Contents lists available at ScienceDirect

Journal of Catalysis

Catalytic ammonia combustion properties and *operando* characterization of copper oxides supported on aluminum silicates and silicon oxides

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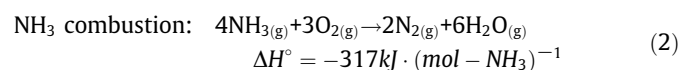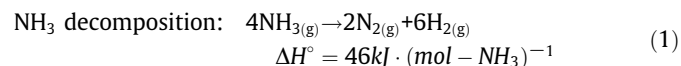
ABSTRACT

Although NH_3 has recently been regarded as a renewable and carbon-free energy source, NH_3 fuel has a high ignition temperature and its use results in the production of N_2O/NO_x. To overcome these issues, in this work, we focused on a novel catalytic combustion system and copper oxides (CuO_x) catalysts supported on aluminum silicates ($Al_6O_{13}Si_2$, $3Al_2O_3 \cdot 2SiO_2$, 3A2S) and silicon oxides (SiO_2). The preparation methods for 3A2S as a support material were optimized to achieve high catalytic NH_3 combustion activity and high N_2 (low N_2O/NO) selectivity. Because the CuO_x supported on 3A2S prepared by an alkoxide method and subsequent calcination at 1200 °C for 5 h in air exhibited high catalytic performance for NH_3 combustion, the properties of the catalyst in addition to CuO_x/SiO_2 thermally aged at 900 °C for 100 h in air were also evaluated using high-angle annular dark-field scanning transmission electron microscopy, energy-dispersive X-ray mapping, *operando* X-ray absorption fine structure analysis, X-ray photoelectron spectroscopy, and gas adsorption techniques. Our findings suggest that the catalytic NH_3 combustion activity, NO selectivity, and N_2O selectivity are closely associated with the reducibility (dispersion) of CuO_x, local structures around Cu, fraction of the oxidation state (Cu^{2+}), and adsorption species of NH_3 (NH, imide). Finally, we propose a reaction mechanism for catalytic NH_3 combustion over not only $CuO_x/3A2S$ but also CuO_x/SiO_2.

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1. Introduction

The demands to realize a low-carbon (low-CO_2-emission) society and address global warming are common issues for developed countries. Recently, NH_3 has been regarded as a renewable and carbon-free energy source because of its high energy density (3160 Wh L^{-1}) and negligible thermal NO_x emission [1,2]. For example, an NH_3-fueled micro gas turbine showed potential as an NH_3-fired power plant at Fukushima Renewable Energy Institute in Japan [2]. However, compared with fossil fuels, NH_3 has the following problems: (1) a high ignition temperature, (2) a low combustion rate, and (3) N_2O/NO_x production. To overcome these issues, the development of a novel NH_3 combustion system is required. One possible route is catalytic combustion, which is regarded as a promising technique for decreasing emissions from hydrocarbon-based fuels and was actively studied for use in gas turbines, boilers, and jet engines in the 1980s [3,4]. This system has many advantages over conventional noncatalytic combustion, as NO_x emission is greatly diminished by the low operating temperatures and high efficiency can be achieved through stable combustion. More recently, RenCat (a start-up company in Denmark) has been commercializing technology to decompose NH_3 into H_2 for use in fuel cells (Fig. 1) [5]. As described below, NH_3 decomposition (cracking) reaction (1) is endothermic, whereas NH_3 combustion reaction (2) is exothermic. Therefore, the system shown in Fig. 1 is expected that NH_3 decomposition can be effectively promoted by the heat produced from NH_3 combustion.

$$NH_3 \text{ decomposition: } 4NH_{3(g)} \rightarrow 2N_{2(g)} + 6H_{2(g)}$$
$$\Delta H^\circ = 46 kJ \cdot (mol-NH_3)^{-1} \quad (1)$$

$$NH_3 \text{ combustion: } 4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(g)}$$
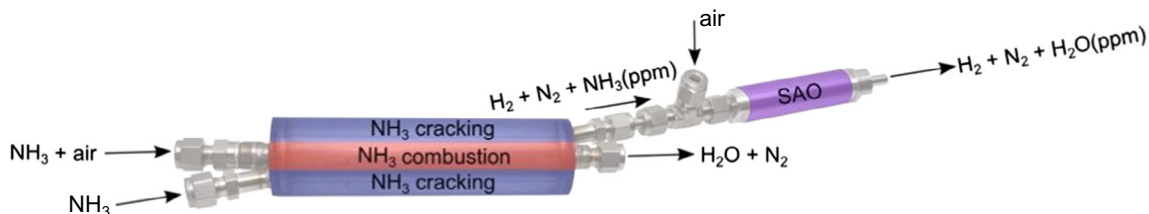$$\Delta H^\circ = -317 kJ \cdot (mol-NH_3)^{-1} \quad (2)$$

Fig. 1. Commercialized technology for NH_3 decomposition (cracking) into H_2 for use in fuel cells. NH_3 decomposition promoted by the heat produced from NH_3 combustion [5]. This is shown with permission from RenCat.

Therefore, to establish the further potentiality of NH_3 fuel, it is desirable to develop a novel catalyst with high thermal stability that enables the use of low ignition temperatures while resulting in negligible N_2O/NO_x emission. In regard to thermal stability, whatever the combustion catalysts are used as already-described potential applications, it is considered that accelerated tests as well as thermal aging at approximately 900 °C are required for the catalysts.

To achieve high performance for catalytic NH_3 oxidation or combustion to N_2, copper oxides (CuO_x)-based catalysts have been widely studied and were reviewed by Jablonska and Palkovits [6]. Chmielarz and Jablonska also reviewed effective catalysts for the selective oxidation of NH_3 (NH_3-SCO) emission in the automotive and energy production sectors [7]. More recently, other novel CuO_x-based catalysts have been reported for selective catalytic NH_3 oxidation to N_2 [8–12]. Zhang et al. prepared several CuO–Fe_2O_3 composites to study their catalytic activity and product selectivity for NH_3-SCO and suggested the synergistic effect between Fe_2O_3 and CuO [8]. Additionally, the mechanism of the NH_3-SCO reaction over CuO–Fe_2O_3 catalysts was investigated using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), revealing that intermediate species of adsorbed NH_3 are a key factor in determining product selectivity. Schiavoni et al. studied the catalytic properties for NH_3-SCO and selective catalytic reduction of NO by NH_3 (NH_3-SCR) over a copper phase deposited on a silico aluminophosphate of chabazite; they concluded that isolated Cu^{2+} centers and small Cu_2O_y (clustered Cu^{2+} species with $y \geq 1$) clusters exhibited high activities for both reactions [9]. Rutkowska et al. also prepared Cu-ZSM-5 zeolite to study its catalytic properties for NH_3-SCO and NH_3-SCR; these researchers surmised that modification of the micro–mesoporous structure enabled tuning of their properties [10]. However, these published studies regarded NH_3 as air pollution, and therefore their NH_3 oxidation tests were evaluated at low NH_3 concentrations and moderate reaction temperatures ($\leq$600 °C). On the other hand, Chakraborty et al. also noted the potentiality of NH_3 fuel as a renewable and carbon-free energy source, and reported a bottom-up approach to design a novel and high performance core–shell Ru–Cu nanoparticle catalyst for the oxidation of NH_3 to N_2 [13]. This is critically advanced study for NH_3 fuel, but the NH_3 oxidation was also evaluated by slightly low NH_3 concentrations (0.2%). Hence, further studies are needed to verify the potential use of the catalytic combustion of NH_3 as a renewable fuel.

Previously, we demonstrated that the NH_3 combustion activity of metal oxides increases with a decrease in their metal–oxygen bond energy [14], unsupported manganese oxides with higher oxidation states tend to exhibit higher activity [15], and sequentially impregnated $CuO_x/Ag/Al_2O_3$ exhibited high performance for catalytic NH_3 combustion among binary CuO_x and Ag supported on Al_2O_3 [16]. In addition, although CuO_x supported on aluminum oxide borates ($10Al_2O_3 \cdot 2B_2O_3$) exhibits higher N_2 selectivity and thermal stability than other CuO_x catalysts supported on various materials, CuO_x/Al_2O_3 and CuO_x/SiO_2 show high activity and N_2 selectivity for catalytic NH_3 combustion, respectively [17]. Local

structures around CuO_x supported on Al_2O_3 and/or $10Al_2O_3 \cdot 2B_2O_3$ during the NH_3 combustion reaction were studied by *operando* XAFS, and we concluded that $CuAl_2O_4$ particles in their catalysts after aging at 900 °C for 100 h in air were preserved during the reaction [18].

In this study, therefore, we focused on CuO_x catalysts supported on composite oxides of Al_2O_3–SiO_2 (aluminum silicates, $Al_6O_{13}Si_2$, $3Al_2O_3 \cdot 2SiO_2$, 3A2S) and SiO_2 after thermal aging at 900 °C to investigate catalytic properties for the combustion of NH_3 as an energy source. Moreover, the preparation methods for 3A2S as support materials were optimized to achieve high catalytic NH_3 combustion activity and high N_2 (low N_2O/NO) selectivity. Because the CuO_x/3A2S catalyst exhibited high thermal stability, activity, and N_2 selectivity as expected, characterization of the local structure and *operando* characterization for CuO_x/3A2S in addition to CuO_x/SiO_2 thermally aged at 900 °C during the catalytic NH_3 combustion were performed using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), energy-dispersive X-ray (EDX) mapping, *operando* X-ray absorption fine structure (XAFS) analysis, X-ray photoelectron spectroscopy (XPS), and gas adsorption techniques. Finally, we discuss the relation between the local structure of not only aged CuO_x/3A2S but also CuO_x/SiO_2 and their catalytic NH_3 combustion properties.

2. Materials and methods

2.1. Catalyst preparation

3A2S as a catalyst support material was prepared using either an alkoxide method or a co-precipitation method.

Alkoxide method: Following a previous report [19], $Si(OC_2H_5)_4$ (TEOS, Wako Pure Chemicals) was dissolved in C_2H_5OH (Wako Pure Chemicals) at 1 M at room temperature. After the addition of H_2O and HCl (Wako Pure Chemicals), the solution was stirred at 70 °C for 5 h, and a Si solution was prepared. The alcohol used was dehydrated. The concentrations of H_2O and HCl were H_2O/TEOS = 2 (mol/mol) and HCl/TEOS = 0.1 (mol/mol), respectively. $Al[OCH(CH_3)_2]_3$ (AIP, Sigma–Aldrich) was refluxed and dissolved in $(CH_3)_2$-$CHCH_2OH$ (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 room temperature·H_2O was added and the solution was stirred for 1 h to prepare a precursor solution. The precursor sols were dried at 110 °C for 48 h to obtain xerogel precursor powders, which were pulverized and calcined at 600 °C for 3 h and finally at 1000, 1200, or 1400 °C for 5 h in air. The 3A2S prepared by the alkoxide method and finally calcined at 1200 °C is abbreviated as 3A2S(A-1200), for example.

Co-precipitation method: Following a previous report [20], an appropriate amount of $Al(NO_3)_3 \cdot 9H_2O$ (Wako Pure Chemicals) and TEOS aqueous solution was combined with 10 wt% NH_3 solution (Wako Pure Chemicals), which was added dropwise under stirring (pH = 8) at room temperature. The precipitate was aged