

ZnO–CuO nanoparticles supported on activated carbon for biogas purification from H₂S at room temperature

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Abstract

Novel sorbents for reactive adsorption of H₂S from biogas at room temperature were prepared by dispersing Zn and Cu oxides nanoparticles onto a commercial activated carbon at fixed total metal loading (10%wt.) and Cu:Zn atomic ratios ranging from 0:1 to 1:1. The functionalized sorbents showed a significantly larger adsorption capacity with respect to the raw activated carbon, and a high utilization factor of the active phase increasing with Cu loading. This was associated to the high dispersion of the metal oxides and the positive interaction with the support. Temperature Programmed Desorption (TPD) of H₂S and SO₂ from saturated sorbents showed that H₂S adsorption was coupled with oxidation phenomena, leading to the formation of metal sulphates apart from metal sulphides and/or elemental sulphur.

Introduction

Biogas deriving from the anaerobic digestion of different biomasses and wastes is mainly composed of CH₄ (50–70%vol.) and CO₂ (30–45%vol.). It represents a valuable energy carrier, which can be used in combined heat and power generation units possibly with fuel cells systems, or further upgraded to biofuels [1]. H₂S is the most harmful and commonly occurring contaminant present in biogas [1], highly toxic even at low concentration, corrosive for engines, poisoning for catalysts in downstream fuel cells or fuel processors. The purification step represents one of the main operational costs of the whole process [2]. A lot of in-situ and ex-situ purification technologies have been proposed [1]. Adsorption has the advantage to couple high selectivity and capture efficiency to process ease. Among the commonly adopted sorbents, Activated Carbons (AC) have been proposed when the sulphur target exit concentration must be of few ppm, thanks to the AC large surface area and pore volume and to the presence of surface functional groups, which can also promote H₂S oxidation [3]. The impregnation of different porous supports with transition metal oxides, hydroxides, and carbonates,

in particular those of Zn, Fe and Cu, is widely used to produce highly performing H₂S sorbents for natural gas processing or, more in general, to reformate gas streams [4]. In particular, promising results were reported for the functionalization of mesoporous silica with a combination of ZnO–CuO, which determined significant synergistic effects in terms of H₂S adsorption capacity [3]. In this work, AC-supported ZnO–CuO sorbents were investigated for room temperature H₂S removal, exploring the effect of the Cu:Zn atomic ratio while keeping the total metal loading fixed at 10%wt.

Materials and Methods

ZnO and CuO oxides were dispersed on a commercial AC (Darco AC 20-40 by Norit) with particle size distribution in the 0.42–0.85 mm range. Five different sorbents were prepared by incipient wet impregnation with aqueous solutions of Zn(NO₃)₂·6H₂O and Cu(NO₃)₂·2.5H₂O (Sigma Aldrich) followed by drying at 120°C and calcination in N₂ flow at 250°C. The nominal total metal loading (as Zn+Cu) was set to 10%wt.. The sorbents were labelled as Cu_xZn_{1-x}/AC, where x represented the atomic fraction of Cu with respect to Cu+Zn and was set to 0, 0.05, 0.1, 0.25 and 0.5, respectively. The actual metal content in the sorbents was determined by ICP spectrometry using an Agilent 7500 ICP-MS instrument. The total S content in spent sorbents was determined with a LECO SC 144-DR analyzer. SEM analysis was carried out with a FEI Inspect instrument equipped with an EDX probe. The textural properties of the sorbents were determined by N₂ adsorption at 77 K with a Quantachrome Autosorb 1-C apparatus (BET, BJH and DA methods employed for specific surface area, mesopores and micropores evaluation, respectively). XRD analysis was performed with a Bruker D2 Phaser diffractometer. H₂S dynamic adsorption tests were carried out at 30°C in a fixed-bed reactor using 5.0 g and 2.5 g of raw and functionalized sorbents, respectively. The H₂S concentration (whose initial value may range from 50 to 3000 ppmv in N₂) was measured by a continuous GAS 3240 R BIOGAS gas analyzer (GEIT Europe). H₂S adsorption capacity at saturation, ω_s [mmol g⁻¹], was determined through a material balance on H₂S over the adsorption column, leading to the following expression:

$$\omega_s = \frac{QC_{H_2S}^{in}\rho_{H_2S}}{M_{H_2S}m} \int_0^{t^*} \left(1 - \frac{C_{H_2S}^{out}(t)}{C_{H_2S}^{in}}\right) dt \quad (1)$$

where Q [L s⁻¹] is the total gas flow rate, C_{H₂S}ⁱⁿ and C_{H₂S}^{out} are the H₂S volumetric fractions in the gas feed and at the bed outlet, respectively; ρ_{H₂S} [mg L⁻¹] is the H₂S density while M_{H₂S} its molecular weight; m [g] is the sorbent dose and t^{*} [s] the time required to reach again, during the adsorption test, 99% of the initial H₂S inlet concentration. TPD tests were carried out to provide insights into H₂S adsorption/desorption mechanisms while evaluating the thermal regenerability of the sorbents. To this end, a known sorbent dose (20–100 mg) was heated at 10°C

min^{-1} up to 620°C under N₂ flow (20 SL h⁻¹). Gas analysis was performed by means of a continuous analyzer (ABB Optima Advance Limas 11 UV), for the simultaneous measurement of H₂S (0–300 ppmv) and SO₂ (0–100 ppmv) concentrations.

Results and Discussion

The Cu+Zn content on sorbents is in the range 10.0±0.5%wt., in good agreement with the target loading as well as the Cu/Zn ratio, which almost corresponds to the nominal value for all the sorbents, thus confirming a good control and repeatability of the preparation procedure. A uniform distribution of Zn throughout the sorbent particle was observed by SEM-EDX, whereas a moderate migration of Cu towards AC particle surface was observed, likely promoted by dehydration of Cu nitrate taking place simultaneously with the decomposition at around 100°C, in contrast to the decomposition of Zn nitrate, which starts above 175°C, i.e. when Cu nitrate dehydration is over [5]. All the Cu_xZn_{1-x}/AC sorbents show a decrease in surface area (520–570 m² g⁻¹) with respect to the raw support (640 m² g⁻¹), which largely corresponded to what expected from the weight increase due to the deposition of the active phase (Table 1). The pore size distribution of the sorbents does not change with respect to the raw support, regardless of the Cu/Zn ratio, indicating a high dispersion of the active phase and no significant occlusion or pores collapse/widening during the impregnation step and the following thermal treatment. Small and broad peaks of ZnO and CuO appear in the XRD patterns of Cu_xZn_{1-x}/AC sorbents (not reported), suggesting nanometric dimensions for the two oxides. From the analysis of the Cu_{0.5}Zn_{0.5}/AC XRD spectrum, after saturation with H₂S the peaks of ZnO completely disappeared, while a small residual CuO signal remained. No formation of new crystalline phases detectable by XRD, such as ZnS and CuS or the corresponding metal sulphates, was detected. The breakthrough curves for Cu_xZn_{1-x}/AC sorbents and their parent support are reported in Figure 1a for an inlet H₂S concentration of 3000 ppmv. From these curves, the dynamic data and the corresponding adsorption capacities (summarized in Table 1) were determined according to Eq. (1).

Table 1. Main parameters for the sorbent under investigation.

Sorbent	BET surface area [m ² g ⁻¹]	t _{br} [s]	ω _s [mmol g ⁻¹]	η [mol mol ⁻¹] ^b
Darco AC	641	198 ^a	0.19	—
Cu ₀ Zn _{1.0} /AC	558	444	0.97	0.51
Cu _{0.05} Zn _{0.95} /AC	520	559	1.28	0.67
Cu _{0.1} Zn _{0.9} /AC	549	597	1.31	0.69
Cu _{0.25} Zn _{0.75} /AC	555	655	1.36	0.71
Cu _{0.5} Zn _{0.5} /AC	570	674	1.46	0.76

^a determined with 5 g sorbent mass.

^b calculated subtracting the contribution of the AC support.

$\text{Cu}_x\text{Zn}_{1-x}/\text{AC}$ sorbents showed a significantly longer breakpoint time t_{br} (for which the ratio of H_2S concentration at the bed outlet relative to that in the feed is 0.05, see Table 1) than AC does (200 s), albeit the tests were carried out with half sorbent mass. The breakpoint time increased monotonically (445–675 s) with the Cu content in the series $\text{Cu}_x\text{Zn}_{1-x}/\text{AC}$. Moreover, the H_2S adsorption capacity ω_s increased along with the Cu content, being 5–7.5 times larger than that for raw AC (Table 1). This effect could be attributed to the faster sulphidation/sulphation rates of CuO with respect to ZnO . To better understand and compare the capture

$$\underline{\eta = \frac{n_{\text{Cu}+\text{Zn}}}{n_{\text{H}_2\text{S}}}}$$

performances, the active phase utilization efficiency $\eta_{\text{Cu}+\text{Zn}}$, corresponding to the molar ratio between sulphur adsorbed as H_2S and $\text{Cu}+\text{Zn}$ content in the sorbent, was estimated (Table 1). It was $\eta > 50\%$ for the sorbent containing only ZnO , and even a small Zn substitution with Cu (5%) enhanced η above 65%, until reaching ca. 76% for $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$. Hence, the effectiveness of dispersing the metal oxides on the surface of the AC support was confirmed. Moreover, the significant impact of Cu addition, even at low content, suggests that copper may contrast/reduce the diffusional limitations responsible for the limited utilization of ZnO and related to the formation of a compact overlayer of ZnS , thus hindering the accessibility to the underlying ZnO core. Considering its highest H_2S adsorption capacity, the $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$ sorbent was selected for further dynamic tests at several inlet concentrations (50–3000 ppmv), to obtain a H_2S adsorption isotherm at 30°C and 1 bar (Figure 1b). For the sake of comparison, the same experimental tests were carried out also on the raw AC. In the range of H_2S concentration investigated, $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$ showed significantly higher adsorption capacity than the raw support: for both the sorbents, ω_s increased slightly with the H_2S equilibrium concentration C (Figure 1b), and an almost asymptotic value was reached at the largest H_2S concentration. Moreover, for $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$, a high adsorption capacity (around 1 mmol g⁻¹) was already achieved in correspondence of rather low H_2S concentrations (50–200 ppmv), as expected for adsorption phenomena involving a predominant contribution of chemical reactions.

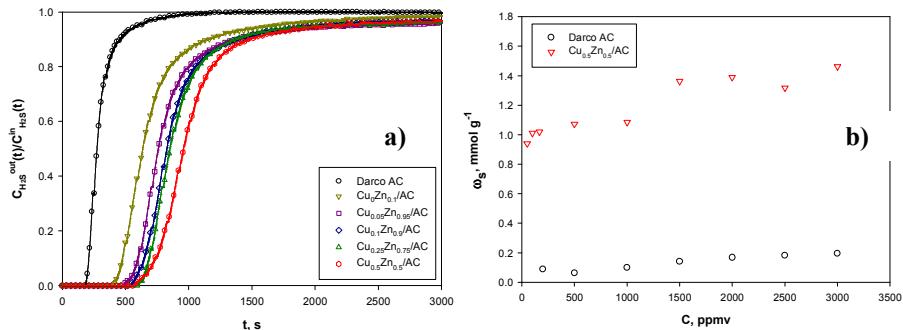


Figure 1. a) H_2S breakthrough curves for $\text{Cu}_x\text{Zn}_{1-x}/\text{AC}$ sorbents (mass: 2.5 g) and the raw AC support (mass: 5 g). Inlet $[\text{H}_2\text{S}] = 3000 \text{ ppmv}$; b) H_2S adsorption

isotherms on the raw AC support and $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$ sorbent. Experiments carried out at 30°C and 1 bar.

The desorption of H_2S during TPD tests was negligible for all the sorbents. The TPD profile for saturated $\text{Cu}_0\text{Zn}_{1.0}/\text{AC}$ shows two main and broad SO_2 emission peaks, respectively centered at ca. 290°C and 500°C (Figure 2). The first peak corresponds to the one observed in the TPD profile of the spent raw Darco AC, whilst the second one can be reasonably assigned to ZnSO_4 on AC, which was tested as reference. A new contribution in the TPD profiles of saturated $\text{Cu}_x\text{Zn}_{1-x}/\text{AC}$ sorbents was observed upon Zn substitution with Cu, initially as a shoulder centered at ca. 330°C, progressively becoming the main signal in the low temperature zone, by increasing the Cu content. Comparison with the TPD profile of a reference CuSO_4 on AC allowed ascribing this peak to supported copper sulphate. As expected, the peak at 500°C, assigned to the decomposition of ZnSO_4 , was progressively reduced. A comparison between the total amount of sulphur calculated from the integration of TPD profiles and that corresponding to H_2S adsorption capacity at saturation revealed that 40–46% of the total adsorbed sulphur was desorbed at 620°C, whereas only 18–27% was released up to 400°C. The remaining sulphur was likely stored as stable Zn and Cu sulphides. Cu-containing sorbents released a larger sulphur quantity, hence Cu-doping favoured the oxidation of H_2S to form sulphates, the final quantity being limited by the oxygen availability on the sorbent.

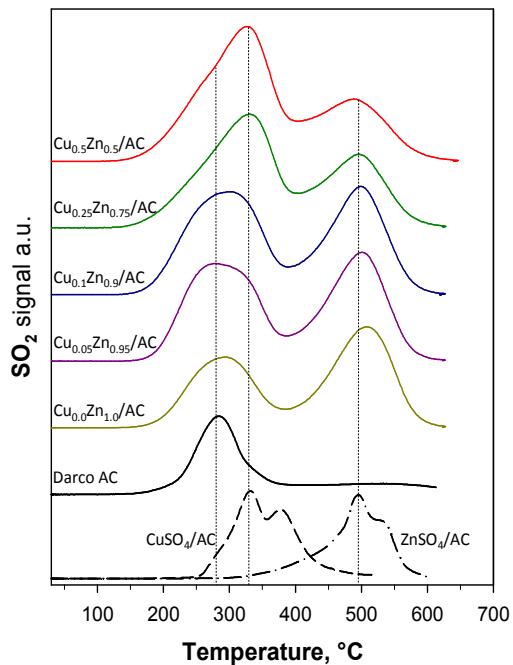


Figure 2. SO₂ released during TPD tests on H₂S-saturated Cu_xZn_{1-x}/AC sorbents and corresponding Darco AC support, as well as on two reference samples of CuSO₄ and ZnSO₄ impregnated on Darco AC.

Conclusions

Novel sorbents for room temperature reactive adsorption of H₂S from biogas or reformate gas streams were prepared by dispersing ZnO and CuO onto a commercial AC at fixed total metal loading (10%wt.) and Cu:Zn atomic ratio ranging from 0:1 to 1:1. A high dispersion of metal oxide nanoparticles without any significant reduction of the pore volume of the AC support was achieved. The functionalized sorbents showed a larger H₂S adsorption capacity with respect to the raw AC. The progressive substitution of Zn for Cu significantly improves the capture performance, reducing diffusional limitations in the reacted overlayer and thus increasing sulphidation/sulphation rates and active phase utilization factors. Moreover, Temperature Programmed Desorption runs from saturated sorbents showed that H₂S adsorption is coupled with oxidation phenomena leading to the formation of metal sulphates apart from metal sulphides and/or elemental sulphur underlying the complexity of the surface reactions.

Acknowledgments

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