

Towards a Deeper Understanding of the H₂S Adsorption Mechanism onto Activated Carbon–Supported Mixed ZnO and CuO.

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Highlights

- ZnO–CuO supported on activated carbon has synergistic effect for H₂S adsorption.
- Cu acts as chemical/structural promoter, accelerating ZnSO₄ formation.
- Sulphur and metal sulphides are formed in the late process stages.

1. Introduction

The efficient removal of H₂S from different gaseous streams (e.g. biogas) at room temperature represents an important technological challenge to face environmental issues, adverse health impacts and operational drawbacks in chemical plants deriving from this compound [1]. Reactive adsorption on metal oxides, hydroxides or carbonates dispersed onto a high surface area support (such as activated carbons) represents a flexible and cost effective purification technique to achieve high selectivity for H₂S capture, while attaining a higher conversion degree of the nano-sized active phase with respect to the unsupported counterpart [2,3]. Recent studies also demonstrated that doping the widely adopted ZnO sorbent with copper ends up in an enhanced reactivity towards H₂S, possibly due to a reduction of solid state diffusion limitations [3,4]. Noteworthy, the type of compounds formed upon adsorption of H₂S onto ZnO–CuO supported systems and the role of Cu on the capture mechanism have been only partially elucidated. However, those aspects are crucial to design optimal chemical formulations and microstructural features of novel sorbents and to set-up regeneration procedures for spent materials. This paper aims at analyzing the intertwining among the properties of an activated carbon functionalized with CuO and ZnO at different compositions, the operating conditions adopted and the H₂S adsorption results in terms of both capture rate/capacity and time evolution of the compounds formed.

2. Methods

Sorbents based on pure or mixed ZnO and CuO supported onto a commercial activated carbon (AC Darco G40; total metals loading fixed at 10% wt.) were produced *via* incipient wetness impregnation with aqueous solutions of metal nitrates followed by calcination at 250 °C under N₂. The sorbents properties were investigated by means of N₂ porosimetry, XRD, SEM-EDX and XPS analyses. H₂S (100–3000 ppmv in N₂) removal tests were run in a fixed bed reactor under dynamic conditions at 30 °C and compared through the analysis of their breakthrough curves, adsorption rates and values of adsorption capacity. TPD/TPO experiments from partially and completely saturated sorbents were performed to enlighten the reactive adsorption mechanism through the speciation of adsorbed sulphur species.

3. Results and discussion

Adsorption tests performed at both low (100 ppmv) and high (3000 ppmv) H₂S concentrations showed a monotonic increase in H₂S capture performance with Cu content, until a maximum for an equimolar Cu and Zn content (sorbent termed Cu_{0.5}Zn_{0.5}/AC), hence witnessing a synergistic effect between CuO and ZnO. For example, at 100 ppmv H₂S in the feed gas, the adsorption capacity at saturation (Q_{ads}) retrieved for

$\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$ was 1 mmol g^{-1} , a figure 12% and 27% greater than those obtained for Cu/AC and Zn/AC , respectively. Figure 1 a) reports the instantaneous adsorption rate r as a function of the adsorption capacity ω . A comparison of the relevant kinetic patterns testifies that even 5% of Zn substitution by Cu (sample $\text{Cu}_{0.05}\text{Zn}_{0.95}/\text{AC}$) produced both an enhanced adsorption rate, in particular for $\omega > 0.3 \text{ mmol g}^{-1}$, and a greater utilization factor of the active phase at saturation. This behavior can be imputed to Cu likely acting as oxygen donor and structural promoter to accelerate the formation of zinc sulphate (as determined from TPD tests). In fact, the pore size distributions for Zn/AC and $\text{Cu}_{0.05}\text{Zn}_{0.95}/\text{AC}$ sorbents were quite similar, thus suggesting that intraparticle transport phenomena equivalently influenced the capture process. $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$ sorbent displayed a further improvement in the adsorption rate, being able to keep the H_2S concentration at the fixed bed outlet at a near-zero level up to $\omega \approx 0.3 \text{ mmol g}^{-1}$. This can be additionally explained by the lower occlusion of micropores observed for this sample (i.e. lower intraparticle diffusion limitations) related to the tendency of zinc and copper to be preferentially located in micropores and mesopores, respectively. Notably, XPS analysis (cf. Figure 1 b)) and TPD/TPO tests performed on sorbents tested at different levels of S-saturation demonstrated that Zn and Cu sulphates were formed with a high rate and at a large extent during the initial phases of the reactive adsorption process. In fact metal sulphides, commonly recognized in the pertinent literature as the main reaction products from metal oxide, started to be formed with slow overall kinetics after the corresponding sulphates probably due to the lack of oxygen available from the sorbent. A deeper experimental campaign coupled with mathematical modelling of dynamic results on the best performing sample ($\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$) highlighted the following aspects: i) the initial stage of the adsorption process proceeded under a prevalent external mass transfer control, whereas the chemical reaction (mainly producing ZnSO_4 for short adsorption times) was very fast; ii) the reduction of the adsorption rate for longer process times could be related to both a partial pore clogging induced by reaction products with large molar volumes (sulphates) and the establishment of different reaction pathways to form S and metal sulphides.

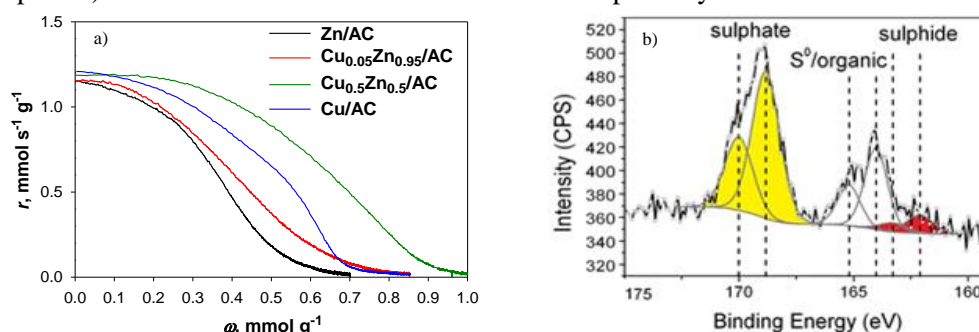


Figure 1. a) Adsorption rates for functionalized sorbents ($\text{H}_2\text{S}=100 \text{ ppmv}$ in N_2 , $T=30 \text{ }^\circ\text{C}$). b) XPS analysis: 2p spectral region of S for a saturated $\text{Cu}_{0.5}\text{Zn}_{0.5}/\text{AC}$ sorbent.

4. Conclusions

This work demonstrated the promoting effect of Cu in enhancing the reactivity of ZnO supported on activated carbon for the H_2S capture at room temperature, in particular to form ZnSO_4 in the initial adsorption stages. The partial pore blocking induced by the formation of large metal sulphates (together with sulphur and metal sulphides) is likely to slow down the capture process for long adsorption times, due to significant diffusion limitations induced.

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Keywords

H_2S adsorption; Supported mixed metal oxides; Activated carbon; Capture mechanism.

Curriculum Vitae

Marco Balsamo, was born in Pomigliano d'Arco (Naples, Italy), on June 6th, 1983. He is Post-Doctoral Research Fellow in Chemical Plants at the Department of Chemical, Materials and Production Engineering of the University of Naples Federico II (Unina, Italy), where he works since 2013. He obtained his Master's Degree in Sciences and Technologies of the Industrial Chemistry (evaluation=110/110 cum laude) in the academic year 2008-2009 at Unina. In 2013, he has got his PhD in Chemical Engineering at Unina with a Thesis entitled "Removal of CO₂ from flue-gas by innovative functionalized sorbents".

His main scientific activities deal with: i) valorization of coal combustion ashes as adsorbent materials; ii) liquid–solid and gas–solid adsorption processes; iii) demulsification of water–in–oil emulsions by means of ionic liquids. He is author of 20 scientific papers published on international peer-reviewed journals. He is reviewer for 10 international peer-reviewed journals among the most important in the field of chemical engineering and chemistry (Chemical Engineering Science; Energy Conversion and Management; Fuel Processing Technology; Journal of Hazardous Materials; Journal of Environmental Chemical Engineering; International Journal of Greenhouse Gas Control; Environmental Science & Technology; Industrial & Engineering Chemistry Research; Desalination and Water Treatment; RSC Advances). In 2017, he was reviewer for the Agence Nationale de la Recherche ANR (France) of scientific projects submitted to the Generic Call 2017.

Since 2013, he is teaching assistant (Cultore della Materia) in Chemical Plants at Unina. He was supervisor of 1 Master Degree Thesis in Materials Engineering, 3 Master Degree Theses in Industrial Chemistry and 9 Master Degree Theses in Chemical Engineering. He is co-author of Web Learning lectures ("Federic@" University of Naples Consortium), retrievable (in Italian) at the websites: <http://www.federica.unina.it/corsi/processi-impianti-trattamento-reflui>
<http://www.federica.unina.it/corsi/processi-termoconversione-solidi>.

List of scientific publications on international peer-reviewed journals:

1. M. Balsamo, F. Di Natale, A. Erto, A. Lancia, F. Montagnaro, L. Santoro, "Arsenate removal from synthetic wastewater by adsorption onto fly ash", *Desalination* 263 (2010) 58–63.
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Participation in Conferences as speaker:

- i. 33rd Meeting of the Italian Section of The Combustion Institute (Ischia, Italy, June 27-30, 2010).
- ii. 7th Mediterranean Combustion Symposium (Chia Laguna, Italy, September 11-15, 2011).
- iii. 22nd International Symposium on Chemical Reaction Engineering (Maastricht, The Netherlands, September 2-5, 2012).
- iv. 8th Mediterranean Combustion Symposium (Çeşme, Turkey, September 8-13, 2013).
- v. 36th Meeting of the Italian Section of The Combustion Institute (Procida, Italy, June 13-15, 2013).
- vi. Joint Meeting of the French and Italian Sections of The Combustion Institute (Pisa, Italy, April 23-24, 2014).
- vii. 2nd International Conference on Ionic Liquids in Separation and Purification Technology (Toronto, Canada, June 29-July 2, 2014).
- viii. International Conference on Shipping in Changing Climates (Glasgow, United Kingdom, November 24-26, 2015).
- ix. 6th International Congress on Ionic Liquids (Jeju, Korea, June 16-20, 2015).

- x. 39th Meeting of the Italian Section of The Combustion Institute (Napoli, Italy, July 4-6, 2016).
- xi. 3rd International Conference on Ionic Liquids in Separation and Purification Technology (Kuala Lumpur, Malaysia, January 8-11, 2017).
- xii. 8th International Conference on Clean Coal Technologies (Cagliari, Italy, May 8-12, 2017).

Awards:

The paper “Alumina-supported [Emim][Gly] ionic liquid for CO₂ capture from model flue-gas”, presented by Marco Balsamo at the 39th Meeting of the Italian Section of The Combustion Institute (Napoli, Italy, July 4-6, 2016), has been awarded as “Best Oral Presentation”.