Comparison of Cu-Mg-Al and Cu/Al_2O_3 catalysts in selective ammonia oxidation into nitrogen and water vapour

Magdalena Jabłońska[a,b*], Bernd Wolkenar[b,c], Andrew M. Beale[d,e], Stefan Pischinger[b,c], Regina Palkovits[a,b]*

[a]*Chair of Heterogeneous Catalysis and Chemical Technology, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany*

[b]*Center for Automotive Catalytic Systems Aachen, RWTH Aachen University, Schinkelstr. 8, 52062 Aachen, Germany*

[c]*Institute for Combustion Engines VKA, RWTH Aachen University, Forckenbeckstr. 4, 52074 Aachen, Germany*

[d]*Research Complex at Harwell, Rutherford Appleton Laboratories, Harwell Science and Innovation Campus, Didcot, Oxon OX11 0FA, UK.*

[e]*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.*

*Corresponding author. Tel: +49 241 80 26497; Fax: -22177. *E-mail address*: Palkovits@itmc.rwth-aachen.de (R. Palkovits), Jablonska@itmc.rwth-aachen.de (M. Jabłońska)

Abstract

Copper-based materials are promising catalysts in the selective catalytic oxidation of ammonia into nitrogen and water vapour (NH_3-SCO). XRD, BET, NH_3-TPD, H_2-TPR and XAFS 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 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 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 the NH_3-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 $NH_3/O_2/N_2$ and $NH_3/O_2/CO_2/H_2O/N_2$ conditions, respectively.

Keywords: copper, alumina, mixed metal oxides, large-scale NH_3-SCO

1. Introduction

Copper-based materials represent a class of the most active and N_2 selective catalysts dedicated to 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 are 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 homogenously dispersed mixed metal oxides with relatively high specific surface areas. Cu-Mg-Al-O_x with 5-8 mol.% of copper was found to be optimal for NH_3-SCO [4]. 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) conditions [5]. Based on 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 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, and found (10 wt.%)Cu/Al_2O_3 as the most efficient among others (full conversion at 350 °C with 90% N_2 selectivity at this temperature). Moreover, based on HREM 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 for (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 acetate precursor favored the formation of crystalline CuO on Cu/Al_2O_3, leading to its superior activity together with 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 presence of typical components of exhaust. Furthermore, majority of the studies in NH_3-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_2O_3, revealing high activities and N_2 selectivities under $NH_3/O_2/N_2$ 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_3-SCO under ~~$NH_3/O_2/N_2$ and~~ $NH_3/O_2/CO_2/H_2O/N_2$ conditions. Furthermore, we applied XRD, BET, NH_3-TPD, H_2-TPR and XAFS to shed light on the active copper oxide species in NH_3-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 $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich), $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) and $Al(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich). 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_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.% was obtained by wetness impregnation using aqueous solutions 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 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-Kα radiation (λ = 1.54056 Å, 45 kV, 40 mA). The specific surface areas (S_{BET}) were determined by low-temperature (-196 °C) N_2 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_{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_3-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_3 in a flow of 1.0 vol.% NH_3/Ar (20 cm^3/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_3 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^3/min). The temperature-programmed reduction (H_2-TPR) experiments were carried out using Quantachrome ChemBET Pulsar TPR/TPD. 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 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. 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 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 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_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 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_2, CO_2, O_2 and H_2O 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 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_x, Cu/Al_2O_3 and γ-Al_2O_3. The Cu-Mg-Al hydrotalcite derived mixed metal oxides revealed only the reflections characteristic for poorly crystalized 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 $CuAl_2O_4$ 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_2O_3 [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_{BET}) and average pore diameter (D_{pore}) for Cu-Mg-Al-O_x and Cu/Al_2O_3. The Cu-Mg-Al hydrotalcite derived mixed metal oxides revealed relatively high specific surface area of about 131 m^2/g. While after deposition of copper on γ-Al_2O_3, its specific surface area significantly decreased from 135 to 114 m^2/g for Cu/Al_2O_3. 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_2O_3 after the deposition of CuO_x. The pore size distribution results suggested that the samples were mesoporous materials.

Fig. 1., Table 1.

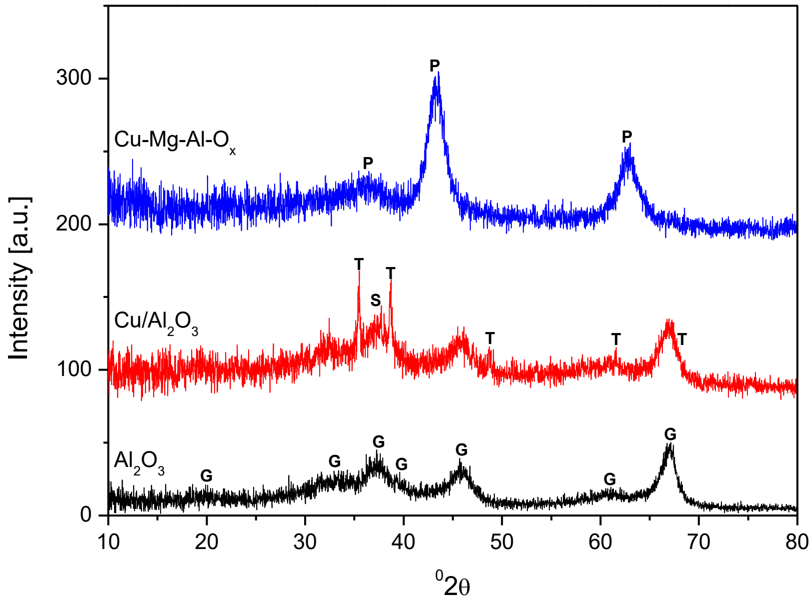

Fig. 1. XRD patterns of Cu-Mg-Al-O_x, Cu/Al_2O_3 and Al_2O_3; P – MgO (periclase), T – CuO (tenorite),

S – $CuAl_2O_4$ (copper aluminate), G – γ-Al_2O_3.

Table 1. Specific surface areas (S_{BET}), average pore diameters (D_{pore}), concentrations of chemisorbed NH_3 and amounts of H_2 consumed during TPR measurements (H_2 uptake) of Cu-Mg-Al-O_x and Cu/Al_2O_3.

Sample codes	S_{BET} /D_{pore} [m^2/g]/[nm]	Concentration of chemisorbed NH_3 [μmol/g]	H_2 uptake [mmol/g][a]
Cu-Mg-Al-O_x	131/6.1	263	0.88
Cu/Al_2O_3	114/4.5	384	1.30

[a]Calculated by equation: Y = 9E-09X + 2E-07, R^2 = 0.9996, and X, Y referred to the area of each reduction peak and the H_2 consumption, respectively.

Fig. S1 (Supplementary Information) presents the NH_3-TPD profiles, while Table 1 summarizes the concentrations of chemisorbed ammonia of Cu-Mg-Al-O_x and Cu/Al_2O_3. 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 γ-Al_2O_3 support showed a substantial amount of chemisorbed NH_3 (321 μmol/g) due to the presence of unsaturated Al^{3+} 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 μmol/g. Thus, Cu/Al_2O_3 revealed a significantly higher amount of chemisorbed ammonia than Cu-Mg-Al-O_x (263 μmol/g). Fig. S2 shows the H_2-TPR profiles, while Table 1 lists the amounts of H_2 consumed during TPR measurements of Cu-Mg-Al-O_x and Cu/Al_2O_3. The peak at about 305 °C in the H_2-TPR profile of Cu-Mg-Al-O_x corresponded to the reduction of Cu^{2+} in highly dispersed CuO_x to metallic copper [16]~~, in agreement with XRD analysis~~. The H_2-TPR profile for Cu/Al_2O_3 revealed low and high temperature reduction peaks at about 261 and 312 °C, respectively. The first peak appeared due to reduction of Cu^{2+} in highly dispersed CuO_x (<300 °C), while the reduction of Cu^{2+} in bulk copper oxide species (CuO and $CuAl_2O_4$) proceeded above 300 °C [17]. The amounts of hydrogen consumed during the measurements (H_2 uptakes) did not varied significantly over the materials and reached 0.88 and 1.30 mmol/g for Cu-Mg-Al-O_x and Cu/Al_2O_3, 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_x and Cu/Al_2O_3 together with those of CuO as a reference. Differences in the rising adsorption edge and XANES region (~ 50 eV above E0) 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_2O_3, the presence of $CuAl_2O_4$ could be inferred based on the similarity of the XANES and EXAFS previously reported for this phase [18]. However, XRD and H_2-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_x the Cu environment could be said to be neither $CuAl_2O_4$ or CuO; the similarity in ionic radius between Mg^{2+} and Cu^{2+} suggested incorporation of the latter into the periclase structure has occurred [19].

Fig. 2 presents the results of catalytic tests for large-scale NH_3-SCO with WHSV = 137-140 L/h·g performed over Cu-Mg-Al-O_x and Cu/Al_2O_3. N_2 was the desired product, while NO, N_2O and NO_2 were undesired by-products. The activity of Cu-Mg-Al-O_x was comparable to this of Cu/Al_2O_3 with full conversion at about 500 °C. The selectivity to N_2 remained above 65% in the studied temperature range over both materials. A slightly higher selectivity to N_2 over Cu-Mg-Al-O_x appeared due to lower reducibility (higher reduction temperature) of ~~bulk~~ copper oxide species present in this catalyst. Also, low-scale NH_3-SCO with WHSV = 24 L/h·g revealed similar activity and selectivity to N_2 over Cu-Mg-Al-O_x and Cu/Al_2O_3 (full conversion at about 400-425 °C with 85-91% N_2 selectivity) as has been presented by Jabłońska et al. [4,20]. ~~Thus, h~~Highly dispersed CuO_x favored high activity and N_2 selectivity up to 500 °C in NH_3-SCO [5]. Similar activities and selectivities over Cu-Mg-Al-O_x and Cu/Al_2O_3 revealed highly dispersed CuO_x as active under $NH_3/O_2/N_2$ conditions ~~over both catalysts~~. NH_3-SCO under $NH_3/O_2/CO_2/H_2O/N_2$ conditions revealed higher activity over Cu/Al_2O_3, indicating an increasing role of bulk copper oxide species (CuO and $CuAl_2O_4$). Furthermore, no significant depletion in conversion was observed in the long-term stability test at 475 °C over Cu/Al_2O_3 under $NH_3/O_2/CO_2/H_2O/N_2$ conditions (Fig. 3). Moreover, the selectivity to N_2 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_x. Similarly, around 5% depletion in conversion was reported earlier at 375 °C over this catalyst in NH_3-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_x.

Fig. 2,3.

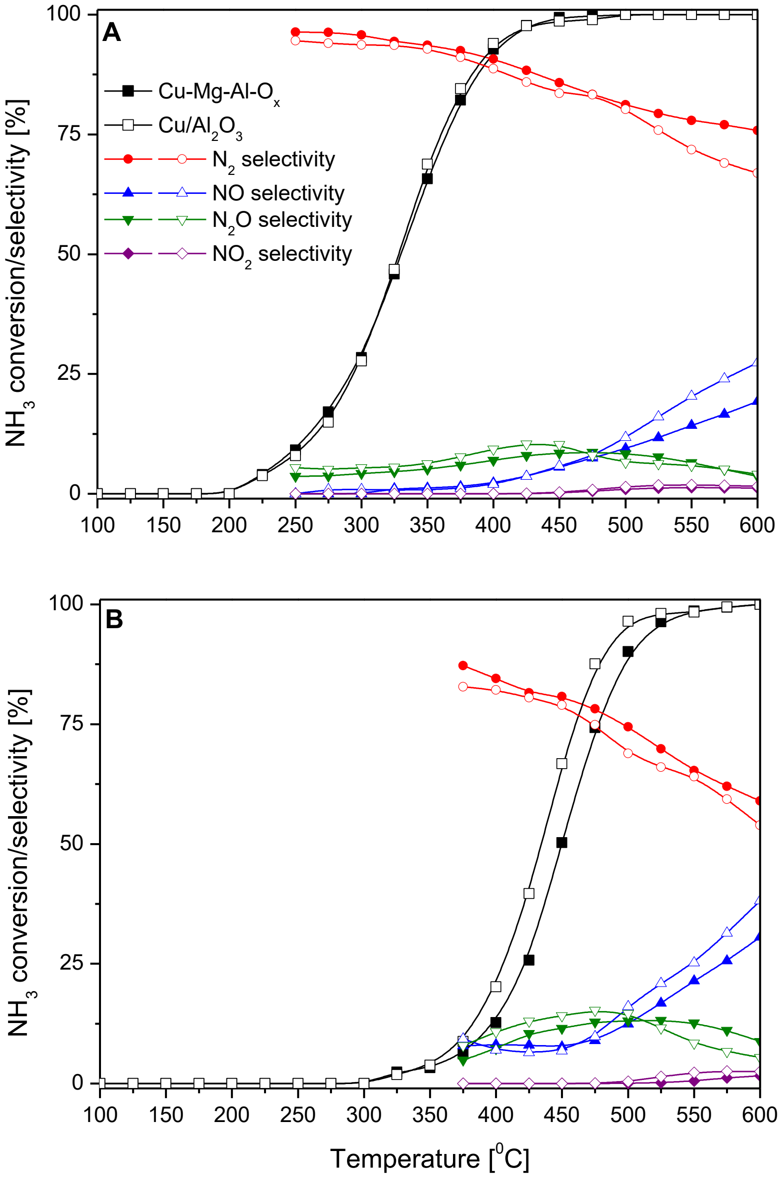

Fig. 2. Results of catalytic tests for NH_3-SCO performed over Cu/Al_2O_3 and Cu-Mg-Al-O_x; experimental conditions: [NH_3] = 0.5 vol.%, [O_2] = 2.5 vol.%, N_2 balance (A), [NH_3] = 0.5 vol.%, [O_2] = 2.5 vol.%, [CO_2] = 10 vol.%, [H_2O] = 5 vol.%, N_2 balance, linear heating rate of 5 K/min and WHSV = 137-140 L/h·g.

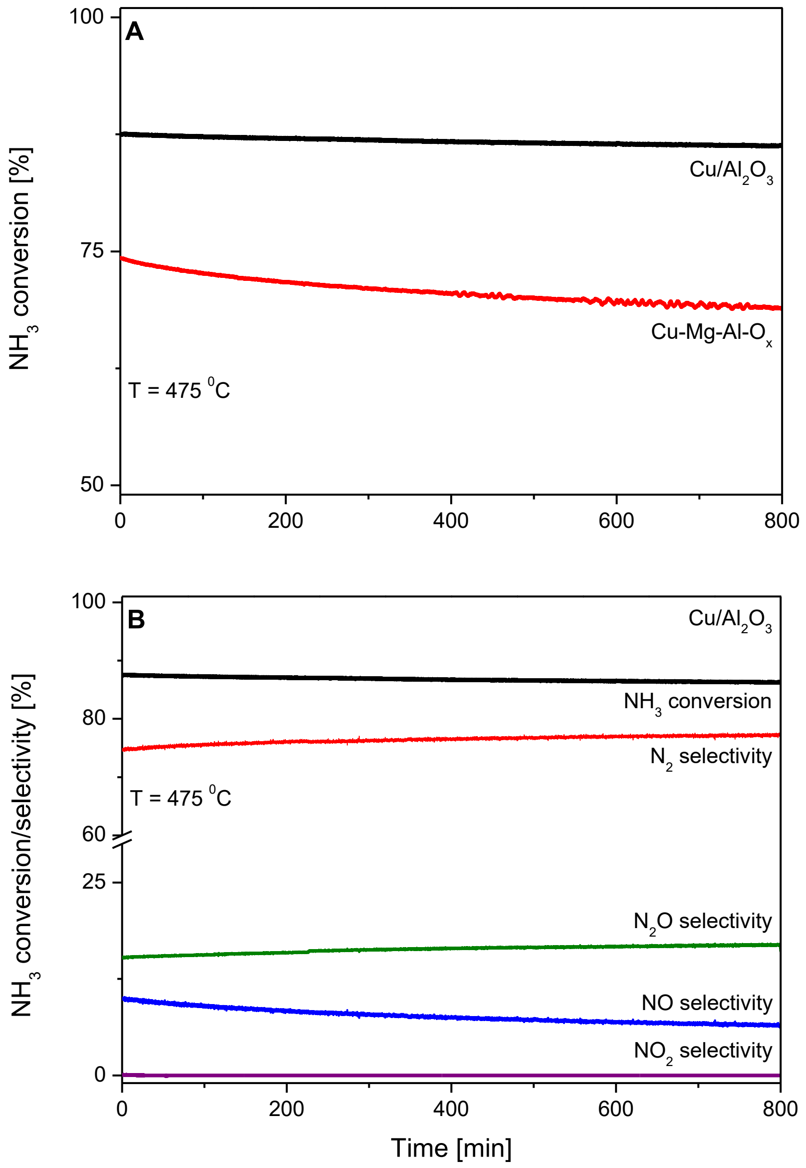

Fig. 3. Results of time-on-stream catalytic tests for NH_3-SCO performed over Cu/Al_2O_3 (A,B) and Cu-Mg-Al-O_x (A); experimental conditions: $[NH_3]$ = 0.5 vol.%, $[O_2]$ = 2.5 vol.%, $[CO_2]$ = 10 vol.%, $[H_2O]$ = 5 vol.%, N_2 balance, linear heating rate of 5 K/min and WHSV = 137-140 L/h·g.

4. Conclusions

The activity and selectivity of Cu-Mg-Al-O_x and Cu/Al_2O_3 in the large-scale NH_3-SCO under $NH_3/O_2/N_2$ and $NH_3/O_2/CO_2/H_2O/N_2$ conditions were investigated and discussed. Our results revealed that different copper oxide species formed on Cu-Mg-Al-O_x (highly dispersed copper oxide species) and Cu/Al_2O_3 (bulk copper oxide species) clearly influence activity and selectivity in NH_3-SCO. The highly dispersed copper oxide species formed on Cu-Mg-Al-O_x and Cu/Al_2O_3 led to similar activity and N_2 selectivity under $NH_3/O_2/N_2$ conditions. Compared to Cu-Mg-Al-O_x, Cu/Al_2O_3 exhibited higher activity under $NH_3/O_2/CO_2/H_2O/N_2$ conditions. Thus, CuO and $CuAl_2O_4$ formed on Cu/Al_2O_3 showed higher activity in NH_3-SCO under $NH_3/O_2/CO_2/H_2O/N_2$ conditions compared with highly dispersed CuO_x.

Acknowledgement

Funded by the Excellence Initiative of the German federal and state governments in the frame of the Center for Automotive Catalytic Systems Aachen (ACA) at RWTH Aachen University. AMB thanks EPSRC for funding. The authors acknowledge the Diamond Light Source (project SP14834) for provision of beamtime on the beamlines B18, and Diego Gianolio and Miren Agote for assistance in performing the XAFS measurements.

References

[1] M. Jabłońska, R. Palkovits, Copper based catalysts for the selective ammonia oxidation into nitrogen and water vapour-Recent trends and open challenges, Appl. Catal. B Environ. 181 (2016) 332–351.

[2] L. Chmielarz, M. Jabłońska, Advances in selective catalytic oxidation of ammonia to dinitrogen: a review, RSC Adv. 5 (2015) 43408–43431.

[3] L. Chmielarz, P. Kuśtrowski, A. Rafalska-Łasocha, D. Majda, R. Dziembaj, Catalytic activity of Co-Mg-Al, Cu-Mg-Al and Cu-Co-Mg-Al mixed oxides derived from hydrotalcites in SCR of NO with ammonia, Appl. Catal. B Environ. 35 (2002) 195–210.

[4] M. Jabłońska, M. Nocuń, K. Gołąbek, R. Palkovits, Effect of preparation procedures on catalytic activity and selectivity of copper-based mixed oxides in selective catalytic oxidation of ammonia into nitrogen and water vapour, Appl. Surf. Sci. 423 (2017) 498–508.

[5] L. Chmielarz, P. Kuśtrowski, A. Rafalska-Łasocha, R. Dziembaj, Selective oxidation of ammonia to nitrogen on transition metal containing mixed metal oxides, Appl. Catal. B Environ. 58 (2005) 235–244.

[6] L. Chmielarz, M. Jabłońska, A. Strumiński, Z. Piwowarska, A. Węgrzyn, S. Witkowski, M. Michalik, Selective catalytic oxidation of ammonia to nitrogen over Mg-Al, Cu-Mg-Al and Fe-Mg-Al mixed metal oxides doped with noble metals, Appl. Catal. B Environ. 130–131 (2013) 152–162.

[7] L. Gang, J. van Grondelle, B.G. Anderson, R.A. van Santen, Selective low temperature NH_3 oxidation to N_2 on copper-based catalysts, J. Catal. 186 (1999) 100–109.

[8] L. Gang, B.G. Anderson, J. van Grondelle, R.A. van Santen, NH_3 oxidation to nitrogen and water at low temperatures using supported transition metal catalysts, Catal. Today. 61 (2000) 179–185.

[90] C. Liang, X. Li, Z. Qu, M. Tade, S. Liu, The role of copper species on Cu/γ-Al_2O_3 catalysts for NH_3-SCO reaction, Appl. Surf. Sci. 258 (2012) 3738–3743.

[10] M. Newville, IFEFFIT: interactive XAFS analysis and FEFF fitting, J. Synchrotron Radiat. 8 (2001) 322–324.

[11] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Radiat. 12 (2005) 537–541.

[12] W. Wang, Y. Zhan, G. Wang, One-step, solid-state reaction to the synthesis of copper oxide nanorods in the presence of a suitable surfactant, Chem. Commun. (2001) 727–728.

[13] H. Wan, D. Li, Y. Dai, Y. Hu, B. Liu, L. Dong, Catalytic behaviors of CuO supported on Mn_2O_3 modified γ-Al_2O_3 for NO reduction by CO, J. Mol. Catal. A Chem. 332 (2010) 32–44.

[14] D. Worch, W. Suprun, R. Gläser, Fe- and Cu-oxides supported on γ-Al_2O_3 as catalysts for the selective catalytic reduction of NO with ethanol. Part I: catalyst preparation, characterization, and activity, Chem. Pap. 68 (2014) 1228–1239.

[15] S. Bai, Q. Dai, X. Chu, X. Wang, Dehydrochlorination of 1, 2-dichloroethane over Ba-modified Al_2O_3 catalysts, RSC Adv. 6 (2016) 52564–52574.

[16] M. Jabłońska, L. Chmielarz, A. Węgrzyn, K. Guzik, Z. Piwowarska, S. Witkowski, R.I. Walton, P.W. Dunne, F. Kovanda, Thermal transformations of Cu-Mg-(Zn)-Al(Fe) hydrotalcite-like materials into metal oxide systems and their catalytic activity in selective oxidation of ammonia to dinitrogen, J. Therm. Anal. Calorim. 114 (2013) 731–747.

[17] L. Jin, M. He, J. Lu, M. Luo, P. Fang, Y. Xie, Comparative Study of CuO Species on CuO/Al_2O_3,

CuO/CeO_2-Al_2O_3 and CuO/La_2O-Al_2O_3 catalysts for CO oxidation, Chinese J. Chem. Phys. 20 (2007).

[18] K. Shimizu, H. Maeshima, H. Yoshida, A. Satsuma, T. Hattori, Ligand field effect on the chemical shift in XANES spectra of Cu (II) compounds, Phys. Chem. Chem. Phys. 3 (2001) 862–866.

[19] J.H. Kwak, R. Tonkyn, D. Tran, D. Mei, S.J. Cho, L. Kovarik, J.H. Lee, C.H.F. Peden, J. Szanyi, Size-dependent catalytic performance of CuO on γ-Al_2O_3: NO reduction versus NH_3 oxidation, ACS Catal. 2 (2012) 1432–1440.

[20] M. Jabłońska, Andrew M. Beale, Marek Nocuń, R. Palkovits, Submitted.