

# Comparison of Cu-Mg-Al and Cu/Al<sub>2</sub>O<sub>3</sub> catalysts in selective ammonia oxidation into nitrogen and water vapour

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## Abstract

Copper-based materials are promising catalysts in the selective catalytic oxidation of ammonia into nitrogen and water vapour (NH<sub>3</sub>-SCO). XRD, BET, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR and XAFS were used to characterize Cu-Mg-Al-O<sub>x</sub> (Cu/Mg/Al = 8/63/29, mol.%) and (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub>. Cu-Mg-Al hydrotalcite derived mixed metal oxides were obtained by coprecipitation, while Cu/Al<sub>2</sub>O<sub>3</sub> was prepared by incipient wetness impregnation. A highly dispersed copper oxide species formed on Cu-Mg-Al-O<sub>x</sub>, while a mixture of highly dispersed and bulk copper oxide species (CuO and CuAl<sub>2</sub>O<sub>4</sub>) formed on Cu/Al<sub>2</sub>O<sub>3</sub>. The comparison of Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> in the NH<sub>3</sub>-SCO gave insight into nature of active species of both copper-based catalysts. Highly dispersed easily reducible copper oxide species and bulk copper oxide species served as active under NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> and NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions, respectively.

*Keywords:* copper, alumina, mixed metal oxides, large-scale NH<sub>3</sub>-SCO

## 1. Introduction

Copper-based materials represent a class of the most active and N<sub>2</sub> selective catalysts dedicated to the selective catalytic oxidation of ammonia into nitrogen (NH<sub>3</sub>-SCO) [1,2] as well as the selective catalytic reduction of NO with ammonia (NH<sub>3</sub>-SCR) [3]. For example, Cu-Mg-Al-O<sub>x</sub> hydrotalcite derived mixed metal oxides are the most active catalysts among copper-modified clays in NH<sub>3</sub>-SCO [1,2]. The unique feature of the hydrotalcite derived catalysts relates mainly to homogeneously dispersed mixed metal oxides with relatively high specific surface areas. Cu-Mg-Al-O<sub>x</sub> with 5-8 mol.% of copper was found to be optimal for NH<sub>3</sub>-SCO [4]. Cu-Mg-Al-O<sub>x</sub> (Cu/Mg/Al = 5/66/29, mol.%) reached full conversion at 500 °C with 86% N<sub>2</sub> selectivity. The increase in copper loading in Cu-Mg-Al-O<sub>x</sub> from 5 to 8 mol.% shifted the temperature for total ammonia conversion to about 100 °C lower temperature; however, the selectivity to N<sub>2</sub> dropped, especially at temperatures above 450 °C [4]. A further decrease of N<sub>2</sub> selectivity was observed with increasing copper loading from 10 up to 20 mol.% in Cu-Mg-Al-O<sub>x</sub> under ideal (NH<sub>3</sub>/O<sub>2</sub>/He) conditions [5]. Based on XRD, UV-vis-DRS and H<sub>2</sub>-TPR analyses, the presence of easily reducible highly dispersed CuO<sub>x</sub> caused the enhanced activity and selectivity to N<sub>2</sub> over Cu-Mg-Al-O<sub>x</sub> (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 supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [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<sub>2</sub> in NH<sub>3</sub>-SCO, and found (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> as the most efficient among others (full conversion at 350 °C with 90% N<sub>2</sub> selectivity at this temperature). Moreover, based on HREM and UV-vis-DRS analyses, the authors claimed that CuAl<sub>2</sub>O<sub>4</sub> was more active than CuO in NH<sub>3</sub>-SCO [7]. Liang et al. [9] extended these studies for (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> obtained by wet impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with various copper salts – Cu(NO<sub>3</sub>)<sub>2</sub>, CuSO<sub>4</sub> and (CH<sub>3</sub>COO)<sub>2</sub>Cu. They reported that the type of copper precursor influenced the contribution of copper oxide species (CuO and/or CuAl<sub>2</sub>O<sub>4</sub>) deposited on alumina, and thus significantly influenced the activity and selectivity to N<sub>2</sub>. The acetate precursor favored the formation of crystalline CuO on Cu/Al<sub>2</sub>O<sub>3</sub>, leading to its superior activity together with poor selectivity to N<sub>2</sub> (below 93% above 350 °C). Significantly higher selectivities to N<sub>2</sub> were

obtained over a mixture of CuO and CuAl<sub>2</sub>O<sub>4</sub>, resulting from nitrate precursors while an excess of CuAl<sub>2</sub>O<sub>4</sub> – formed from a sulfate precursor – was believed to suppress the activity in NH<sub>3</sub>-SCO under NH<sub>3</sub>/O<sub>2</sub>/He conditions. However, the authors did not clarify the active copper oxide species for NH<sub>3</sub>-SCO in presence of typical components of exhaust. Furthermore, majority of the studies in NH<sub>3</sub>-SCO were carried out for model gas stream (typically containing ammonia and oxygen diluted in inert gas). Further studies under more applied reaction conditions and a comprehensive understanding of the involved active copper oxide species could facilitate a knowledge-based catalyst optimization. Therefore, ~~inspired by the aforementioned studies~~, we selected among Cu-containing catalysts – ~~we prepared~~ Cu-Mg-Al hydrotalcite derived mixed metal oxides and Cu/Al<sub>2</sub>O<sub>3</sub>, revealing high activities and N<sub>2</sub> selectivities under NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> conditions ~~by coprecipitation and wetness impregnation, respectively~~, and tested them as catalysts in large-scale (reactor consisted of 6.5-6.7 g of catalyst, pelletized and sized to 1-1.3 mm) NH<sub>3</sub>-SCO under ~~NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> and~~ NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions. Furthermore, we applied XRD, BET, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR and XAFS to shed light on the active copper oxide species in NH<sub>3</sub>-SCO, and thus allow for the design of active, selective and stable copper-based catalyst.

## 2. Experimental

### 2.1. Catalysts preparation

Cu-Mg-Al hydrotalcite-like compounds with intended molar ratio of Cu/Mg/Al = 8/63/29, mol.% were synthesized by coprecipitation using 1 M aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Sigma-Aldrich), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma-Aldrich). A solution of NaOH (Chemsolute) was used as a precipitating agent. Metal nitrate solutions were added to a vigorously stirred solution containing a slight over-stoichiometric excess of Na<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>O<sub>3</sub> with intended loading of 10 wt.% was obtained by wetness impregnation using aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Sigma-Aldrich). The weight ratio of metal was

measured with respect to the mass of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Merck). Both obtained samples were calcined in static air at 600 °C for 6 h. Cu-Mg-Al mixed metal oxides obtained from hydrotalcite-like compounds were kept in a desiccator in order to avoid reconstruction of the hydroxide-like structure. For catalytic experiments, a fraction of particle size in the range of 1-1.3 mm was used.

## ***2.2. Catalysts characterization***

The X-Ray diffraction measurements (XRD) were performed using a Siemens D5000 XRD diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ , 45 kV, 40 mA). The specific surface areas ( $S_{\text{BET}}$ ) were determined by low-temperature (-196 °C) N<sub>2</sub> sorption using Quantachrome Quadrasorb SI. Prior to nitrogen adsorption the samples were outgassed at 250 °C for 12 h using a Quantachrome Flovac degasser. The specific surface areas ( $S_{\text{BET}}$ ) were calculated using the Brunauer-Emmett-Teller (BET) multiple point method at partial pressures from  $p/p_0$  range from 0.05 to 0.3. Pore size distributions were obtained from analysis of the desorption branches of the nitrogen isotherms using the Barrett-Joyner-Halenda method. The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) experiments were performed in a fixed-bed flow microreactor system equipped with QMS MKS, Cirrus 2 detector. Prior to the analysis, the sample (100 mg) was 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<sub>3</sub> in a flow of 1.0 vol.% NH<sub>3</sub>/Ar (20 cm<sup>3</sup>/min) for about 2 h. After that the sample was purged with pure Ar (about 2 h) in order to remove physisorbed ammonia. Finally, the desorption of NH<sub>3</sub> was measured in a temperature range of 70-600 °C with a linear heating rate of 5 K/min in a flow of pure argon (20 cm<sup>3</sup>/min). The temperature-programmed reduction (H<sub>2</sub>-TPR) experiments were carried out using Quantachrome ChemBET Pulsar TPR/TPD. H<sub>2</sub>-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<sup>3</sup>/min) of 5.0 vol.% H<sub>2</sub>/Ar. Water vapour was removed from effluent gas by means of a cold trap placed in an ice-water bath. The H<sub>2</sub> consumption was detected and recorded using a TCD detector. The X-ray absorption spectra (XAS) 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  $\mu\text{m}$ ) 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 atmospheric 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<sub>2</sub> (WHSV = 137-140 L/h·g). Two sets of tests were performed with: (i) 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub> and 97 vol.% N<sub>2</sub>, and (ii) 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, 10 vol.% CO<sub>2</sub>, 5 vol.% H<sub>2</sub>O and 82 vol.% N<sub>2</sub> in the temperature range of 100-600 °C with a linear heating rate of 5 K/min and WHSV = 137-140 L/h·g. The stability tests were carried out at a constant temperature of 475 °C for 800 min and the following composition of the (ii) gas mixture. Water vapour was supplied by a HovaPOR LF-1200, IAS GmbH. N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O 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<sub>3</sub>, NO, N<sub>2</sub>O, NO<sub>2</sub>, CO and H<sub>2</sub>O were continuously monitored by FTIR type MKS Multigas 2030. After separating H<sub>2</sub>O from the outlet gases, subsequently CO<sub>2</sub> and O<sub>2</sub> were detected applying 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 reactor prior and after each test.

## **3. Results and discussion**

Fig. 1 shows the XRD patterns for Cu-Mg-Al-O<sub>x</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub>. The Cu-Mg-Al hydrotalcite derived mixed metal oxides revealed only the reflections characteristic for poorly crystallized magnesium oxide (2θ of 36, 43 and 63°) [6]. Otherwise, the reflections characteristic for CuO (2θ of 35, 38, 48, 62 and 68°) [12] appeared after deposition of 10 wt.% of copper on alumina. Besides the diffraction peaks ascribed to CuO, the XRD peak attributable to CuAl<sub>2</sub>O<sub>4</sub> at 37° 2θ could not be excluded [9]. The pure support showed reflections located at about 20, 33, 38, 40, 46, 61 and 67° 2θ, corresponding to γ-Al<sub>2</sub>O<sub>3</sub> [13]. Thus, coprecipitation favored formation of the well dispersed copper oxide species, while impregnation of alumina led also to formation of bulk copper oxide species. Table 1 lists specific surface areas (S<sub>BET</sub>) and average pore diameter (D<sub>pore</sub>) for Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>. The Cu-Mg-Al hydrotalcite derived mixed metal oxides revealed relatively high specific surface area of about 131 m<sup>2</sup>/g. While after deposition of copper on γ-Al<sub>2</sub>O<sub>3</sub>, its specific surface area significantly decreased from 135 to 114 m<sup>2</sup>/g for Cu/Al<sub>2</sub>O<sub>3</sub>. Thus, the coverage of the support surface by the low surface area clusters of active component resulted in a decrease in the specific surface area of Al<sub>2</sub>O<sub>3</sub> after the deposition of CuO<sub>x</sub>. The pore size distribution results suggested that the samples were mesoporous materials.

**Fig. 1., Table 1.**

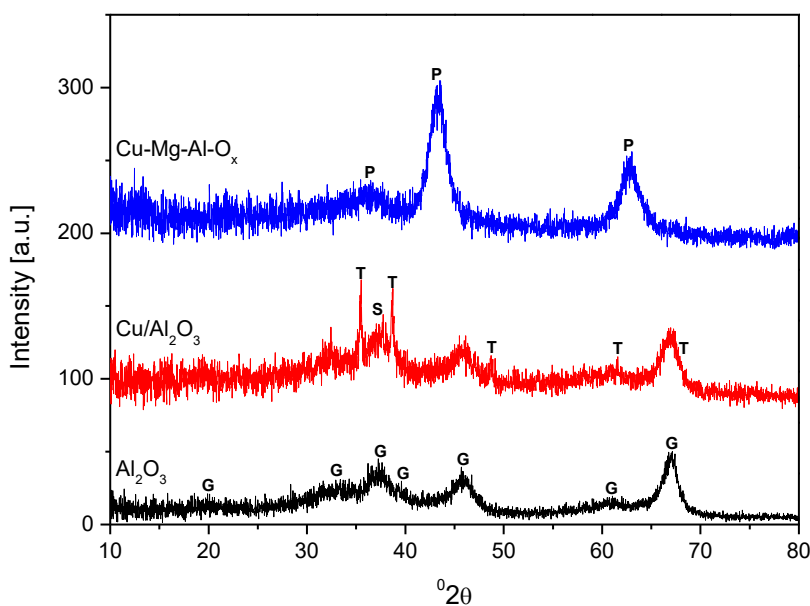


Fig. 1. XRD patterns of Cu-Mg-Al-O<sub>x</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>; P – MgO (periclase), T – CuO (tenorite),

S – CuAl<sub>2</sub>O<sub>4</sub> (copper aluminate), G –  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Table 1. Specific surface areas ( $S_{\text{BET}}$ ), average pore diameters ( $D_{\text{pore}}$ ), concentrations of chemisorbed NH<sub>3</sub> and amounts of H<sub>2</sub> consumed during TPR measurements (H<sub>2</sub> uptake) of Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>.

Sample codes	$S_{\text{BET}}/D_{\text{pore}}$ [m <sup>2</sup> /g]/[nm]	Concentration of chemisorbed NH <sub>3</sub> [ $\mu\text{mol/g}$ ]	H <sub>2</sub> uptake [mmol/g] <sup>a</sup>
Cu-Mg-Al-O <sub>x</sub>	131/6.1	263	0.88
Cu/Al <sub>2</sub> O <sub>3</sub>	114/4.5	384	1.30

<sup>a</sup>Calculated by equation:  $Y = 9\text{E-}09X + 2\text{E-}07$ ,  $R^2 = 0.9996$ , and X, Y referred to the area of each reduction peak and the H<sub>2</sub> consumption, respectively.

Fig. S1 (Supplementary Information) presents the NH<sub>3</sub>-TPD profiles, while Table 1 summarizes the concentrations of chemisorbed ammonia of Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>. The ammonia desorption for examined materials appeared below 350 °C with the maximum centered at about 157 °C, indicating the presence of mainly weak and medium acid sites [14]. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support showed a substantial amount of chemisorbed NH<sub>3</sub> (321  $\mu\text{mol/g}$ ) due to the presence of unsaturated Al<sup>3+</sup> acting as strong Lewis acid sites over a high specific surface area [15]. Furthermore, the amount of surface acid sites increased for copper-modified alumina up to 384  $\mu\text{mol/g}$ . Thus, Cu/Al<sub>2</sub>O<sub>3</sub> revealed a significantly higher amount of chemisorbed ammonia than Cu-Mg-Al-O<sub>x</sub> (263  $\mu\text{mol/g}$ ). Fig. S2 shows the H<sub>2</sub>-TPR profiles, while Table 1 lists the amounts of H<sub>2</sub> consumed during TPR measurements of Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>. The peak at about 305 °C in the H<sub>2</sub>-TPR profile of Cu-Mg-Al-O<sub>x</sub> corresponded to the reduction of Cu<sup>2+</sup> in highly dispersed CuO<sub>x</sub> to metallic copper [16], in agreement with XRD analysis. The H<sub>2</sub>-TPR profile for Cu/Al<sub>2</sub>O<sub>3</sub> revealed low and high temperature reduction peaks at about 261 and 312 °C, respectively. The first peak appeared due to reduction of Cu<sup>2+</sup> in highly dispersed CuO<sub>x</sub> (<300 °C), while the reduction of Cu<sup>2+</sup> in bulk copper oxide species (CuO and CuAl<sub>2</sub>O<sub>4</sub>) proceeded above 300 °C [17]. The amounts of hydrogen consumed during the measurements (H<sub>2</sub> uptakes) did not varied significantly over the materials and reached 0.88 and 1.30 mmol/g for Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>, respectively. Fig. S3 presents XANES around

Cu K-edge and isolated  $k^3\chi(k)$  EXAFS data (and the associated Fourier Transforms (FTs)) of Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> together with those of CuO as a reference. Differences in the rising adsorption edge and XANES region (~ 50 eV above E<sub>0</sub>) were suggestive of slight differences in the Cu environment. However, the similarity of the EXAFS oscillation frequency in the  $k$ -plot and the FTs suggested the Cu environment to possess similar near-neighbour distances and that the likely oxidation state of Cu to be 2+. The lower FT peak intensity for the samples (versus CuO) was consistent with there being less uniformity in these samples. For Cu/Al<sub>2</sub>O<sub>3</sub>, the presence of CuAl<sub>2</sub>O<sub>4</sub> could be inferred based on the similarity of the XANES and EXAFS previously reported for this phase [18]. However, XRD and H<sub>2</sub>-TPR analyses revealed CuO to also be present. The domination of the EXAFS by the spinel phase suggested that there was more of this phase present than CuO. For Cu-Mg-Al-O<sub>x</sub> the Cu environment could be said to be neither CuAl<sub>2</sub>O<sub>4</sub> or CuO; the similarity in ionic radius between Mg<sup>2+</sup> and Cu<sup>2+</sup> suggested incorporation of the latter into the periclase structure has occurred [19].

Fig. 2 presents the results of catalytic tests for large-scale NH<sub>3</sub>-SCO with WHSV = 137-140 L/h·g performed over Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>. N<sub>2</sub> was the desired product, while NO, N<sub>2</sub>O and NO<sub>2</sub> were undesired by-products. The activity of Cu-Mg-Al-O<sub>x</sub> was comparable to this of Cu/Al<sub>2</sub>O<sub>3</sub> with full conversion at about 500 °C. The selectivity to N<sub>2</sub> remained above 65% in the studied temperature range over both materials. A slightly higher selectivity to N<sub>2</sub> over Cu-Mg-Al-O<sub>x</sub> appeared due to lower reducibility (higher reduction temperature) of bulk copper oxide species present in this catalyst. Also, low-scale NH<sub>3</sub>-SCO with WHSV = 24 L/h·g revealed similar activity and selectivity to N<sub>2</sub> over Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> (full conversion at about 400-425 °C with 85-91% N<sub>2</sub> selectivity) as has been presented by Jabłońska et al. [4,20]. Thus, highly dispersed CuO<sub>x</sub> favored high activity and N<sub>2</sub> selectivity up to 500 °C in NH<sub>3</sub>-SCO [5]. Similar activities and selectivities over Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> revealed highly dispersed CuO<sub>x</sub> as active under NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> conditions over both catalysts. NH<sub>3</sub>-SCO under NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions revealed higher activity over Cu/Al<sub>2</sub>O<sub>3</sub>, indicating an increasing role of bulk copper oxide species (CuO and CuAl<sub>2</sub>O<sub>4</sub>). Furthermore, no significant depletion in conversion was observed in the long-term stability test at 475 °C over Cu/Al<sub>2</sub>O<sub>3</sub> under NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions (Fig. 3). Moreover, the selectivity to N<sub>2</sub> over this catalyst slightly increased from about 75 up to 77% after 800 min. Higher depletion in conversion – from 74 to 69% – was recorded over Cu-Mg-Al-O<sub>x</sub>. Similarly, around 5% depletion in



conversion was reported earlier at 375 °C over this catalyst in NH<sub>3</sub>-SCO with WHSV = 24 L/h·g in the presence of water vapour (3.2 vol.%) [4]. After 400 min the conversion reached a stable level of about 89% over Cu-Mg-Al-O<sub>x</sub>.

Fig. 2,3.

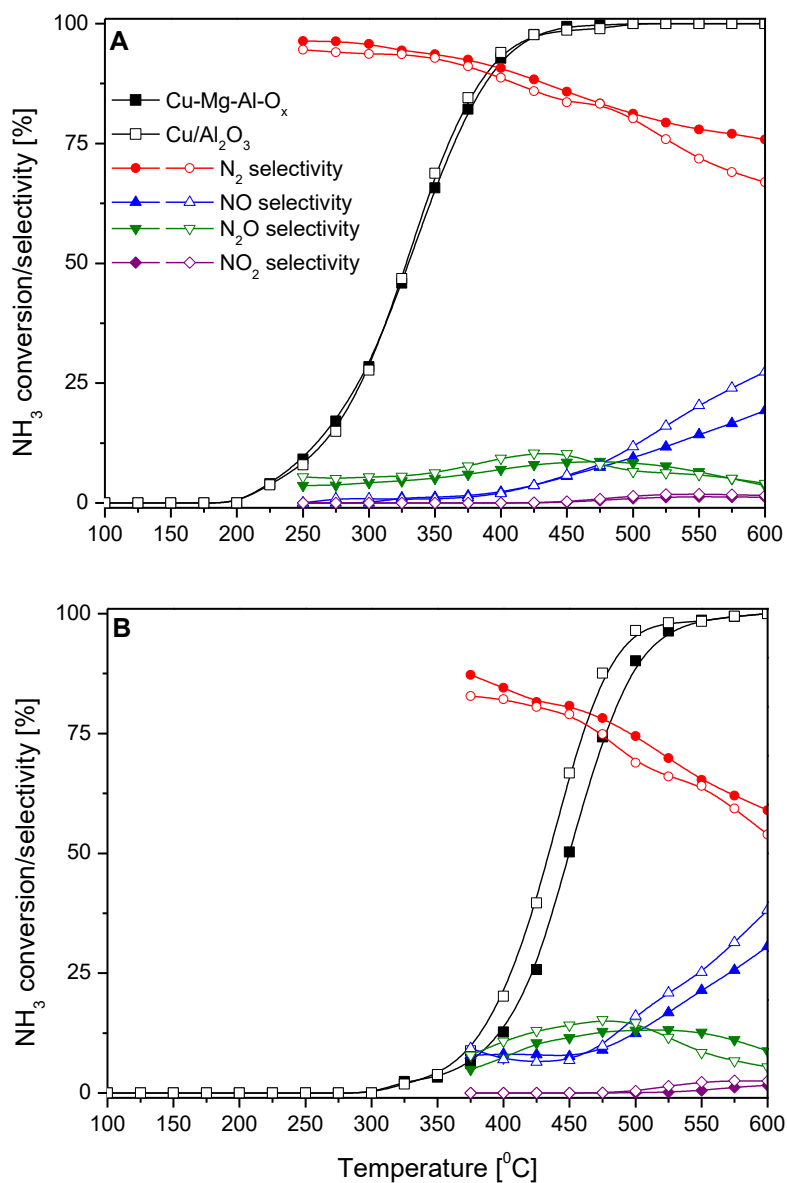


Fig. 2. Results of catalytic tests for NH<sub>3</sub>-SCO performed over Cu/Al<sub>2</sub>O<sub>3</sub> and Cu-Mg-Al-O<sub>x</sub>; experimental conditions: [NH<sub>3</sub>] = 0.5 vol.%, [O<sub>2</sub>] = 2.5 vol.%, N<sub>2</sub> balance (A), [NH<sub>3</sub>] = 0.5 vol.%, [O<sub>2</sub>] = 2.5 vol.%, [CO<sub>2</sub>] = 10 vol.%, [H<sub>2</sub>O] = 5 vol.%, N<sub>2</sub> balance, linear heating rate of 5 K/min and WHSV = 137-140 L/h·g.

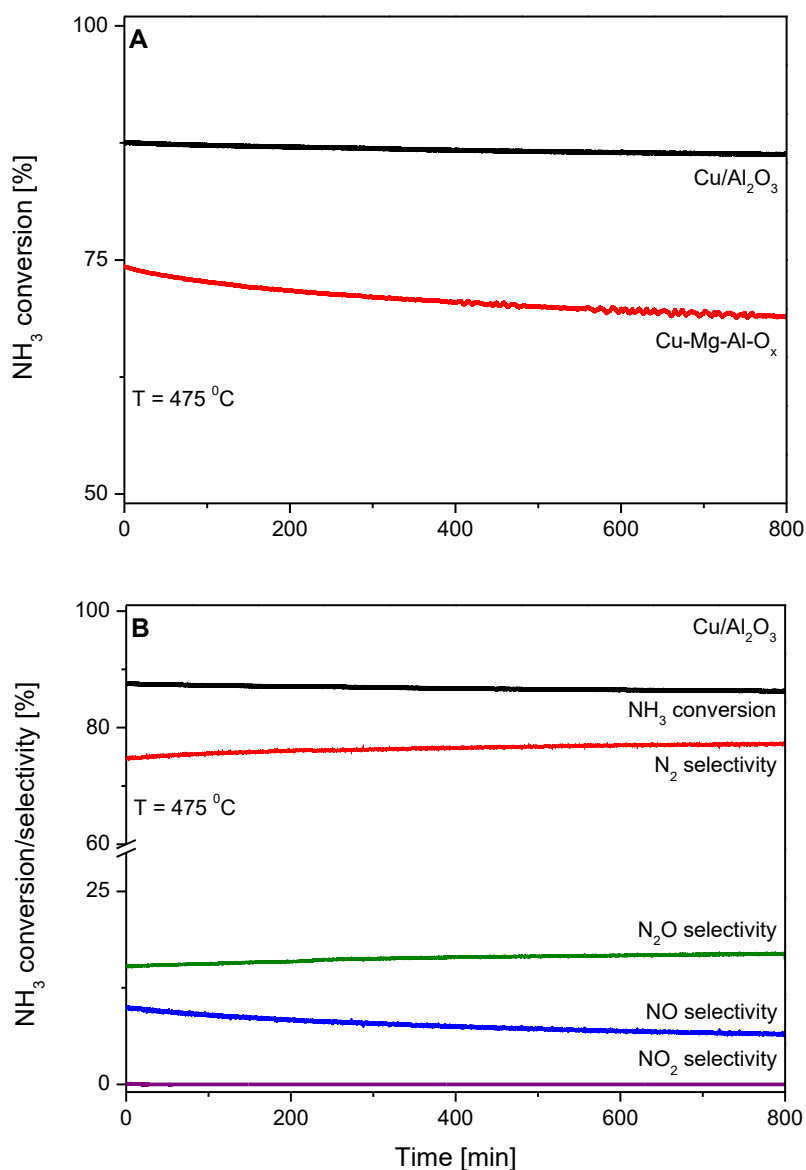


Fig. 3. Results of time-on-stream catalytic tests for NH<sub>3</sub>-SCO performed over Cu/Al<sub>2</sub>O<sub>3</sub> (A,B) and Cu-Mg-Al-O<sub>x</sub> (A); experimental conditions: [NH<sub>3</sub>] = 0.5 vol.%, [O<sub>2</sub>] = 2.5 vol.%, [CO<sub>2</sub>] = 10 vol.%, [H<sub>2</sub>O] = 5 vol.%, N<sub>2</sub> balance, linear heating rate of 5 K/min and WHSV = 137-140 L/h·g.

#### 4. Conclusions

The activity and selectivity of Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> in the large-scale NH<sub>3</sub>-SCO under NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> and NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions were investigated and discussed. Our results revealed that different copper oxide species formed on Cu-Mg-Al-O<sub>x</sub> (highly dispersed copper oxide species) and Cu/Al<sub>2</sub>O<sub>3</sub> (bulk copper oxide

species) clearly influence activity and selectivity in NH<sub>3</sub>-SCO. The highly dispersed copper oxide species formed on Cu-Mg-Al-O<sub>x</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> led to similar activity and N<sub>2</sub> selectivity under NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> conditions. Compared to Cu-Mg-Al-O<sub>x</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> exhibited higher activity under NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions. Thus, CuO and CuAl<sub>2</sub>O<sub>4</sub> formed on Cu/Al<sub>2</sub>O<sub>3</sub> showed higher activity in NH<sub>3</sub>-SCO under NH<sub>3</sub>/O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> conditions compared with highly dispersed CuO<sub>x</sub>.

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