Effects of support materials and silver loading on catalytic ammonia combustion properties

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ABSTRACT

In this research, the effects of support materials and silver (Ag) loading on catalytic NH_3 combustion properties were studied. Among the Ag supported on various metal-oxide materials, Ag/Al_2O_3 exhibited high catalytic NH_3 combustion activity and high N_2 (low $N_2O \cdot NO$) selectivity. The combustion activity is closely associated with the Ag dispersion which is estimated using the O_2–H_2 titration technique. Thus, highly dispersed Ag nanoparticles on supports play a crucial role in the low-temperature light-off of NH_3, implying that the support materials significantly affect the Ag dispersion. Although Ag/Al_2O_3 with higher amounts of Ag loading tended to exhibit higher combustion activity, the optimum Ag loading was found to be approximately 10 wt.%. At the optimum Ag loading concentration, Ag/Al_2O_3 performed well during the catalytic NH_3 combustion reaction. The local structures of the catalysts were investigated *via* transmission electron microscopy, X-ray absorption fine structure and gas adsorption techniques. After an NH_3 combustion reaction at a temperature of 900 °C, Ag/Al_2O_3 slightly deactivated because of the sintering of metallic Ag nanoparticles and the decreased surface area.

1. Introduction

The excessive consumption of finite fossil fuels and the risks associated with the use of nuclear power indicate that the exploration of cleaner and more efficient alternative fuel sources is crucial. Recently, NH_3 has been considered as a renewable and carbon-free energy source owing to its high energy density (3160 Wh L^{-1}) and negligible thermal NO_x emission [1]. However, in comparison to fossil fuels, NH_3 poses the following problems: (1) high ignition temperature, (2) low combustion rate and (3) production of N_2O and fuel NO_x. Thus, the development of new NH_3 combustion systems is necessary. One possible candidate is catalytic combustion, a promising technique for decreasing emissions from hydrocarbon-based fuels. It was actively studied for use in gas turbines, boilers and jet engines in the 1980s [2,3]. Catalytic combustion has multiple advantages over conventional non-catalytic combustion because NO_x emission is greatly diminished by the low operating temperatures and high efficiency can be attained through stable combustion. By applying a novel catalytic combustion system to the NH_3 fuel, it is expected that low-temperature ignition and negligible NO_x emission can be achieved.

Previously, we demonstrated that the catalytic NH_3 combustion activity of metal oxides increases as their metal-oxygen bond energy decreases [4] and that copper oxides (CuO_x) supported on aluminium oxide borates exhibit higher N_2 selectivity and thermal stability than CuO_x supported on other materials [5]. In addition, the catalytic properties for NH_3 combustion over Ag/Al_2O_3 were reported [6]. For the selective catalytic oxidation (SCO) of NH_3 to N_2, supported Ag catalysts, particularly Ag/Al_2O_3, have been studied because these catalysts exhibited high activity. Previously, Gang et al. reported that Ag/Al_2O_3 shows higher NH_3 oxidation activity and N_2 selectivity than Ag/SiO_2 and Ag powder catalyst and concluded that their catalytic properties were induced by the interaction between Ag and Al_2O_3 [7]. Lippits et al. reported the catalytic properties for NH_3-SCO over single Ag/Al_2O_3 and suggested the effects of adding Li_2O (increasing the Ag dispersion) and/or CeO_2 (increasing the Ag activity) [8]. The role of Ag species in Ag/Al_2O_3 for NH_3-SCO was studied by Zhang et al., who maintained that Ag^0 and Ag^+ act as the main active species at reaction temperatures < 140 °C and > 140 °C, respectively [9]. Zhang and He also studied the reaction mechanism of NH_3-SCO over Ag/Al_2O_3 [10]. Recently, Qu et al. reported the effect of support materials (e.g. Al_2O_3,

SiO_2, NaY and TiO_2) on the NH_3-SCO properties of Ag-based catalysts [11]. In addition, Ag/Al_2O_3 has been widely studied for the selective catalytic reduction of NO_x by NH_3 [12–26]. However, these studies regarded NH_3 as air pollution, and therefore, their oxidation tests for the low concentation of NH_3 (approximately < 0.1% NH_3) were evaluated at low reaction temperatures (approximately < 400 °C), studies of which have been reviewed by Chmielarz and Jablonska [27].

In this study, we focused on Ag catalysts that are supported on several materials to study their catalytic combustion properties towards high concentration of NH_3 (as an energy source) at high reaction temperatures (≤ 900 °C). Because Ag/Al_2O_3 exhibited high activity and N_2 selectivity in comparison to Ag supported on other materials, the effects of Ag loading were also studied. In addition, the local structures of Ag/Al_2O_3 were characterised using transmission electron microscopy (TEM), X-ray absorption fine structure (XAFS) and gas adsorption techniques. Finally, the thermal stability and reproducibility of Ag/Al_2O_3 were considered.

2. Materials and methods

2.1. Catalyst preparation

A wide variety of commercially available metal oxides (Table 1) were used as support materials for Ag. Supported Ag (5 wt.% loading as metallic Ag) was prepared by impregnation of an aqueous solution of $AgNO_3$ (Wako Pure Chemicals), followed by drying and calcination at 600 °C for 3 h in air. To study the effects of Ag loading, 0.1 wt.%–15 wt. % Ag/Al_2O_3 (γ-Al_2O_3: JRC-ALO-8, supplied by Catalysis Society of Japan; Brunauer–Emmett–Teller (BET) surface area (S_{BET}) = 173 $m^2\,g^{-1}$) with high performance in NH_3 combustion was prepared in a similar manner. Catalyst preparation methods for the other catalysts are explained in the Supporting Information.

2.2. Characterisation

Powder X-ray diffraction (XRD) measurements were performed using monochromated Cu Kα radiation (30 kV; 20 mA; Multiflex, Rigaku). Ag loading was determined through X-ray fluorescence (XRF; EDXL-300; Rigaku) measurements. The XAFS measurements of Ag K-edge were performed at the NW10A station of the Photon Factory (PF), High Energy Accelerator Research Organization (KEK) and at the BL01B1 station of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI). The Ag K-edge XAFS spectra were recorded in the transmission mode using an ionisation chamber filled with Ar, another chamber filled with Kr and an Si(311) monochromator. Reference samples (Ag_2O and $AgAlO_2$) were mixed with boron nitride (BN) powder to give an appropriate absorbance at the edge energy, whereas the catalysts were used without mixing with BN. The XAFS data were processed using the IFEFFIT software package (Athena and Artemis). High-resolution TEM (HRTEM) observations were performed using an

FEI Tecnai F20 electron microscope operated at 200 kV. The S_{BET} calculations were performed using N_2 adsorption isotherms, which were obtained at −196 °C (Belsorp, Bel Japan, Inc.). The Ag dispersion of supported catalysts was estimated by O_2–H_2 titration (Bel-cat, Bel Japan, Inc.), as per the method used by Seyedmonir et al. [28]. The catalysts were reduced (bulk: metallic Ag and/or AgO_x → metallic Ag) by flowing 5% H_2/Ar at 300 °C for 1 h, subsequently purged with Ar, cooled to 170 °C and reoxidised (surface: metallic Ag → Ag_2O). Reoxidation was performed by flowing 2.5% O_2/He at the same temperature for 10 min. The catalyst cell was purged with Ar. Finally, pulsed H_2 (5% H_2/Ar) was supplied to supported Ag catalysts and the Ag dispersion was expressed in terms of the consumption H_2/surface Ag (1:1).

2.3. Catalytic NH_3 combustion tests

Catalytic NH_3 combustion (NH_3–O_2 reaction) was performed in a flow reactor at atmospheric pressure. Catalysts (10–20 mesh; 50 mg) were fixed in a quartz tube (OD = ϕ6 mm and ID = ϕ4 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 room temperature to 900 °C at a constant rate of 10 °C·min^{-1} while a gas mixture containing 1.0% NH_3, 1.5% O_2 and He (balance) at 100 cm^3·min^{-1} (W/F = 5.0 × 10^{-4} g·min·cm^{-3}) was supplied. The O_2-excess ratio of NH_3 combustion was expressed as $\lambda = (pO_2/pNH_3)_{exp.}/(pO_2/pNH_3)_{stoichiom.}$. The concentrations of NH_3, N_2, N_2O/NO and NO_2 gas were analysed using a nondispersive infrared (NDIR) gas analyser (EIA-51d; Horiba), gas chromatography (GC-8A; Shimadzu), NDIR (VA-3011; Horiba) and chemiluminescence analyser (NOA-7000; Shimadzu). The calculation formulae for the concentration ratios are shown in the Supporting Information.

3. Results and discussion

3.1. Effects of support materials on catalytic NH_3 combustion properties

Fig. 1 shows the XRD patterns of as-prepared 5 wt.% Ag supported on various oxide materials. For all supported catalysts, the diffraction peaks were identified as belonging to each support material. The XRD patterns of Ag supported on MgO, $10Al_2O_3$·$2B_2O_3$ (denoted as 10A2B), SiO_2, and ZrO_2 showed peaks ascribable to the metallic Ag; however, these diffraction peaks could not be observed for the other support materials (Al_2O_3, $AlPO_4$, anatase TiO_2), probably because of the high dispersion of the Ag species. These trends are almost in agreement with their Ag dispersions, as summarised in Table 1. Indeed, from HRTEM observations (Supporting Information), as-prepared Ag supported on Al_2O_3 and TiO_2 could be characterised as highly dispersed and small Ag nanoparticles, whereas Ag supported on MgO and SiO_2 with low dispersion exhibited large Ag particles on each support.

Table 1 summarises the catalytic properties of as-prepared 5 wt.% Ag supported on various oxide materials. The activity was expressed in terms of the light-off temperature at which 10% conversion of NH_3 was reached (T_{10}), and the product selectivities were evaluated at the reaction temperature when NH_3 conversion was 90% (T_{90}). The temperature dependence of the product selectivities for NH_3 combustion over the catalysts is shown in the Supporting Information. The combustion activity decreased in the following order: Al_2O_3 ≈ TiO_2 > 10A2B > SiO_2 > MgO > ZrO_2 > $AlPO_4$, which bears no relation to the S_{BET} value of their catalysts. However, the activity order is almost same as the order of Ag dispersion (D_{Ag}: TiO_2 ≈ Al_2O_3 > 10A2B > $AlPO_4$ > SiO_2 ≈ ZrO_2 > MgO) estimated by O_2–H_2 titration technique, suggesting that the Ag dispersion is closely associated with the combustion activity. In addition, it is believed that the highly dispersed (small) Ag nanoparticles on supports are considered to play a crucial role in the low temperature light-off of NH_3. This correlation between the activity and Ag dispersion is almost consistent with our previous report for binary CuO_x–Ag/Al_2O_3 systems,

Table 1
Catalytic properties of as-prepared 5 wt.% Ag supported on various metal oxide materials.

Support	T_{10}[a]/°C	T_{90}[a]/°C	Selectivity at T_{90}[a]/%			S_{BET} /$m^2\,g^{-1}$	D_{Ag}[b]/%
			N_2	N_2O	NO		
MgO	292	398	72	25	3	53	< 1
Al_2O_3	229	396	89	11	< 1	150	25
10A2B	233	361	86	14	< 1	82	9
$AlPO_4$	349	713	78	< 1	22	66	7
SiO_2	259	401	87	12	1	172	3
TiO_2	229	521	88	2	10	39	26
ZrO_2	339	559	84	< 1	16	9	2

[a] Temperature at which NH_3 conversion reached 10% and 90%.

[b] Estimated by O_2–H_2 titration.