The role of silver species on Ag/Al$_2$O$_3$ catalysts for the selective catalytic oxidation of ammonia to nitrogen

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A B S T R A C T

The role of Ag species on Ag/Al$_2$O$_3$ catalyst for the selective catalytic oxidation (SCO) of NH$_3$ to N$_2$ was studied using 10 wt% Ag/Al$_2$O$_3$ catalysts prepared with impregnation, incipient wetness impregnation and sol–gel methods. The catalyst characterization was preformed using N$_2$ adsorption–desorption, UV/Vis, TEM and XRD. O$_2$-chemisorption and H$_2$–O$_2$ titration were measured to confirm the metal dispersion on the catalyst. The Ag species state and Ag particle size have significant influence on the Ag/Al$_2$O$_3$ activity and N$_2$ selectivity of the SCO of NH$_3$ at low temperature. Ag^0 is proposed to be an active species on the H$_2$ pretreated catalyst at low temperature ($<140\,°C$). It is evident that well-dispersed and small particle Ag^0 enhances catalytic activity at low temperature, whereas large particle Ag^0 is relate to a high N$_2$ selectivity. In contrast, Ag$^+$ could also be the active species at temperatures above 140 °C.

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1. Introduction

The removal of NH$_3$ from waste gas streams is becoming increasingly important because of environmental concerns. Selective catalytic oxidation (SCO) of NH$_3$ to N$_2$ is an ideal technology for removing NH$_3$ from waste gases, and it has been of increasing interest in recent years [1–3]. The application areas for the SCO of NH$_3$ include the treatment of waste gases from various NH$_3$ emission sources, such as chemical production processes, the selective catalytic reduction (SCR) of NO$_x$ by urea for diesel powered vehicles, the purification of reformate for fuel-cell systems and the gasification/combustion of biomass for combined heat and power generation.

Previous studies showed that noble metals such as Pt, Ir and Au were active for the reaction of SCO of NH$_3$ at low temperature, however, the selectivity of N$_2$ was not satisfied for the reason that the main by-product at low temperature was N$_2$O [4–8]. Metal oxide catalysts, namely, MnO$_2$, Co$_3$O$_4$, CuO, CaO, NiO, Bi$_2$O$_3$, Fe$_2$O$_3$, V$_2$O$_5$ [9–17], and many ion-exchanged zeolite catalysts [18–22], have also been investigated for the SCO of NH$_3$, but NH$_3$ conversion levels of these catalysts at low temperature were not high enough to be of practical use.

The Ag-based catalyst used for NH$_3$ oxidation has been studied by some researchers previously [2,4,5,23,24]. In earlier work, Il'chenko et al. have reported that the specific catalytic activity of metal Ag at 300 °C is lower than that of the precious metals Pt

and Pd [4,5]. Recently, it was reported by Gang et al. that alumina supported Ag (Ag/Al$_2$O$_3$) catalysts were extremely active for NH$_3$ oxidation at low temperature, and the performance of the Ag/Al$_2$O$_3$ catalyst was even superior to noble metal catalysts [2, 23]. However, the nature of Ag/Al$_2$O$_3$ for the NH$_3$ oxidation has not been studied in detail, such as the valence state of Ag species and particle size effect on the activity and selectivity of SCO of NH$_3$. In addition, the reduced Ag catalysts for NH$_3$ oxidation are mainly used in oxygenous environment, it is important to investigate the real performance of Ag species under reaction conditions.

In this article, we prepared the Ag/Al$_2$O$_3$ catalysts by different methods and investigated the role of Ag species on the Ag/Al$_2$O$_3$ for its catalytic activity and selectivity of NH$_3$ oxidation. It has been discovered that the Ag species state and Ag particle size of the Ag/Al$_2$O$_3$ have significant influence on the activity and N$_2$ selectivity for the SCO of NH$_3$. Ag^0 has been proposed as the active species at low temperature, and Ag$^+$ as the active species at high temperature for the SCO of NH$_3$, with the changeover at approximately 140 °C.

2. Experimental

2.1. Catalyst preparation and H$_2$ pretreatment

We prepared 10 wt% Ag/Al$_2$O$_3$ catalysts using three different methods: impregnation, incipient wetness impregnation, and sol–gel methods, denoted IM, IW and SOL, respectively. The catalysts prepared by the IM and IW methods were produced using γ-Al$_2$O$_3$ powder (250 m^2 g^{-1}) with an appropriate amount of silver nitrate aqueous solution. The samples were dried at 120 °C overnight and

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then calcined at 600 °C for 3 h in air. The preparation method for the SOL was the same as that in the literature [25] and it was calcined at 600 °C for 6 h in air. The catalysts were sieved into 20–40 mesh powders and pretreated in flowing H_2/N_2 (20 vol% H_2, 60 $cm^3 min^{-1}$) at 400 °C for 2 h before testing.

2.2. Catalytic tests

2.2.1. Catalytic activity test
The SCO activity measurement was carried out in a fixed-bed quartz reactor. In this work, 0.2 g catalyst was used. The reactant gas was obtained by blending different gas flows. The typical reactant gas composition was as follows: 500 ppm NH_3, 10 vol% O_2, and balance N_2. The total flow rate was 200 $cm^3 min^{-1}$ ($W/F = 0.06$ g s cm^{-3}). NH_3, O_2, and N_2 flow rates were controlled by mass flow controllers. The inlet and outlet gas compositions were analyzed by an on-line NEXUS 670-FTIR spectrophotometer fitted with a gas cell of volume 200 cm^3. These conditions are defined as standard conditions.

In order to investigate the pre-treatment effects, we tested the activity of the fresh Ag/Al_2O_3 (IM) under the standard conditions and compared it with the activity of the H_2 pretreated Ag/Al_2O_3 (IM).

2.2.2. Evolution with time-on-stream at 160 °C
The H_2 pretreated Ag/Al_2O_3 (IM) catalyst was fed with the reactant mixture (standard conditions) at 160 °C, and the evolution of the NH_3 conversion and N_2 selectivity were recorded for the next 48 h at 160 °C.

2.2.3. Temperature cycle
The H_2 pretreated Ag/Al_2O_3 (IM) catalyst was heated from room temperature to 220 °C and cooled to room temperature under the standard conditions for 5 times.

2.3. Characterization of catalysts

The N_2 adsorption–desorption isotherms were obtained at −196 °C over the whole range of relative pressures, using a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co.). Specific areas were computed from these isotherms by applying the Brunauer–Emmett–Teller (BET) method. The pore size distribution was calculated by the BJH method. Before measurement, the samples were treated by degassing at 300 °C for 4 h.

Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a Rigaku D/max-RB X-Ray Diffractometer (Japan) using Cu$K\alpha$ radiation and operating at 40 kV and 40 mA. The patterns were taken over the 2θ range from 20 to 70° at a scan speed of 6° min^{-1}.

Diffuse-reflectance UV/Vis spectra (UV/Vis) were recorded under ambient conditions on a U-3010 (Hitachi) spectrometer with a standard diffuse reflectance unit. The range was 190–850 nm and the scan rate was 300 nm min^{-1}. The measured spectra were converted into Kubelka–Munk functions and deconvoluted into Gaussian subbands that could be quantitatively assigned to the different Ag species [26–33].

Transmission electron microscopy (TEM) characterizations were carried out using an H-7500 (Hitachi) instrument. The accelerating voltage for the microscope was 80 kV and the point resolution was 0.36 nm. 200–300 particles were counted to evaluate the particle size (diameter) distribution.

The global dispersion (%) of Ag and the mean particle size (MPS) (nm) in the prepared catalysts were determined by O_2-chemisorption at 170 °C using a Quantasorb-18 (Quanta Chrome Instrument Co.) at a pressure range of 40 to 200 Torr of O_2, according to Ref. [34]. Before the O_2-chemisorption experiments, the

samples were reduced in a 5 vol% H_2/Ar stream (40 $cm^3 min^{-1}$) by heating from room temperature to 400 °C with a heating rate of 10 °C min^{-1}, and then holding at this temperature for 2 h. Metal dispersion and MPS were calculated by the Langmuir method according to a method adapted from the literature [35]. For dispersion measurements, we relied on the total adsorption isotherms and stoichiometries of $Ag/O_2 = 2$ [34,35].

H_2–O_2 titration has also been a common method for the detection of Ag dispersion. We therefore measured the Ag dispersion using a H_2–O_2 titration pulse method in a homemade pulse flow system equipped with a computer-interfaced quadruple mass spectrometer (Hiden HPR 20). Prior to the H_2–O_2 titration, 100 mg of sample was reduced in 5 vol% H_2/Ar (40 $cm^3 min^{-1}$, 10 °C min^{-1}) at 400 °C for 2 h. Then He gas (40 $cm^3 min^{-1}$) was passed over the sample for 1 h. After cooling to 170 °C in He, the O_2 adsorption experiment was performed, followed by flushing with He (40 $cm^3 min^{-1}$), then the introduction of H_2 pulses (1 cm^3 of 5 vol% H_2/Ar). The stoichiometries of $Ag/O_2 = 2$, $Ag/H_2 = 1$ were assumed [34]. On the basis of these dispersion (D) data, the crystallite size could be estimated from the expression d (nm) $= 1.34/D$, assuming spherical Ag crystallites [36]. We note that there have been a number of studies of O_2-chemisorption and H_2–O_2 titration on Ag. We selected the reduction temperature 400 °C (10 °C min^{-1}) to ensure that the degree of reduction in these conditions was approximately 100%, the same condition as before the activity test.

3. Results

3.1. NH_3 oxidation over 10 wt% Ag/Al_2O_3 catalysts

To elucidate the effects of the preparation methods, 10 wt% Ag/Al_2O_3 catalysts prepared using three different methods were tested for the SCO of NH_3 at various temperatures. As can be seen in Fig. 1, IW and IM behaved similarly and they had higher NH_3 conversions at low temperature, quite different from SOL. However, the SOL showed better selectivity to N_2 than the other two catalysts. It is noteworthy that N_2O was the main by-product produced over the catalysts IM and IW at lower temperatures.

As shown in Fig. 2, H_2 pretreatment significantly improved the low temperature activity of the Ag/Al_2O_3 (IM), showing over 95% conversion of NH_3 at 140 °C and reaching 100% at 160 °C. However, no NH_3 conversion was obtained over fresh Ag/Al_2O_3 (IM) at 140 °C, but complete conversion at 220 °C.

Since the NH_3 conversion reached 100% at 160 °C over the H_2 pretreated Ag/Al_2O_3 (IM) catalyst, we kept the temperature at 160 °C for more than 48 h to continuously test the activity of the reduced Ag/Al_2O_3 catalyst (shown in Fig. 3). It was discovered that high NH_3 conversion over the H_2 pretreated Ag/Al_2O_3 at 160 °C was retained for at least 48 h, while the selectivity of N_2 increased slightly (from 46% to 50%).

As shown in Fig. 2, the NH_3 conversion over the fresh and H_2 pretreated Ag/Al_2O_3 catalysts increased with the temperature; complete conversions of NH_3 were obtained at 220 and 160 °C. Temperature cycle test was performed on the H_2 pretreated Ag/Al_2O_3 from room temperature to 220 °C for 5 times under the standard conditions. The SCO of NH_3 over the catalyst was tested at various temperatures. The result is shown in Fig. 4. It is significant that the NH_3 conversion at low temperature decreased gradually over the 5 reaction cycles, but the selectivity for N_2 formation showed the opposite behavior. In all the 5 cycles, the NH_3 conversion reached 100% at 220 °C.

We compared the performance of our Ag/Al_2O_3 catalysts with the results of the reported highly active noble metal catalysts [3,8,15] in Table 1. Since the reaction conditions of NH_3 oxidation used in these literatures were different with this work, we also