] Temperature at which NH_3 conversion reached 10% and 90%. [b] Temperature of the first H_2 consumption peak determined by H_2-TPR. [c] Calculated from H_2-TPR after H_2 reduction and subsequent N_2O reoxidation.

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4. Conclusions

During the NH_3 combustion reaction, the local structure of $CuAl_2O_4$ nanoparticles in CuO_x/3A2S(aged) was preserved, whereas that of CuO nanoparticles in CuO_x/SiO_2(aged) was partly changed to that of Cu_2O. The catalytic NH_3 combustion activity of supported CuO_x was closely associated with the reducibility and particle size of CuO_x, which implies that NH_3 adsorbed on CuO_x reacts primarily with the lattice oxygen. Thus, catalytic NH_3 combustion proceeds *via* the Mars–van Krevelen mechanism.

References

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