Highly dispersed Cu$_y$AlO$_x$ mixed oxides as superior low-temperature alkali metal and SO$_2$ resistant NH$_3$-SCR catalysts

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ABSTRACT

For NO$_x$ removal from the exhaust gases of municipal solid waste (MSW) incinerators by selective catalytic reduction (SCR) technology, a suitable SCR catalyst which is active at low temperatures and robust to the presence of alkali metals and SO$_2$ is highly desired. In this contribution, we report the successful fabrication of a highly dispersed Cu$_y$AlO$_x$ (y = 2–4) mixed oxides for NH$_3$-SCR catalyst using high surface area, flower-like highly dispersed AMO-Cu-Al-CO$_3$ LDHs precursors. The influence of the Cu/Al ratio (2, 3, 4, and 5), calcination temperature (400, 500, 600, and 700 °C), and testing temperature (150, 200, 250, and 300 °C) on the activity of the Cu$_y$AlO$_x$ mixed oxide catalysts were systematically investigated. Among all samples, Cu$_4$AlO$_x$ showed the highest NO$_x$ conversion of 91.1% at 200 °C. After being thermally treated at 700 °C, the NO$_x$ conversion of Cu$_4$AlO$_x$ was still as high as 84.7%, which is much higher than that of the control catalyst 10 wt% CuO/γ-Al$_2$O$_3$ (57.5%). XRD and HR-TEM analyses suggested that the highly dispersed CuO nanoparticles are the active species for the SCR reaction. The catalytic De-NO$_x$ performance of Cu$_4$AlO$_x$ in the presence of alkali metals (K and Na) and SO$_2$ was also studied. In the presence of 50 ppm SO$_2$, the NO$_x$ conversion of Cu$_4$AlO$_x$ (78.4%) was much higher than that of CuO/γ-Al$_2$O$_3$ (48%). The selectivity of NO$_x$ conversion to N$_2$ and resistance to H$_2$O (and co-existence of H$_2$O and SO$_2$) for Cu$_4$AlO$_x$ catalyst were also evaluated. In all, we have demonstrated that the newly obtained Cu$_4$AlO$_x$ catalyst not only possesses higher thermal stability and higher low temperature (150–250 °C) catalytic activity, but also has much better alkali metal (K and Na), SO$_2$, and H$_2$O resistance than a conventional CuO/γ-Al$_2$O$_3$ catalyst.

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1. Introduction

For the sustainable development of society, municipal solid waste (MSW) has to be managed to avoid the exclusive use of landfills. Waste incineration is an increasingly used route to get rid of MSW due to the primary advantages of weight reduction, volume reduction, hygienic control, and energy recovery [1]. However, the main problem for the incineration treatment is the release of significant amounts of harmful pollutants, including heavy metals (e.g., Cd, Pb, and Hg), acid gases (e.g., NO$_x$, CO, SO$_x$, and HCl), and hydrocarbons [2]. In recent years, with the regulations for NO$_x$ emission becoming more and more stringent, the NO$_x$ abatement technologies for MSW incineration flue gases are receiving more

and more attention. In China, for instance, the NO$_x$ emission limit of hourly average was reduced from 400 mg/m^3 in GB18485-2001 to 250 mg/m^3 in DB11 502-2008. In addition, the actual implemented NO$_x$ emission limit of hourly average for new plants that are under construction in Beijing is even lower, which is 80 mg/m^3. With more stringent regulations on NO$_x$ emission from MSW incineration flue gases, efficient and reliable De-NO$_x$ technologies are highly desirable [3].

As the concentration of NO$_x$ emitted from MSW incineration plants is in the similar range as that from coal-fired power plants, selective catalytic reduction (SCR) technology has been systematically investigated because of its good selectivity, high efficiency, low cost, and is currently applied in MSW incineration plants in some countries such as Japan, Denmark, and Sweden [4]. The mostly adopted SCR catalysts for practical applications are V$_2$O$_5$-MoO$_3$/TiO$_2$ and V$_2$O$_5$-WO$_3$/TiO$_2$, with an active temperature range of 300–400 °C [5,6]. However, for the MSW incineration flue gases, because the concentration of SO$_2$ is normally very high, the SCR unit is preferred to be placed in downstream of the desulfurizer.

For such configuration, the temperature of the exhaust gases is much lower and the vanadium-based high-temperature SCR catalysts do not work properly under this condition [7–10]. Reheating the exhaust gases is not economical. In addition, the vanadium-based SCR catalysts also suffer from the poisoning effects by other harmful pollutants such as alkali metals and SO_2 that exit in the MSW flue gases [11,12]. Thus, developing novel SCR catalysts that are highly active at relatively lower temperatures and are resistant to alkali metals and SO_2 is of great importance for NO_x emission control from MSW flue gases.

To date, several types of low-temperature NH_3-SCR catalysts have been reported, including noble metals-based [13], zeolite-based [14,15], MnO_x-based [16], and CuO-based catalysts [17,18]. Among these catalysts, noble metals-based catalysts are expensive while zeolite-based catalysts have relatively poor stability in the presence of HCl [19–21]. MnO_x-based catalysts have good activity but suffer from SO_2 poisoning [22,23]. Comparing to other catalysts, CuO catalysts supported on various supports, such as CuO/ZrO_2 [24–26], CuO/γ-Al_2O_3 [27], CuO/SiO_2 [28] and CuO/TiO_2 [29,30] showed good NH_3-SCR activities. It was believed that the activity and selectivity of CuO-based catalysts are highly dependent on the texture and dispersion state of CuO species, which are importantly influenced by the preparation method [31]. In addition, for the supported CuO catalysts, the active CuO is often associated with sintering and aggregation when being exposed to high temperatures, leading to reduced SCR activity.

Recently, the synthesis of highly dispersed mixed metal oxides based catalysts via the careful calcination of a highly dispersed layered double hydroxide (AMO-LDH) precursors has attracted great attention [32–34]. Using this approach the dispersion of active metal species can be controlled at the atomic level [35–39]. Inspired by these studies, we now report the successful preparation of novel highly dispersed Cu_yAlO_x ($y = 2$–4) mixed oxides as NH_3-SCR catalysts from AMO-Cu-Al-CO_3 LDHs. Due to the better dispersion of active CuO species, these Cu_yAlO_x mixed oxide catalysts showed much higher De-NO_x activity and better resistance to alkali metals and SO_2 than those of the supported CuO/γ-Al_2O_3 catalyst. The influences of Cu/Al ratio, calcination temperature and reaction temperatures were systematically investigated. In addition, the poisoning effects of alkali metals and SO_2 on the surface acidity and reducibility were evaluated.

2. Experimental

2.1. Preparation of highly dispersed Cu_yAlO_x (y = 2–5) mixed oxide catalysts

First, conventional Cu-Al-CO_3 LDHs, $[Cu_{1-x}Al_x(OH)_2]_x(CO_3)_{x/2}$ were synthesized via a standard co-precipitation method. For instance, for the synthesis of Cu_2Al-CO_3 LDH, $\{[Cu_{0.66}Al_{0.33}(OH)_2](CO_3)_{0.165}\}$ an 100 mL aqueous solution containing 0.025 mol $Al(NO_3)_3 \cdot 9H_2O$ and 0.05 mol $Cu(NO_3)_2 \cdot 6H_2O$ and was added drop-wise into a vigorously stirred basic solution (100 mL) including 0.05 mol Na_2CO_3. During the synthesis, the pH of solution were maintained at 10 by addition of a NaOH solution (4 M). The slurry was stirred continuously for another 12 h. After aging, the resulting precipitate was filtered, washed several times with deionized water until pH = 7. The damp solids were then exposed to the Aqueous Miscible Solvent Treatment Method (AMOST), which involved washing and stirred for 2 h with acetone to give highly dispersed AMO-Cu-Al-CO_3 LDHs [32–34]. Finally, the AMO-Cu_2Al-CO_3 LDH was obtained by drying at 60 °C in the oven for another 24 h. Similarly other AMO-Cu-Al-CO_3 LDHs with different Cu/Al ratios of 3, 4, and 5 can be prepared by simply changing the $Cu(NO_3)_2 \cdot 6H_2O$ amount. After being calcined

at different temperatures (400–700 °C), various Cu_yAlO_x mixed oxides were obtained, which were denoted as Cu_2AlO_x, Cu_3AlO_x, Cu_4AlO_x, and Cu_5AlO_x, respectively.

The conventional supported catalyst 10 wt% CuO/γ-Al_2O_3 was prepared by incipient wetness impregnation method with an aqueous solution of $Cu(NO_3)_2 \cdot 6H_2O$. After being dried at 60 °C in the oven for 12 h, the samples were calcined at different temperatures (400–700 °C) in air for 5 h.

2.2. Characterization of catalysts

The X-ray diffraction (XRD) patterns of all synthesized samples were characterized using a Shimadzu XRD-7000 instrument in reflection mode with Cu Kα radiation ($\lambda = 1.542$ Å). The accelerating voltage was set at 40 kV with 30 mA current. Diffraction patterns were recorded within the 2θ range of 5–70° with the setting scan speed of 5°/min and a step size of 0.02°. The morphology of samples was characterized using field emission scanning electron microscope (FE-SEM, SU-8010, Hitachi). High resolution transmission electron microscopy (HR-TEM) analyses were performed on JEM-2100 microscope (JEOL, Japan) with an accelerating voltage of 200 kV. Fourier transform infrared spectrometer (FT-IR) experiments were performed on a FTS 3000 MX FT-IR (Bruker Vertex 70) spectrophotometer. BET specific surface areas (SSA) of samples were measured with a physisorption analyser (SSA-7000, Builder). The calcined Cu_yAlO_x mixed oxides samples were degassed at 220 °C for 4 h. Thermogravimetric analyses (TGA) of samples were conducted on a Q50 TGA analyzer from the TA Instruments. The samples were loaded onto the sample holder, and the temperature of the TGA furnace was increased to 800 °C in a flowing air (60 mL/min) with a rate of 5 °C/min.

The surface acidity of Cu_yAlO_x mixed oxides catalysts was measured by temperature-programmed desorption of ammonia (NH_3-TPD) in a fixed-bed continuous flow microreactor system. The desorbed molecules were monitored on-line using a quadrupole mass spectrometer (QGA, Hidden, UK). Before NH_3-TPD measurement, the catalyst (0.15 g) was purged in a flow of pure Ar at 400 °C for 30 min. Then, the furnace temperature was cooled down to 100 °C, and the samples were saturated in a flow of 1% NH_3/Ar (40 mL/min) for about 1 h. Subsequently, the sample was purged in Ar to remove weakly bound (physisorbed) NH_3, until a stable baseline level was achieved. TPD of ammonia was detected from 100 to 600 °C in a flow of Ar (40 mL/min) with a linear heating rate of 2 °C/min. The temperature in the catalyst bed was controlled using a K-type thermocouple immersed in the catalyst bed. The temperature-programmed reduction (TPR) of samples was detected from 100 to 600 °C in a fixed-bed flow microreactor (10 mm internal diameter). The hydrogen consumption was monitored using a quadrupole mass spectrometer (QGA, Hidden, UK). Prior to the TPR experiment, the sample (0.15 g) was purged in a flow of pure Ar at 400 °C for 30 min until a stable baseline level was achieved. Then, the furnace temperature was cooled down to 100 °C. The TPR runs were carried out in a flow of 5% H_2 in Ar (100 mL/min) with a linear heating rate of 2 °C/min.

2.3. NH_3-SCR activity tests

The NH_3-SCR catalytic activities of synthesized catalysts were performed at atmospheric pressure in a fixed-bed stainless steel reactor with an internal diameter of 10 mm. For each test, 0.15 g of catalyst was charged. After the reactor was heated up to the desired reaction temperature, the gas mixture was fed to the reactor. The reaction gas mixture normally consisted of 500 ppm NO_x, 500 ppm NH_3, 5% O_2, and Ar in balance, with a flow rate of 200 mL/min. All the gas flows were controlled independently by mass flow controllers (Brooks Instruments). The change of NO_x concentration was contin-