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Technical Note CRYOFRABR#002/2021: Activated-copper-coated alumina granules synthesis

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Detailed experimental studies of oxygen capture in the argon purification process using activated-copper on alumina and layered double hydroxide (LDH) were carried out, and the results were compared to the BASF commercial copper material Cu-0226 S performance. Here, we report the following main findings: i) the desired crystal structures for the studied materials were obtained after the synthesis process, ii) the use of the LDH structure promoted greater dispersion of the CuO phase when compared to BASF commercial catalyst, iii) alumina impregnated with copper demonstrated a similar result as the BASF sample for O_2 capture, and iv) among the three samples evaluated, the LHD sample demonstrated the best results regarding oxygen capturing performance becoming a promising structure for further studies.

INTRODUCTION

This technical note is part of the studies proposed in the CRADA No. FRA-2016-0017 Annex B for purification media.

The synthesis method choice is fundamental to control the final properties of the media material, such as pore size, specific surface area, and interaction strength between support and active phase. Among the main methods of preparing diluted copper-based media candidate materials, wet methods are the most used, with emphasis on the methods of wet impregnation, co-precipitation, and sol-gel.

Thus, we propose the use of the impregnation of Cu on Al_2O_3 by the sol-gel method, using copper salt and poly (ethylene oxide) polymer (PEO) as a dispersing agent and co-precipitation of layered double hydroxide (LDH) as an intermediate structure (Figure 1) to increase the dispersion of the active phase Cu^0. In this work, all catalysts have 10% w/w copper as nominal content. For comparison, BASF commercial copper material (Cu-0226 S) is used as a reference.

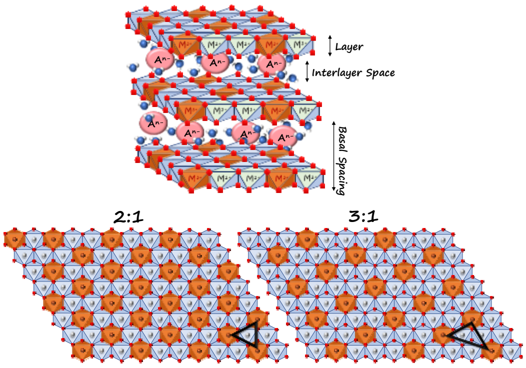

Figure 1: The idealized crystal structure of LDH with different M^{2+}:M^{3+} molar.

MATERIALS AND METHODS

LAYERED DOUBLE HYDROXIDE (LDH)

The LDH samples were prepared by a coprecipitation method at a constant pH value as follows: a solution containing $Cu(NO_3)_2\ 3H_2O$ (8.0 mmol), $Mg(Cl)_2\ 6H_2O$ (84.3 mmol), and $Al(Cl)_3\ 6H_2O$ (30.8 mmol) in water (250 mL) was added dropwise under vigorous stirring to a solution containing Na_2CO_3 (90.0 mmol) in water (1000 mL). A NaOH solution (2.0 mol L^{-1}) was added dropwise to keep the pH value constant at 10. After synthesis, the solid in suspension was

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washed with deionized water and dried at 70 °C. To prepare the calcined LDH sample (CLDH), it was heated at 500 °C for 2 h under ambient atmosphere[1].

$CuAl_2O_3$ PEO

Based on the work developed by Tokudome and collaborators [2], a meso/macroporous alumina was prepared using $Al(Cl)_3\ 6H_2O$. In this synthesis PEO (Mw = 100000 g mol^{-1}) and $Al(Cl)_3\ 6H_2O$ were dissolved in a mixture of deionized water and ethanol under stirring at room temperature. Then, propylene oxide (PO) was added to the system under agitation. The homogeneous sol formed after the PO addition was sealed at 40 °C for gelatinization and aging. Then they were dried and calcined at 700 °C in air. To perform the deposition, a solution containing the precursor ($Cu(NO_3)_2\ 3H_2O$) dissolved in water was used. Then, meso/macroporous Al_2O_3 was dispersed in water, and the two solutions were mixed under vigorous stirring, and then dried. The dry samples were calcined at 500 ºC with a synthetic airflow to decompose the salt and promote the deposition of the active phase over the entire surface of the support.

CHARACTERIZATION

The X-ray powder diffraction (XRD) data were obtained using a Rigaku Multiflex diffractometer operated in the range $5° < 2\theta < 80°$, with Cu Kα radiation (40 kV, 30 mA).

N_2 adsorption/desorption isotherms were carried out in a Quantachrome NOVA 1000e volumetric adsorption analyzer at -196 °C. First, the samples were outgassed under vacuum at 200 °C, and the N_2 isotherm was obtained by successive steps of adsorption and desorption of this gas. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method by using data of the adsorption branch of the isotherm in the relative pressure P/P_0 range of 0.05-0.2. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method.

Temperature-programmed reduction (TPR) analyses were performed in a Micromeritics Pulse ChemiSorb 2750 equipment. The hydrogen consumption was monitored by a thermal conductivity detector (TCD).

REDUCTION/OXIDATION CYCLES

Reproducibility tests of the materials in sequential reduction and oxidation cycles were performed. Samples with 100 mg of the materials were placed in a U-shaped quartz tube reactor and reduced under 10% H_2/Ar (v/v) mixture flowing at 25 mL min^{-1}, from room temperature to 310 °C at a heating rate of 10 °C min^{-1}. After the reduction, the sample oxidation was performed under a 5% O_2/Ar (v/v) mixture flowing at 20 mL min^{-1} for 30 min at room temperature and atmospheric pressure. Temperature Programmed Reduction (TPR) of the oxidized samples was performed to estimate the amount of copper oxidized. The hydrogen consumed (determined by the area under of TPR profile) was compared before and after the oxidation cycles for all studied samples.

RESULTS

In Figure 2, the XRD pattern of the LDH shows the presence of basal reflections (00ℓ), (003) e (006) [3,4], which are related to the lamellar stacking plane characteristic of LDH structure. For this material, the interlayer space (d) calculated from the Bragg equation is roughly 7.7 Å [1], which can be assigned to the intercalation of carbonate ions between the inorganic lamellae. The alumina XRD data (Figure 2 B) presented diffraction peaks corresponding to poorly crystallized γ-Al_2O_3 (2θ = 37,5°, 45,9° e 67,0° (JCPDS 04-0880)) [5,6] .

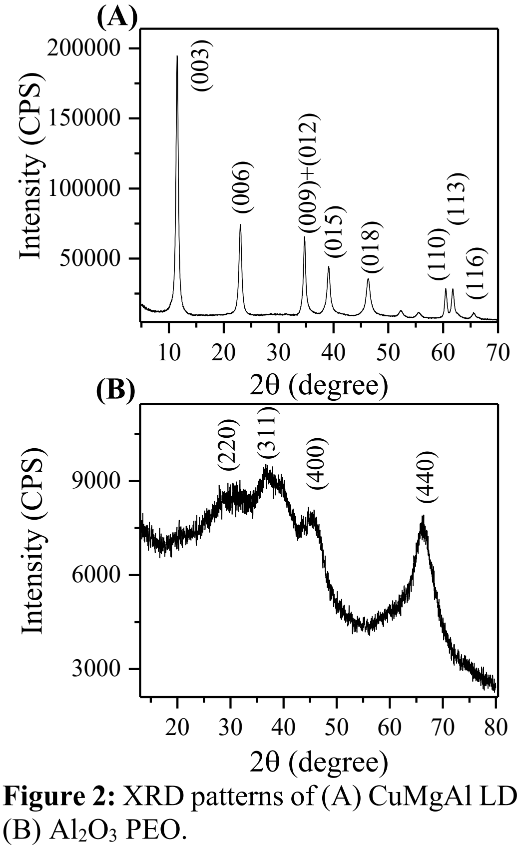

Figure 2: XRD patterns of (A) CuMgAl LDH and (B) Al_2O_3 PEO.

For calcined samples, the XRD analysis (Figure 3) showed the collapse of the layered structure due to the disappearance of the basal reflections and the typical formation of the defect periclase MgO structure (Mg(Al)O)[7]. For $CuAl_2O_3$ PEO, can be observed that the addition of 10 wt% of copper did not cause any significant change in the diffraction patterns of the poorly crystallized γ-Al_2O_3. Furthermore, in the XRD of CuO BASF, one can see that in addition to the relative peaks of the γ-Al_2O_3 phase, two peaks correspond to the CuO crystalline structure what can indicate less dispersion of the CuO phase. Thus the absence of XRD peaks related to the formation of a crystalline CuO phase in the CuMgAl LDH and $CuAl_2O_3$ PEO is a strong indication that the copper species were well dispersed on the support [8].

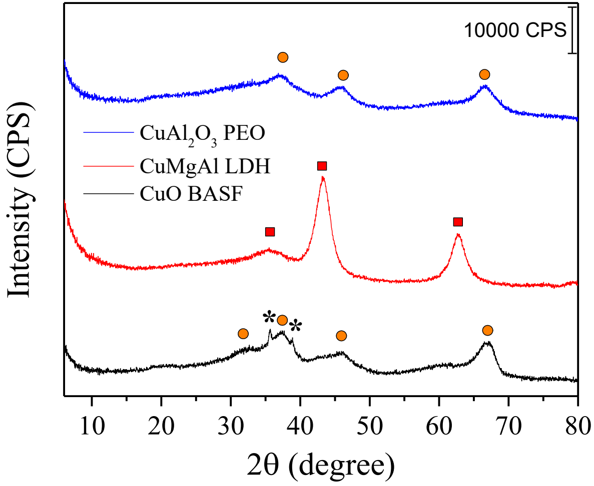

Figure 3: XRD patterns of CuO BASF, CuMgAl LDH, and $CuAl_2O_3$ PEO.

The study of the textural properties of the samples is of great importance since the accessibility of the oxygen to the active sites (Cu^0) is directly related to the specific surface and the pore size. Figure 4 shows the N_2 adsorption /desorption isotherms of the calcined samples. From these results, it is noted that the Cu BASF, Al_2O_3 PEO, and $CuAl_2O_3$ PEO samples have a similar shape in terms of the hysteresis loop between the adsorption/desorption branches, being classified as Type IV isotherms according to IUPAC, characteristic of mesoporous materials[9]. The N_2 adsorption/desorption isotherms of CuMgAl LDH is type III, according to the IUPAC classification [10], characterized by the absence of a plateau at relative pressure close to 1, evidencing the presence of macropores.

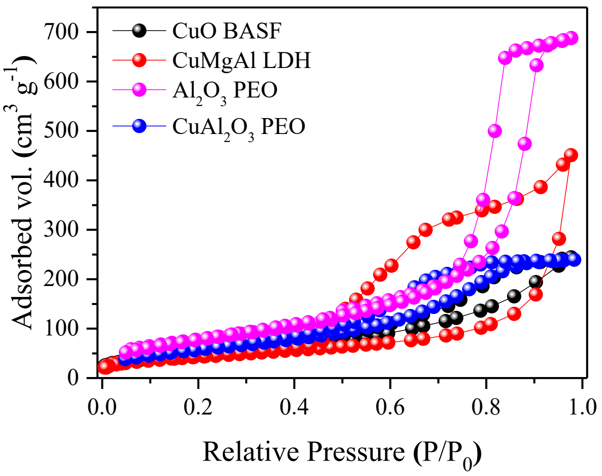

Figure 4: N_2 adsorption/desorption isotherms of CuO BASF, CuMgAl LDH, Al_2O_3 PEO, and $CuAl_2O_3$ PEO.

Table 1 shows the values of the textural properties of the investigated materials. These results show that all Cu-based samples have a close specific surface area and average pore sizes and that the addition of copper promoted a decrease in the surface area, pore size, and pore volume. The relative decrease in pore size and volume pore of the sample with the highest Cu-content, relative to the bare support, was related to partial blockage of the pores, as well as the collapse of the thin mesopore walls during the processes of impregnation and calcination [11].

Table 1: Surface area and porosity characteristics.

Sample	Specific surface ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore size (nm)
CuO BASF	166	0.39	3.5
CuMgAl LDH	152	0.92	3.8
Al_2O_3 PEO	286	1.12	10
$CuAl_2O_3$ PEO	200	0.38	5.4

To evaluate the O_2 capture capacity through the oxidation of the Cu^0 species ($2Cu^0 + O_2 \rightarrow 2CuO$), fresh samples were first reduced from 30 - 310 °C under 10% H_2/Ar (v/v) mixture. Then, the furnace was cooled to 30°C to perform the oxidation process under the 5% O_2/Ar (v/v) mixture for 30 min. After the oxidation process, a new reduction step ($CuO + H_2 \rightarrow Cu^0 + H_2O$) was performed to determine the amount of copper oxidized in relation to the fresh sample.

Figure 5 shows the % ratio between the area under the TPR profile of the sample after oxidation by the area under the TPR profile of the fresh sample. For this result, it is observed that after 3 oxidation cycles no deactivation occurs in any sample.

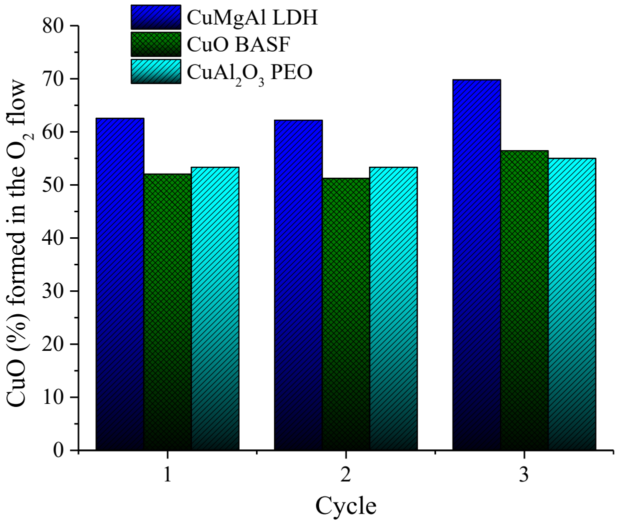

Figure 5. % of the area under TPR profiles after the oxidation cycle ((area after/area before) *100).

Besides, it is shown in figure 5 that the sample impregnated with copper prepared in the laboratory ($CuAl_2O_3$ PEO) has equivalent results to that commercial sample the BASF, in terms of O_2 capture efficiency, and that the CuMgAl LDH has the highest O_2 capture capacity. This enhanced performance found for LDH can be explained by the probable better dispersion of the Cu^0 particles between the two compared materials here since the dispersion of the LDH copper occurs at an atomic level in layers [3,11].

CONCLUSION

The results obtained so far by this work show that the CuMgAl LDH and $CuAl_2O_3$ PEO samples prepared by our research group have excellent structural characteristics such as good dispersion of the CuO phase, high porosity, and high O_2 capture capacity. By comparison with the commercial CuO BASF, it was observed that the sample $CuAl_2O_3$ PEO presented similar results regarding the capture of O_2 and that the CuMgAl LDH sample has the highest O_2 capture capacity among these evaluated materials.

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