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Nawel Jraba, Thabet Makhlouf, Gérard Delahay, Hassib Tounsi. Catalytic activity of Cu/ η -Al₂O₃ catalysts prepared from aluminum scraps in the NH₃-SCO and in the NH₃-SCR of NO. Environmental Science and Pollution Research, 2022, 29, pp.9053-9064. 10.1007/s11356-021-16206-1 . hal-03517496

HAL Id: hal-03517496

<https://hal.science/hal-03517496>

Submitted on 7 Jan 2022

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Catalytic activity of Cu/ η -Al₂O₃ catalysts prepared from aluminum scraps in the NH₃-SCO and in the NH₃-SCR of NO

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[‡]This paper is dedicated to the memory of our dear colleague, Prof. Thabet Makhoulf, who passed away in March 19, 2020.

Abstract

Copper loaded η -alumina catalysts with different copper contents were prepared by impregnation/evaporation method. The catalysts were characterized by XRD, FTIR, BET, UV-vis, H₂-TPR and evaluated, for the first time, in the selective catalytic reduction of NO by NH₃ and in the selective catalytic oxidation of NH₃. The characterization techniques showed that the impregnation/evaporation method permits to obtain highly dispersed copper oxide species on the η -alumina surface when low amount of copper is used (1wt. % and 2 wt.%). The wet impregnation method made it possible to reach a well dispersion of the copper species on the surface of the alumina for the low copper contents Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃. The latter justifies the similar behavior of Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ in the selective catalytic oxidation of NH₃ where these catalysts exhibit a conversion of NH₃ to N₂ of the order of 100% at T> 500 °C.

Keywords: Cu/ η -Al₂O₃; NH₃-SCR; NH₃-SCO; H₂-TPR; TEM

1 Introduction

The selective catalytic reduction (SCR) of NO by ammonia in the presence of excess oxygen is considered a mature technology for the removal of NO from stationary sources (Forzatti, 2001; Usberti et al. 2015). Moreover, this technology has been adapted for the modern diesel exhaust after treatment system using urea as the ammonia precursor (urea-SCR) (Goldbach et al., 2017; Jung et al., 2017; Kröcher, 2018; Nova and Tronconi, 2014; Piumetti et al., 2015; Yuan et al., 2015). This system contains besides the urea delivery device, a catalyst for the selective catalytic reduction of NO with NH₃ (NH₃-SCR) combined with an ammonia slip catalyst (ASC) for the selective catalytic oxidation of ammonia (NH₃-SCO) (Piumetti et al., 2015; Walker, 2016).

Vanadium-based catalysts (V-catalysts) V₂O₅-WO₃/TiO₂ or V₂O₅-MoO₃/TiO₂ are widely employed in stationary applications since the 1970s (Lai and Wachs, 2018). However, the major drawbacks bounded to the toxicity of vanadium and its weaker activity at low temperature limit the utilization of V-catalysts in automotive applications. Besides, some country regulations such as USA forbid the use of V-catalysts for automotive applications. Therefore, Cu/Fe-exchanged zeolites have been reported as alternative to vanadium-based catalysts because they are active and N₂ selective for the NH₃-SCR (Boron et al., 2019; Villamaina et al., 2019; Xin et al., 2018) and for the NH₃-SCO (Jablonska, 2020). Among all the zeolite-catalysts, Cu/Fe-ZSM-5 and Fe/Cu-BEA are the most extensively investigated in the past 30 years (Hamoud et al., 2019; Villamaina et al., 2019; Xin et al., 2018). Copper-based zeolites are usually more active in the low-temperature (<350°C) range while iron-based zeolites are more active at higher temperatures (>350°C). Small-pore zeolite Cu-SSZ-13 has received great attention due to its higher activity and selectivity at low temperatures and improved hydrothermal stability for diesel vehicles. (Gao and Szanyi, 2018; Lambert, 2019; Shibata et al., 2019)

On the other hand, noble metals (Pt, Pd, and Rh) supported on metal oxides have been studied for the diesel exhaust after treatment system. Common metal oxides such as Al₂O₃, SiO₂, CeO₂, TiO₂, and ZrO₂ are used as support materials for the diesel oxidation catalyst (Jablonska, 2015;

53 Sun et al., 2019). Nevertheless, γ -Al₂O₃ due to its high surface area (100–200 m²/g) and its good
 54 thermal stability is preferred to all other metal oxides (Kong et al., 2020; Panahi and Delahay,
 55 2017). For instance, Pt- γ -Al₂O₃ is used in the diesel oxidation catalyst (DOC) and ammonia slip
 56 catalyst (ASC) (svintsitskiy et al., 2020). The DOC oxidizes CO, unburnt hydrocarbons and NO
 57 in the exhaust gas to CO₂, H₂O and NO₂, respectively. The ASC removed the excess of NH₃ by
 58 selective catalytic oxidation (SCO) with oxygen to N₂ and H₂O. Pt- γ -Al₂O₃ catalyst is considered
 59 to be the most active for ammonia oxidation below 300 °C than the other noble metals (Pd, and
 60 Rh). However, Pt- γ -Al₂O₃ catalyst has high selectivity towards N₂O and NO over 300°C (Hansen
 61 et al. 2017). The drawbacks of noble-metal catalysts motivate the vehicle manufacturers to reduce
 62 their content or substitute them with cheaper Mn/Cu-based oxides catalysts (Damma et al., 2019).
 63 Cu based systems are discussed more comprehensively in the review of (Jablonska and Palkovits,
 64 2016). Among Cu based systems, CuO/Al₂O₃ catalyst has been proposed to substitute the noble
 65 metal-based emission control catalysts in the NH₃-SCR (Jeong et al., 1999; Kwak et al., 2012;
 66 Xie et al., 2004) and NH₃-SCO (Gang et al., 1999; Jablonska et al., 2018; Jablonska, 2015;
 67 Strom et al., 2018). In the early research of (Il'chenko and Ivanovna 1976), CuO was found as
 68 one of the most efficient oxide in selective ammonia oxidation into nitrogen and water vapour.
 69 Further studies over preoxidised polycrystalline copper foil proved that CuO is an active phase
 70 for NH₃-SCO (Mayer et al. 2003). However, due to unsatisfying selectivity to N₂, further studies
 71 concerning ammonia oxidation were carried out over CuO supported e.g. on Al₂O₃ (Jones et al.,
 72 2005). It should be mentioned that all cited studies have used γ -Al₂O₃ to support copper oxide. To
 73 our best knowledge, η -Al₂O₃ has never been employed as support for the preparation of
 74 CuO/Al₂O₃ catalysts for the NH₃-SCR of NO and for the NH₃-SCO. Gang et al., 1999 studied
 75 supported CuO/ γ -Al₂O₃ catalysts containing 5, 10 and 15 wt.% of copper. They found that the
 76 best catalytic results in the NH₃-SCO were obtained for the sample loaded with 10 wt.% of Cu
 77 (90% of NH₃ conversion with 97% selectivity to N₂ at 300°C). This effect was explained by the

78 formation of the surface CuAl_2O_4 -like species, active in NH_3 -SCO, in the catalyst containing 10
79 wt.% of copper. Liang et al., 2012 obtained similar results for $\text{Cu}(10\%)/\gamma\text{-Al}_2\text{O}_3$ catalysts
80 prepared by different copper precursors (nitrate, acetate and sulfate). They showed that a mixture
81 of CuO and CuAl_2O_4 species is formed on the various $\text{Cu}(10\%)/\gamma\text{-Al}_2\text{O}_3$ catalysts.

82 In our previous work (Jraba et al., 2018), we reported the preparation of $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$
83 Al_2O_3 with high surface areas using aluminum chips collected from metal manufacturing industry
84 as starting materials. $\eta\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ were obtained by calcination at 500 °C of bayerite ($\alpha\text{-Al}(\text{OH})_3$) and pseudo-boehmite, respectively. $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ are considered to be the most
85 important among other alumina's due to their high specific surface area (200–500 m^2/g) and acid-
86 base properties. The two alumina polytypes $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ have the same non-
87 stoichiometric spinel structure. $\eta\text{-Al}_2\text{O}_3$ has a higher population of stronger Lewis acid sites and a
88 slightly higher activity than $\gamma\text{-Al}_2\text{O}_3$ as an acid catalyst (Jraba et al., 2018). On one hand, $\gamma\text{-Al}_2\text{O}_3$
89 counts for the most important industrial applications as adsorbents, catalysts and catalyst supports
90 but on the other hand the application of $\eta\text{-Al}_2\text{O}_3$ is rarely reported (Peintinger et al., 2014). The
91 literature showed that $\eta\text{-Al}_2\text{O}_3$ is mostly used as catalyst in the dehydration of methanol to
92 Dimethyl Ether (DME) (Osman et al., 2017; Osman et al., 2018; Hoyong et al., 2017). Osman et
93 al., (2017) showed that loading $\eta\text{-Al}_2\text{O}_3$ with 10 wt.% of silver enhanced both surface Lewis
94 acidity and the hydrophobicity of the carrier. Accordingly, they obtained a catalyst with high
95 degree of activity and stability under steady-state conditions for the production of DME. Le et
96 al., (2017) investigated the methanation of CO and CO_2 using Ni catalysts supported by alumina
97 with different crystalline phases ($\alpha\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$, $\delta\text{-Al}_2\text{O}_3$, $\eta\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, and $\kappa\text{-Al}_2\text{O}_3$).
98 Among these catalysts, $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ showed the highest activity for both CO and CO_2 methanation.
99 Nikoofar et al., (2019) published a review which describes the various organic reactions
100 promoted by nano alumina catalysts ($\eta\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, $\theta\text{-Al}_2\text{O}_3$,...) relevant up to 2017.

102 Herein, $\text{CuO}/\eta\text{-Al}_2\text{O}_3$ catalysts were prepared by impregnation/evaporation method using
103 copper acetate as precursor. Then, these catalysts were tested for the first time in the reactions of

104 NH₃-SCR of NO and of NH₃-SCO in presence of water vapour. The prepared CuO/ η -Al₂O₃
105 catalysts were characterized by XRD, SEM, TEM, NH₃-TPD, H₂-TPR, UV-vis and N₂
106 adsorption-desorption techniques.

107

108 **2 Experimental**

109 **2.1 Preparation of the catalysts**

110 Five copper loaded η -alumina catalysts Cu(x)-Al₂O₃, with x theoretical copper loadings
111 were prepared by wet impregnation/evaporation technique. In a flask containing 100 mL of
112 distilled water, the desired amount of copper acetate Cu(CO₂CH₃)₂·H₂O (Sigma Aldrich, ACS
113 reagent, $\geq 98\%$) was added to obtain the copper contents of 1 wt.%, 2 wt.%, 3wt.%, 5 wt.% and
114 7.5 wt%. After the total dissolution of the copper acetate, a mass of 1.5 g of alumina η -Al₂O₃ was
115 added. The flask is then mounted on a rotary evaporator and the suspension is stirred for 4 hours
116 at 80 °C. After this step, the water was evaporated under reduced pressure for about 1 hour. Once
117 dry, the solid was placed in an oven at 80 °C overnight and finally calcined at 500 °C under an air
118 stream (2 °C/min) for 10 hours. In **figure 1** are reported the photographs of the prepared
119 catalysts.

Figure 1: Colors of the prepared catalysts after copper loading and calcination.

126 **2.2 Characterization of Cu(x)-Al₂O₃ catalysts**

127 X-ray powder diffraction patterns were obtained using a D8 ADVANCE BRUKER 40 Kv
128 40 mA Detector Lynx eye Geometrie Bragg Brentano (ICGM MAES) using Cu K α (λ = 0.15418
129 nm) incident radiation. The diffractograms were recorded at room temperature (RT) between 4°
130 and 70 ° counted in 2 θ at a scan speed of 0.02°/s.

131 The textural properties, surface area and porosity of the support and the catalysts were
132 determined from nitrogen adsorption–desorption isotherms measured at -196 °C using the
133 “micrometrics Tristar Surface Area and Porosity analyzer”. The sample (approximately 100 mg)
134 was weighed exactly in a glass tube lined with an "insert" to reduce the void volume. Before all
135 measurements, the samples were treated under high vacuum overnight at 150 °C.

136 H₂-TPR profiles were carried out with an automated Micromeritics Autochem 2910
137 analyzer. Before H₂-TPR measurements, samples (50 mg) were pretreated in a quartz U-tube
138 reactor under 5%O₂/He flow (30 cm³/min) at 550 °C (10 °C/min) for 30 min and then cooled
139 under helium to 60 °C. The samples were then reduced from 60 °C to 800 °C (5 °C/min) under
140 3% H₂/Ar atmosphere (30 cm³/min). The reduction gas H₂/Ar, was passed after the reactor
141 through a freezing trap (propan-2-ol + liquid nitrogen) kept at -80°C to remove the formed water.
142 Hydrogen consumption was monitored continuously by a thermal conductivity detector.

143 The ammonia desorption programmed as a function of the temperature (NH₃-TPD) was
144 carried out using the same H₂-TPR equipment. A mass of 30 mg of catalyst is pretreated at 450
145 °C for 30 min, under air flow (30 cm³/min), then saturated with ammonia at 100 °C and purged
146 with helium for 45 min. Following this adsorption, the physisorbed ammonia is removed by
147 leaving the sample for 2 h at 100 °C, under a helium flow rate of 30 cm³/min. Finally, the
148 temperature was raised to 550 °C (10 °C/min), under a helium flow rate of 30 cm³/min.

149 The Selective Catalytic Reduction of NO by NH₃ was carried out in a fixed-bed quartz
150 flow reactor operating at atmospheric pressure. The catalyst (24 mg) was activated in-situ at
151 550°C for 1 hour under a flow of O₂/He (20/80, v/v) and then cooled to 180°C. A feed mixture of

1000 ppm NO, 1000 ppm NH₃, 8% O₂ in He and 3.5% H₂O was then passed through the catalyst at a flow rate of 100 cm³/min (GHSV = 250000 cm³/g. h). The NH₃-SCR was carried out on programmed temperature from 180 °C to 500 °C with the heating rate of 5 °C/min.

For the Selective Catalytic Oxidation of ammonia (NH₃-SCO), the test was carried out on the catalysts already tested in the NH₃-SCR of NO. At 550 °C, the NO flow is cut off and the NH₃-SCO experiments were carried out adjusting He flow and by decreasing the temperature from 500 °C to 180 °C with the heating rate of 5 °C/ min.

The reactants and products were analysed by a quadruple mass spectrometer (Pfeiffer Omnistar) equipped with Channeltron and Faraday detectors (0–200 amu) following these characteristic masses: NO (30), N₂ (14, 28), N₂O (28, 30, 44), NH₃ (15, 17, 18), O₂ (16, 32) and H₂O (17, 18).

The percentages of NO (X_{NO}) and NH₃ (X_{NH3}) conversions were calculated on the basis of the differences in their concentrations measured before and after the catalyst bed.

$$X_{NO} = \frac{(NO)_0 - (NO)_T}{(NO)_0} \times 100$$

$$X_{NH3} = \frac{(NH_3)_0 - (NH_3)_T}{(NH_3)_0} \times 100$$

3 Results and discussion

3.1 Characterization of the catalysts

The XRD patterns of the support η-Al₂O₃, CuO (Sigma Aldrich, ACS reagent 99.0 %) and the prepared catalysts Cu(x)-Al₂O₃ are shown in **figure 2**. The characteristic peaks at angles in 2θ 19.5°, 37.5°, 39.7°, 45.8°, 60.8° and 67.2° correspond to η-Al₂O₃ phase having spinel lattice (JCPDS, No. 04-0875). The introduction of copper leads to the destruction of the structure of η-Al₂O₃ for the catalysts with higher copper contents Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ and Cu (7.5)-Al₂O₃.

175 These catalysts showed the characteristic peaks of CuO (JCPDS, No. 80-0076) at the angles in 20
 176 32.6°, 35.6°, 38.8° and 48.8°, 58.3° and 61.5° (Liang et al., 2012). On the other hand, for the
 177 Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ catalysts, there is a slight decrease in the intensity of the peaks of
 178 the support and particularly the peak at 19.5 ° and the absence of the diffraction peaks of CuO. It
 179 appears that the copper species present in the Cu(1)-Al₂O₃ and Cu (2)-Al₂O₃ catalysts are small
 180 and well dispersed on the surface of the support. Friedman et al., (1978) showed that the
 181 saturation of the CuO/ γ -Al₂O₃ catalyst surface a CuO monolayer occurs for a Cu content of about
 182 4-5% by weight for every 100 m²/g of alumina. Beyond this threshold, crystalline CuO was
 183 observed.

184
 185 **Figure 2:** XRD patterns of η -Al₂O₃, CuO and the prepared catalysts Cu(x)-Al₂O₃.

186 The SEM micrographs of the η -Al₂O₃ and the catalysts Cu(2)-Al₂O₃ and Cu(3)-Al₂O₃ are
 187 illustrated in **figure 3**. The SEM micrograph of alumina η -Al₂O₃ is made up small agglomerate
 188 particles. The introduction of copper leads to a change in the morphology of η -Al₂O₃ particles.
 189 For example, the Cu(2)-Al₂O₃ catalyst presents a sponge-like morphology, which reveals a high
 190 level of porosity. On the other hand, for the Cu(3)-Al₂O₃ catalyst, one can see two phases. The

191 first one is relative to sintered alumina particles and the second is related to CuO particles. It
192 appears that high levels of copper favor the sintering of alumina at lower temperatures than usual.
193 Sintering leads to the drop of the specific surface and the deterioration of the dispersion state of
194 the copper species on the surface of the support.

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Figure 3: SEM images of the support η -Al₂O₃ (A₁, A₂) and the catalysts Cu(2)-Al₂O₃ (B₁, B₂), Cu(3)-Al₂O₃ (C₁, C₂) with different magnifications.

268 The TEM images of the Cu(1)-Al₂O₃, Cu(2)-Al₂O₃ and Cu(3)-Al₂O₃ catalysts are reported
 269 in **figures 4**. For (Cu(1)-Al₂O₃ catalyst, we note that the copper particles are very small and well
 270 dispersed on the support η -Al₂O₃. The increase of the amount of copper leads to the increase of
 271 copper species size. For Cu(2)-Al₂O₃ catalyst, copper particles have size about 5-10 nm. Whereas
 272 for the Cu(3)-Al₂O₃ catalyst, we note the presence of black spherical particles exceeding 70 nm
 273 attributed to copper oxide CuO as shown by XRD.

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 275
 276 **Figure 4:** TEM images of Cu(1)-Al₂O₃ Cu(2)-Al₂O₃ and Cu(3)-Al₂O₃ catalysts.

277 Textural properties of the support η -Al₂O₃ and the prepared catalysts Cu(x)-Al₂O₃ are
 278 presented in **Table 1** and **figure 5**. It is noted that the specific surface area S_{BET} of the catalysts
 279 decrease after the wet impregnation/evaporation with copper acetate. For example, the specific
 280 surface area of the support ($S_{\text{BET}} = 417 \text{ m}^2/\text{g}$) decreases by 18% when 1% of copper was added

281 ($S_{\text{BET}} = 343 \text{ m}^2/\text{g}$) and 60% with the higher content of copper 7.5% ($S_{\text{BET}} = 169 \text{ m}^2/\text{g}$). Indeed, the
282 XRD technique has shown that Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ and Cu(7.5)-Al₂O₃ catalysts contain
283 large CuO particles which block the porous structure of η -Al₂O₃. On the other hand, for Cu(1)-
284 Al₂O₃ and Cu (2)-Al₂O₃ catalysts the copper species are well dispersed on the surface of the
285 support and the decrease of S_{BET} was moderate (only 16% for Cu(2)-Al₂O₃ catalyst). On the other
286 hand, we notice an increase in the pore volume up to a copper quantity of 2% wt. and then a
287 decrease beyond this value. Actually, the pore volume of the support which was $V_p = 0.295$
288 cm^3/g increases by about 30% ($V_p = 0.387 \text{ cm}^3/\text{g}$) for 1% Cu and 40% ($V_p = 0.411 \text{ cm}^3/\text{g}$) for 2%
289 Cu. This result could explain the morphology of η -Al₂O₃ and the formation of macropores as
290 shown by SEM technique. On the other hand, increasing the copper content from 3% to 7.5%
291 induces a reduction in the pore volumes of the catalysts due to the sintering of η -Al₂O₃ particles.

292 In **figure 5** are reported the N₂ adsorption-desorption isotherms of η -Al₂O₃ and Cu(x)-
293 Al₂O₃ catalysts. All adsorption isotherms are of type IV having hysteresis loops characteristics for
294 mesoporous solids (Petitto et al., 2013). Nevertheless, we note that the addition of copper to the
295 η -Al₂O₃ changes the hysteresis loop from H3 to H2(b) type. This behavior could reflect a change
296 in the pore shape and distribution with the introduction of copper. Indeed, H3 type hysteresis loop
297 indicates the presence of narrow slit-like pores particles with internal voids of irregular shape and
298 broad size distribution but the H2(b) hysteresis loop type shows a narrow distribution of pore
299 shape with a wide neck size distribution (Cychosz and Thommes, 2018). Likewise, when the
300 amount of copper increases there is a decrease in the adsorbed volume at low relative pressure
301 (P/P°), indicating the decrease in microporosity and the increase in mesoporosity.

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Table 1: Textural parameters of the prepared catalysts Cu(x)-Al₂O₃

Sample	S _{BET} (m ² /g)	BJH Pore	BJH pore
		volume (cm ³ /g)	diameter (nm)
η-Al ₂ O ₃	417	0.295	4.50
Cu(1)-Al ₂ O ₃	343	0.387	4.79
Cu(2)-Al ₂ O ₃	351	0.411	4.85
Cu(3)-Al ₂ O ₃	226	0.319	4.27
Cu(5)-Al ₂ O ₃	229	0.229	4.67
Cu(7.5)-Al ₂ O ₃	169	0.165	4.69

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Figure 5: Adsorption–desorption isotherms of η-Al₂O₃ and Cu(x)-Al₂O₃ catalysts.

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313 H₂-TPR profiles of the studied samples are shown in **figure 6**. It is observed that Cu(1)-Al₂O₃ and
314 Cu(2)-Al₂O₃ catalysts have similar reduction profiles. With the increase of copper amount there is
315 an increase of the intensity of the peaks. For Cu(2)-Al₂O₃ catalyst, the first peak around 130 °C
316 was attributed according to Yan et al., (1996) to the reduction of well dispersed CuO clusters on
317 the surface of the support. The second peak extending from 300 °C to 500 °C corresponds to the
318 reduction of highly dispersed Cu²⁺ cations in the structure of the alumina forming a surface spinel
319 CuAl₂O₄ type (Aguila et al., 2008; Il'chenko et al., 1976). On the other hand, when the copper
320 content was increased above 3 wt%, there are changes in the catalyst reduction profiles. Indeed,
321 Cu(3)-Al₂O₃, Cu(5)- Al₂O₃ and Cu(7.5)- Al₂O₃ profiles consist only of a broad peak extending
322 from 140–380°C. This reduction peak can be attributed to the reduction of CuO. In fact, Fierro et
323 al., 1994 reported that the supported CuO particle reduction temperature range extends from
324 200 to 300°C depending on the type of support. The analysis of the deconvolution (not shown) of
325 the reduction profiles of Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ and Cu(7.5)-Al₂O₃ was reported in Table 2.
326 For Cu(3)- Al₂O₃, for example, the central peak was deconvoluted into three peaks. The first is
327 located around 209°C with a relative surface area of around 11%, the second around 232°C
328 (15%) and the last around 274°C. The presence of these peaks could be due to CuO aggregates
329 with different sizes interacting differently with the support.

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Figure 6: H₂-TPR profiles of Cu(x)-Al₂O₃ catalysts.

Table 2: Results of H₂-TPR profiles deconvolution of Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ et Cu(7.5)-Al₂O₃ catalysts

Catalysts	Maximum reduction temperature T _m (°C)		
	Peak I	Peak II	Peak III
Cu(3)-Al₂O₃	209 (11%)	232 (15%)	274 (74%)
Cu(5)-Al₂O₃	—	220 (46%)	282 (54%)
Cu(7.5)-Al₂O₃	179 (11%)	222 (41%)	268 (48%)

The nature and environment of copper species present in the prepared catalysts have been studied by UV-vis spectroscopy. The UV-vis spectra of the carrier η -Al₂O₃ and the Cu(x)-Al₂O₃ catalysts are shown in **figure 7**. Generally, alumina is transparent in the UV-visible range.

340 Nevertheless, the absorption band around 370 nm of support that could be attributed to
 341 impurities. The spectra of the Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ catalysts have the same profile
 342 characterized by a broad absorption band that extends from 350 to 650 nm and centered around
 343 490 nm. This band could be attributed according to the literature (Buvaneswari, 2015; Chaudhary
 344 et al., 2018) to CuO or surface spinel type CuAl₂O₄ species. The catalysts Cu(3)-Al₂O₃, Cu(5)-
 345 Al₂O₃ and Cu(7.5)-Al₂O₃ exhibit characteristic spectra of well-crystallized CuO.

346
 347 **Figure 7:** UV-vis spectra of η -Al₂O₃ and Cu(x)-Al₂O₃ catalysts.

348 The NH₃-TPD profiles of η -Al₂O₃ and the prepared Cu(x)-Al₂O₃ catalysts are reported in
 349 **figure 8**. The support η -Al₂O₃ has broad ammonia desorption peak which extends from 110 °C to
 350 475 °C with a maximum at around 180 °C. The catalysts Cu(1)-Al₂O₃ and Cu (2)-Al₂O₃ show
 351 similar desorption profiles to the support but with a higher intensity of the peaks. For the other
 352 catalysts Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ and Cu(7.5)-Al₂O₃, a peak around 300 °C is observed which
 353 increases in intensity with the increase of the copper amounts. Generally, the temperature of
 354 desorbed ammonia is related to the strength of acidic sites in the samples. So, according to the
 355 maximum desorption temperature of ammonia (T_d) (Carre et al., 2010), there are three types of

356 acidic sites: *i*) weak acidic sites ($150 \leq T_d (^{\circ}\text{C}) \leq 250$), *ii*) average acidic sites ($250 < T_d (^{\circ}\text{C}) \leq$
 357 350) *iii*) strong acidic sites $T_d (^{\circ}\text{C}) > 350$. The NH_3 desorption at $T \leq 150 ^{\circ}\text{C}$ could be attributed to
 358 the NH_3 molecules weakly bound to the surface of the support which have not been evacuated at
 359 $100 ^{\circ}\text{C}$.

360
 361 **Figure 8:** NH_3 -TPD profiles of $\eta\text{-Al}_2\text{O}_3$ and $\text{Cu}(x)\text{-Al}_2\text{O}_3$ catalysts.

363 3.2 Evaluation of the catalytic activity of $\text{Cu}(x)\text{-Al}_2\text{O}_3$ catalysts

364 3.2.1 Selective Catalytic Reduction of NO by NH_3

365 The prepared catalysts were tested in the NH_3 -SCR of NO in the presence of an excess of
 366 oxygen and of water vapor according to reaction (I):

368 In **figures 9** and **10** are reported the NO conversion and NH_3 conversion of the prepared
 369 $\text{Cu}(x)\text{-Al}_2\text{O}_3$ catalysts in the NH_3 -SCR of NO. The NO conversion increased initially with
 370 increasing temperature, then reached a maximum and decreased. The evolution of the NO
 371 conversion passing through a maximum reflects the existence of a competition between two

reactions; the first concerning the reduction of NO and the second the oxidation of NH₃ by the oxygen present in the gas mixture. The competition between the two reactions is in favor of the oxidation of NH₃ at high temperatures which explains the decline in NO conversion. The decrease in the NO conversion is also accompanied with some formation of N₂O according to the two the following reaction:

It should be mentioned that Reaction III implied ammonium nitrate intermediate formed at temperature below 180°C and which starts to decompose above this temperature.

Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ catalysts have similar NO and NH₃ conversion profiles up to 475 °C. Beyond this temperature, the NO conversion decreases for the Cu(2)-Al₂O₃ catalyst, whereas it continues to increase for Cu(1)-Al₂O₃ up to 500 °C where a maximum NO conversion is about 91%. If we look to the conversion of NO to N₂, we notice that these two catalysts are almost selective towards N₂ (**figure 11**), due to the fact that the oxidation of NH₃ is less favored due to the better dispersion of copper. The others catalysts, (Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ and Cu(7.5)-Al₂O₃, display a volcano-shape curve of NO conversion as temperature increases while NH₃ conversion continue to increase with the temperature. For example (**Fig. 9**), the catalyst Cu(7.5)-Al₂O₃ has a maximum NO conversion of the order of 40% at 350 °C which is accompanied with small N₂O production. Therefore, the large drop in NO conversion on this catalyst above 350°C is due to the NH₃ oxidation into NO. Moreover, above 425°C, no NO reduction by ammonia occurs since NO concentration in the outlet gas is superior at the NO concentration in the inlet gas. The behavior of these catalysts could be related to the presence of large CuO particles. One can conclude that the two catalysts Cu(1)-Al₂O₃ and Cu (2)-Al₂O₃ are the most efficient in the reduction of NO by NH₃ in the presence of 3.5% of water vapor. Nevertheless, the Cu(1)-Al₂O₃ has a slightly better NO reduction behavior at high temperature. It has been found that the high

398 NO conversion of these two catalysts can be related to the presence of small CuO clusters
399 deposited on the surface of η -Al₂O₃ alumina and to CuAl₂O₄ surface spinel. We believe that small
400 CuO clusters deposited on the surface and easily reduced at low temperatures are responsible for
401 high temperature N₂ selectivity. In fact, according to the H₂-TPR results, the quantity of these
402 copper species is greater in the case of Cu(2)-Al₂O₃ the and Cu(1)-Al₂O₃ catalysts.

403 Kwak et al., 2012 investigated the NH₃-SCR of NO reaction under lean conditions on CuO- γ -
404 Al₂O₃ catalysts (350 ppm NO, 350 ppm NH₃, 14% O₂, 2% H₂O, and the balance N₂). They
405 showed that on 10 wt % CuO/ γ -Al₂O₃, the NO_x conversion is about 30% at 350°C and NH₃ reacts
406 primarily with oxygen to produce NO_x. However, on a 0.5 wt CuO/ γ Al₂O₃ catalyst, NH₃ reacts
407 with NO to form N₂ and the NO_x conversion to N₂ was almost 80% at 450 °C. Jeong et al., 1999;
408 carried out the NH₃-SCR of NO over sulphated CuO/ γ -Al₂O₃ in a fixed-bed reactor (400 ppm
409 NO, 400 ppm, 4% O₂ and the balanced N₂). They found that the optimum temperatures of the
410 fresh and sulphated CuO/ γ -Al₂O₃ in the NH₃-SCR of NO are 350 and 450 °C, respectively. Also,
411 NO conversion over the sulphated catalyst is somewhat higher than that over the fresh catalyst.
412 The amount of N₂O formation in NO reduction over the fresh and the bulk sulphated catalysts is
413 below 10% of NO in the feed.

Figure 9: NO conversion profiles of the prepared Cu(x)-Al₂O₃ catalysts in the NH₃-SCR of NO.

Figure 10: NH₃ conversion profiles of the prepared Cu(x)-Al₂O₃ catalysts in the NH₃-SCR of NO.

Figure 11: N₂O emission profiles during the NH₃-SCR of NO on Cu(x)-Al₂O₃ catalysts.

3.2.2 Selective catalytic Oxidation of NH₃

The oxidation profiles of NH₃ in the presence of 3.5% water vapor of the prepared catalysts Cu(x)-Al₂O₃ are presented in **figure 12**. The studied reaction is as follows (IV):

For all catalysts, it is noted that ammonia oxidation increases with the increase in temperature. For the Cu(3)-Al₂O₃, Cu (5)-Al₂O₃ and Cu(7.5)-Al₂O₃ catalysts, a gradual increase in NH₃ oxidation from 200 °C to 400 °C was recorded. But above 400 °C, the oxidation of NH₃ decreases slightly. On the other hand, for Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ a gradual slower increase of the NH₃ conversion was recorded from 250 °C to 550 °C. These two catalysts are much less active towards ammonia oxidation as we have already seen previously in NH₃-SCR of NO. The catalytic activity of the catalyst Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ in the oxidation of NH₃ could be related to the highly dispersed CuO on the support which are reduced at low temperature T = 130 °C. According to (Gang et al., 1999) complete oxidation of NH₃ was obtained at 350 °C on

445 Cu(10%)- γ -Al₂O₃ catalyst with N₂ selectivity of 90%. Liang et al., 2012 obtained similar results
446 for Cu(10%)- γ -Al₂O₃ catalysts prepared by different copper precursors (nitrate, acetate and
447 sulphate) and calcined at 500 °C and 600 °C. They showed that a mixture of CuO and CuAl₂O₄
448 species is formed on the various Cu(10%)- γ -Al₂O₃ catalysts. On the other hand, the dispersion and
449 the nature of the copper species have a significant influence on the activity of the catalysts.
450 Indeed, the highly dispersed CuO nanoparticles on the support are responsible for the high
451 activity of Cu(10%)- γ -Al₂O₃ catalysts. Lenihan and Curtin (2009) using lower levels of copper
452 (Cu(3.4%)/ γ -Al₂O₃) found conversions of the order of 100% in NH₃.

453 The nature of the copper precursor and the method of preparation were found to be
454 determinants in the formation of active copper species in the NH₃-SCO. For example, a sulphate
455 precursor leads to the formation of CuAl₂O₄, whereas CuO of higher crystallinity is formed using
456 an acetate compared to a nitrate precursor (Jung et al., 2017). However, the nature of the active
457 species in NH₃- SCO has not been fully verified yet. Gang et al., 2000 claimed that the surface
458 CuAl₂O₄ spinel phase is responsible for the higher catalytic activity relative to CuO. A study
459 conducted by Liang et al., 2012 has shown that a mixture of CuO and CuAl₂O₄ phases is formed
460 on the various Cu (10%) - γ -Al₂O₃ catalysts. On the other hand, the dispersion and the nature of
461 the copper species have a significant influence on the activity of the catalysts. Indeed, CuO
462 nanoparticles highly dispersed on the support and easily reduced at low temperature are
463 responsible for the high conversion of NH₃.

Figure 12: NH₃ oxidation profiles of Cu(x)-Al₂O₃ catalyst.

Figures 13, 14 and figure 15 presents the selectivity profiles towards NO, N₂O and N₂ respectively obtained in the NH₃-SCO reaction. N₂ is the desired gas product, while NO and N₂O are undesired by-products. The Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ catalysts have N₂ selectivity close to 95% over the temperature range of 200-400 °C. Additionally, the transition metal oxides have been widely studied in the scientific literature (Jablonska and Palkovits, 2016; Sazonova et al., 1996). This type of catalysts showed higher selectivity to N₂, however, they need significantly higher operation temperatures as high as 300–500 °C than noble metal catalysts. For the three others Cu(x)-Al₂O₃, selectivities towards N₂ are much lower. At 550 °C (**Figure 16**), 48%, 40%, 30% of selectivity towards NO were measured for (Cu(7.5)-Al₂O₃, Cu(5)-Al₂O₃, Cu(3)-Al₂O₃) respectively.

The NH₃-SCO method is an effective method for oxidizing NH₃ into N₂. The overall selectivity into N₂ was close to 100% for Cu(1)-Al₂O₃ and above 95% for Cu(2)-Al₂O₃ over all the temperature while for the other three catalysts, N₂ selectivity remains as high as 95% only at

479 temperature below 350°C, as reported by (Jabłońska et al., 2017; 2018). Highly dispersed CuOx
 480 favor moderate activity but N₂ selectivity up to 550 °C in NH₃-SCO (Chmielarz et al., 2005). In a
 481 similar work (Dong et al. 2013) showed that nitrogen gas was primarily formed by the direct
 482 dissociation of the NO produced by the oxidation of the adsorbed NH₃ (Dong et al., 2014).

483
 484 **Figure 13:** NO selectivity profiles obtained for NH₃-SCO performed over Cu(x)-Al₂O₃ catalysts.
 485

486

487 **Figure 14:** N₂O selectivity profiles obtained for NH₃-SCO performed over Cu(x)-Al₂O₃ catalysts.

488

489 **Figure 15:** N₂ selectivity profiles obtained for NH₃-SCO performed over Cu(x)-Al₂O₃ catalysts.

490

491

492 **4 Conclusion**

493 Copper-supported η -Al₂O₃ catalysts have prepared and tested in the selective catalytic
494 reduction of NO by NH₃ and in the selective catalytic oxidation of NH₃. The
495 impregnation/evaporation method has successfully dispersed the copper species on the surface of
496 the alumina for the low copper contents; Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ catalysts. The XRD
497 showed that the introduction of an additional amount of copper leads to the destruction of the
498 alumina structure when copper content exceeded 3% wt.%. The Cu(3)-Al₂O₃, Cu(5)-Al₂O₃ and
499 Cu (7.5) -Al₂O₃ catalysts contain mainly large CuO particles. Cu(2)-Al₂O₃ and Cu(1)-Al₂O₃
500 catalysts have interesting NO conversion to N₂ in the NH₃-SCR of NO. This activity could be
501 related essentially to the small CuO clusters deposited on the alumina surface and CuAl₂O₄
502 species. For NH₃-SCO, the catalyst Cu(1)-Al₂O₃ and Cu(2)-Al₂O₃ exhibit similar behavior
503 resulting in the conversion of NH₃ to N₂ of about 100% at T > 500 ° C. This conversion could be
504 attributed to CuO nanoparticles highly dispersed on the support and easily reduced at low
505 temperature.

506 **Ethics approval and consent to participate** “Not applicable.

507 **Consent for publication** “Not applicable”.

508 **Competing interests** The authors declare that they have no known competing financial
509 interests or personal relationships that could have appeared to influence the work reported in this
510 paper.

511 **Availability of data and materials** “Not applicable”.

512 **Funding** “Not applicable”.

513 **Authors' contributions**

514 Nawel Jraba: analyzed the data and write the complete paper.

515 HassibTounsi, Thabet Makhlouf and Gerard Delahay: gave this idea of work.

516 All authors read and approved the final manuscript.

517

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