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Short communication

Comparison of Cu-Mg-Al-O_x and Cu/Al_2O_3 in selective catalytic oxidation of ammonia (NH_3-SCO)

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ABSTRACT

Copper-based materials are promising catalysts in the selective catalytic oxidation of ammonia into nitrogen and water vapour (NH_3-SCO). Investigations under applied reaction conditions over such materials seem to be rare and a comprehensive understanding of the involved active copper oxide species could facilitate a knowledge-based catalyst optimization. In the present work, Cu-Mg-Al-O_x mixed metal oxides and Cu/Al_2O_3 active catalysts in NH_3-SCO were investigated under $NH_3/O_2/CO_2/H_2O/N_2$ reaction conditions. Powder XRD, BET, NH_3-TPD, H_2-TPR and XAFS methods were used to characterize Cu-Mg-Al-O_x (Cu/Mg/Al = 8/63/29, mol%) and 10 wt% Cu/Al_2O_3. Cu-Mg-Al-O_x hydrotalcite derived mixed metal oxides were obtained by coprecipitation, while Cu/Al_2O_3 was prepared by incipient wetness impregnation. A highly dispersed copper oxide species formed on Cu-Mg-Al-O_x, while a mixture of highly dispersed (CuO_x) and bulk copper oxide species (CuO and $CuAl_2O_4$) formed on Cu/Al_2O_3. The comparison of Cu-Mg-Al-O_x and Cu/Al_2O_3 in NH_3-SCO provided good insight into the nature of the active species present in both copper-based catalysts. It was found that highly dispersed easily reducible copper oxide species and bulk copper oxide species appear as active species under $NH_3/O_2/N_2$ and $NH_3/O_2/CO_2/H_2O/N_2$ reaction conditions, respectively.

1. Introduction

Copper-based materials represent a class of the most active and N_2 selective catalysts towards the selective catalytic oxidation of ammonia into nitrogen (NH_3-SCO) [1,2] as well as the selective catalytic reduction of NO with ammonia (NH_3-SCR) [3]. For example, Cu-Mg-Al-O_x hydrotalcite derived mixed metal oxides appear as the most active catalysts among copper-modified clays in NH_3-SCO [1,2]. The unique feature of the hydrotalcite derived catalysts relates mainly to the homogenously dispersed mixed metal oxides present with relatively high specific surface areas. Cu-Mg-Al-O_x with 5–8 mol% copper was found to be optimal for NH_3-SCO [4]. In particular, Cu-Mg-Al-O_x (Cu/Mg/Al = 5/66/29, mol%) reached full conversion at 500 °C with 86% N_2 selectivity. The increase in copper loading in Cu-Mg-Al-O_x from 5 to 8 mol% shifted the temperature for total ammonia conversion to about 100 °C lower temperature; however, the selectivity to N_2 dropped, especially at temperatures above 450 °C [4]. A further decrease of N_2 selectivity was observed with increasing copper loading from 10 up to 20 mol% in Cu-Mg-Al-O_x under ideal (NH_3/O_2/He) feed composition [5]. Based on powder XRD, UV–vis-DRS and H_2-TPR analyses, the presence of easily reducible highly dispersed CuO_x caused the enhanced activity and selectivity to N_2 over Cu-Mg-Al-O_x (Cu/Mg/Al = 5–8/66–63/29, mol%) [4,6]. Another widely studied and one of the most efficient catalysts among transition metal-based systems is copper oxide (CuO) supported on γ-Al_2O_3 [7–9]. For example, Gang et al. [7,8] investigated the effect of copper loading (5–15 wt%) supported on alumina on activity and selectivity to N_2 in NH_3-SCO. They found that 10 wt% Cu/Al_2O_3 is the most efficient among others (full conversion at 350 °C with 90% N_2 selectivity). Moreover, based on HRTEM and UV–vis-DRS analyses, the authors claimed that $CuAl_2O_4$ was more active than CuO in NH_3-SCO [7]. Liang et al. [9] extended these studies over 10 wt% Cu/Al_2O_3 obtained by wet impregnation of γ-Al_2O_3 with various copper salts – $Cu(NO_3)_2$, $CuSO_4$ and $(CH_3COO)_2Cu$. They reported that the type of copper precursor influenced the contribution of copper oxide species (CuO and/or $CuAl_2O_4$) deposited on alumina, and thus significantly influenced the activity and selectivity to N_2. The

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acetate precursor favored the formation of crystalline CuO on Cu/Al_2O_3, leading to its superior activity but poor selectivity to N_2 (below 93% above 350 °C). Significantly higher selectivities to N_2 were obtained over a mixture of CuO and $CuAl_2O_4$, resulting from nitrate precursors, while an excess of $CuAl_2O_4$ – formed from a sulfate precursor – was believed to suppress the activity in NH_3-SCO under $NH_3/O_2/He$ conditions. However, the authors did not clarify the active copper oxide species for NH_3-SCO in the presence of typical flue gas compositions.

Furthermore, the majority of studies on NH_3-SCO were carried out using model feed gas streams (typically containing ammonia and oxygen diluted in inert gas). Investigations under more applied reaction conditions appear to be rare, and a comprehensive understanding of the involved active copper oxide species could facilitate a knowledge-based catalyst optimization. Therefore, we selected among Cu-containing catalysts – Cu-Mg-Al hydrotalcite derived mixed metal oxides and Cu/Al_2O_3, revealing high activities and N_2 selectivities under $NH_3/O_2/N_2$ conditions, and tested them in large-scale (ca. 6.5–6.7 g of catalyst, pelletized and sieved to 1–1.3 mm) NH_3-SCO under $NH_3/O_2/CO_2/H_2O/N_2$ feed gas compositions. Furthermore, powder XRD, BET, NH_3-TPD, H_2-TPR and XAFS techniques were applied to shed some light on the active copper oxide species in NH_3-SCO, and thus to allow for the design of an active, selective and stable copper-based catalyst.

2. Experimental

2.1. Catalysts preparation

Cu-Mg-Al-O_x hydrotalcite-like compounds with intended molar ratio of Cu/Mg/Al (8/63/29, mol%) were synthesized by co-precipitation using 1 M aqueous $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich), $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) and $Al(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich) solutions. A NaOH (Chemsolute) solution was used as a precipitating agent. Metal nitrate solutions were added to a vigorously stirred solution containing a slight over-stoichiometric excess of Na_2CO_3 (Sigma-Aldrich). The pH was maintained at 10.0 ± 0.2 by dropwise addition of 1 M NaOH solution. The obtained slurry was aged at 60 °C for 0.5 h, filtered, washed with distilled water and dried at room temperature. Cu/Al_2O_3 with intended loading of 10 wt% Cu was obtained after applying the wetness impregnation using aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich). The weight ratio of metal was measured with respect to the mass of γ-Al_2O_3 (Merck). Both obtained samples were calcined in static air at 600 °C for 6 h. Cu-Mg-Al-O_x mixed metal oxides obtained from hydrotalcite-like compounds were kept in a desiccator in order to avoid reconstruction of the hydroxide-like structure. For NH_3-SCO experiments, a fraction of particle size in the range of 1–1.3 mm was used.

2.2. Catalysts characterization

Powder X-ray diffraction measurements (XRD) were performed using a Siemens D5000 diffractometer (Cu-Kα radiation (λ = 1.54056 Å, 45 kV, 40 mA)). The specific surface areas (S_{BET}) of solids were determined by low-temperature (−196 °C) N_2 physical adsorption using Quantachrome Quadrasorb SI instrumentation. Prior to nitrogen adsorption, the samples were outgassed at 250 °C for 12 h using the supplied Quantachrome Flovac degasser unit. The S_{BET} areas were estimated using the Brunauer-Emmett-Teller (BET) multiple point method at partial pressures in the range of 0.05–0.3 P/P_0. Pore size distributions were obtained from the analysis of the desorption branches of the nitrogen isotherms using the Barrett-Joyner-Halenda method. Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were performed in a fixed-bed flow microreactor system equipped with QMS MKS, Cirrus 2 gas detector. Prior to the analysis, the sample (100 mg) was first outgassed in a flow of pure Ar at 600 °C for 1 h, and afterwards cooled down to 70 °C. Subsequently, the sample was saturated with NH_3 in a flow of 1.0 vol% NH_3/Ar (20 cm^3/min) for ~2 h. After that the sample was purged with pure Ar (~2 h) in order to remove weakly adsorbed ammonia. Finally, the desorption of NH_3 was measured in the temperature range of 70–600 °C with a linear heating rate of 5 K/min in a flow of pure argon (20 cm^3/min). Temperature-programmed reduction (H_2-TPR) experiments were carried out using Quantachrome ChemBET Pulsar TPR/TPD apparatus. The H_2-TPR run for the sample (50 mg) was performed starting from room temperature to 1000 °C, with a linear heating rate of 10 K/min and in a flow (25 cm^3/min) of 5.0 vol% H_2/Ar. Water vapour was removed from the effluent gas by means of a cold trap placed in an ice-water bath. The H_2 consumption was detected and recorded using a TCD detector. X-ray absorption spectroscopy (XAS) experiments were performed at room temperature on station B18 at the Diamond Light Source. The measurements were carried out in transmission mode using a Si (111) monochromator at the Cu K-edge (8979 keV) with the respective Cu monometallic foil (10 μm) used as an energy calibrant for the monochromator, and performed in quick scanning mode; the time taken for each scan was ca. 5 min (a step size of 0.5 eV and counting time of 150 ms/point was used for collection of data around the edge). To improve the signal-to-noise ratio, multiple scans were taken. Prior to the measurements, samples were pressed into 13 mm pellets using an appropriate amount of cellulose as binder. All data were subjected to background correction using the Athena program (i.e. IFFEFFIT software package for pre and post edge background subtraction and data normalization [10,11]). The Fourier transforms of the k^3-weighed data were phase corrected before plotting.

2.3. Catalytic studies

The catalytic experiments were carried out under 1 atm total pressure in a fixed-bed flow reactor (i.d.: 15 mm; L.: 62 mm). Prior to the reaction the catalyst was outgassed at 600 °C for 1 h in a flow of pure N_2 (WHSV = 137–140 L/h·g). Two sets of tests were performed with: (i) 0.5 vol% NH_3, 2.5 vol% O_2 and 97 vol% N_2, and (ii) 0.5 vol% NH_3, 2.5 vol% O_2, 10 vol% CO_2, 5 vol% H_2O and 82 vol% N_2 in the temperature range of 100–600 °C and using a linear heating rate of 5 K/min and WHSV = 137–140 L/h·g. Stability tests were carried out at the constant temperature of 475 °C for 800 min and the composition of the (ii) gas mixture mentioned above. Water vapour was supplied by the HovaPOR LF-1200, IAS GmbH apparatus. N_2, CO_2, O_2 and H_2O gas flows were convectively heated to meet the desired test temperature and mixed with the other gases (pre-heated to 180 °C) directly in front of the reactor. The concentrations of NH_3, NO, N_2O, NO_2, CO and H_2O were continuously monitored by FTIR type MKS Multigas 2030. After separating H_2O from the outlet gases, subsequently CO_2 and O_2 were detected after using a combined measurement system (type ColdUnit by FEV Europe GmbH) consisting of a non-dispersive infrared spectrometer (NDIR) and a paramagnetic detector (PMD), respectively. The signals were corrected for cross-sensitivities and normalized to the concentrations upstream of the reactor prior and after each test.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of Cu-Mg-Al-O_x, Cu/Al_2O_3 and γ-Al_2O_3. The Cu-Mg-Al hydrotalcite derived mixed metal oxides reveal only reflections characteristic of a poorly crystalized magnesium oxide (2θ of 36, 43 and 63°) [6]. Otherwise, the reflections characteristic of CuO (2θ of 35, 38, 48, 62 and 68°) [12] appear after deposition of 10 wt% of copper on alumina. Besides the diffraction peaks ascribed to CuO, the XRD peak attributable to $CuAl_2O_4$ at 37° 2θ may not be excluded [9]. The pure alumina support show reflections located at about 20, 33, 38, 40, 46, 61 and 67° 2θ, corresponding to γ-Al_2O_3 [13]. Thus, co-precipitation favored the formation of well dispersed copper oxide species, while impregnation of alumina led also to the formation of bulk copper oxide species. Table 1 lists specific surface areas (S_{BET})