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Highlighting the effect of the support during H_2S adsorption at low temperature over composite Zn-Cu sorbents

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ABSTRACT

Reactive adsorption of hydrogen sulphide (H_2S) from gaseous streams at room temperature with mixed Zn and Cu active phase supported onto γ-alumina is dealt in this manuscript. Sorbents with a fixed total metal content and variable Cu:Zn ratios were prepared by impregnation of commercial γ-alumina spheres in order to investigate the role of the support and the possible synergic effect between the two metals on the adsorption mechanism and performance. H_2S (500–3000 ppmv in N_2) removal tests were run under dynamic conditions at 30 °C. Experimental techniques such as BET and pore size distribution by N_2-adsorption, SEM-EDX, XRD and DRIFT analysis were coupled for the characterization of fresh and spent sorbents. TPD/TPO experiments on saturated sorbents were performed to assess their regenerability and allowed the speciation of adsorbed sulphur species, testifying the complexity of the surface reactions and the effect of the support.

1. Introduction

The removal of H_2S from a fuel gas stream (crude petroleum, natural gas and biogas) represents a crucial stage in the industrial practice because the gas can corrode pipelines and poison catalysts used in fuel cells, even at a few ppm levels [1,2]. Many purification technologies have been proposed to remove H_2S, including chemical absorption into basic solutions (e.g. NaOH), membrane separation, biological filtration and adsorption [3–5]. Among them, adsorption is very attractive due to its potentially high removal efficiency/operating flexibility and generally low maintenance costs. The adoption of reactive nano-sized active phases (such as metal oxides, hydroxides, carbonates) dispersed onto highly porous substrates allows to attain H_2S capture performances typically higher than their unsupported form also at relatively low temperatures [5–10]. In particular, different porous supports such as activated carbons, mesoporous silicas (e.g., SBA-15, MCM-41) and three-dimensionally ordered macroporous structure (3DOM) have been employed to disperse ZnO and CuO or mixtures thereof for the selective removal of hydrogen sulphide from different gaseous streams [5,9–13]. Contextually, we have recently investigated the application of mixed Zn and Cu oxides supported onto a commercial activated carbon (at Cu:Zn molar ratios varying from 0:1 to 1:0) for H_2S reactive adsorption [9,10]. The beneficial role of Cu, even at low loadings, in determining a better utilization of the active phases has been ascribed to a reduction of the diffusional limitations in the lattice of the composite active phase and through the reacted overlayer. Moreover, the strong interaction of the composite oxides with the activated carbon support improved metal dispersion and significantly reduced the stability and the decomposition temperature of metal sulphates formed during reactive adsorption.

However, inorganic supports offer the advantage of high thermal stability and they are potentially regenerable after the sulphation stage via thermal treatments, usually carried out under oxygen/air streams [5,11]. Elyassi et al. observed that a sequence of oxidation (in a 5/95% O_2/N_2 mixture @ 400 °C) followed by reduction (in a 10/90% H_2/He mixture @ 400 °C to reduce $CuSO_4$ species) of a spent Cu-ZnO-SBA-15 sorbent was effective in fully restoring the H_2S capture capacity of the adsorbent [5]. On the other hand, the feasibility of a regeneration process for an exhaust sorbent is not trivial and might depend on different factors including the nature of the substrate/sulphation products, their chemical interactions and possible sintering phenomena of the active phase induced by the high temperature treatment. For instance, Wang et al. observed that the H_2S capture capacity at ambient temperature of CuO-SiO_2 3DOM sorbents was significantly reduced when performing the regeneration stage at 650 °C in air [13], due to the aggregation of CuO upon exposure to high temperature. Consequently, the analysis of the sorbent regenerability has to be verified case by case.

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Following the path drawn in our previous papers, in which a carbonaceous support was employed for the dispersion of Zn/Cu mixed phases [9,10], this contribution aims at elucidating the role of a different support such as mesoporous γ-alumina spheres for the same active species for the H_2S capture process. H_2S adsorption tests onto the alumina both raw and functionalized with 8% wt. total metal content and various Cu:Zn proportions were carried out at room temperature under dynamic conditions in a lab-scale fixed-bed adsorption column. A thorough sorbent characterization was carried out by SEM, XRD and N_2 adsorption at −196 °C analyses. Finally, DRIFT analysis and temperature programmed desorption (TPD) or oxidation (TPO) tests were performed to shed light on the type of compounds formed upon the H_2S reactive adsorption process and to assess the sorbent regenerability.

2. Materials and method

The porous substrate adopted for the deposition of Zn- and Cu-based active phase was a commercial γ-Al_2O_3 (SASOL PURALOX 1-160, spheres with 1 mm diameter, $Al_2O_3 \geq 98\%$ wt.). The functionalization procedure included an impregnation step of alumina spheres (12.5 g) at ambient conditions with an aqueous solution (10 mL, 1.72 mol L^{-1}) of metal nitrates precursors ($Zn(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}2.5H_2O$, Aldrich, respectively with purity of 99.3% and 98.6% wt.). Thereafter, the sorbents were dried at 120 °C in air and eventually calcined for 2 h at 250 °C, in analogy to our previous work in which the same precursors dispersed onto an activated carbon support were used [9]. In this case, the low calcination temperature allowed preventing the undesired formation of superficial metal aluminates [14 and refs. therein]. The nominal metal loading (Zn + Cu) was set at 8% wt., whereas the Cu:Zn atomic ratio was varied in the range 0:1–1:1. The sorbents were labelled as Cu_xZn_{1-x}/Als, with x representing the atomic fraction of Cu with respect to the total metal content.

The actual metal loading on the sorbents was verified by ICP-MS using an Agilent 7500 instrument. Scanning electron microscopy (SEM) was carried out with a FEI Inspect instrument equipped with an EDX probe. The textural properties of the sorbents were determined by N_2 adsorption at −196 °C from P/P_0 10^{-5} using a Quantachrome Autosorb 1-C (BET method for specific surface area, Barrett-Joyner-Halenda (BJH) method applied to the desorption branch for pore size distribution, PSD). XRD analysis was performed with a Bruker D2 Phaser diffractometer operated at diffraction angles ranging between 10° and 90°2θ with a scan rate of 0.02° s^{-1}.

H_2S dynamic adsorption tests at initial pollutant concentration ranging from 500 to 3000 ppmv in N_2 (90 SL h^{-1}) were carried out at 30 °C in a fixed-bed reactor using 5.0 g of either raw alumina spheres or functionalized sorbents. The dynamic evolution of H_2S concentration was measured by a continuous GAS 3240 R BIOGAS gas analyzer (GEIT Europe). H_2S adsorption capacity at saturation, ω_s [mmol g^{-1}], was determined through a material balance on H_2S over the adsorption column, leading to the following expression:

$$\omega_s = \frac{Q^t C^{in}_{H_2S} \rho_{H_2S}}{m M_{H_2S}} \int_0^{t^*} \left(1 - \frac{C^{out}_{H_2S}(t)}{C^{in}_{H_2S}}\right) \mathrm{d}t \quad (1)$$

where Q^t [L s^{-1}] is the total gas flow rate, $C^{in}_{H_2S}$ [−] is the H_2S volumetric fraction in the gas feed, $C^{out}_{H_2S}$ [−] is the H_2S volumetric fraction at the bed outlet, ρ_{H_2S} [mg L^{-1}] is the H_2S density (at 30 °C and 1 bar) while M_{H_2S} [mg mmol $^{-1}$] is its molecular weight; m [g] is the sorbent dose and t^* [s] represents the saturation time for which $C^{out}_{H_2S}/C^{in}_{H_2S} \approx 0.99$.

Temperature Programmed Desorption (TPD) tests were carried out in a lab-scale rig [9], in order to analyze the residual presence of nitrates on the calcined sorbents (TPD-NO_x) and to shed light on the species formed upon the sulphidation process, while evaluating the thermal regenerability of the spent sorbents. Temperature Programmed Oxidation (TPO) tests were also performed on spent sorbents in order to further explore their thermal regenerability. To this end, a known sorbent amount (20–150 mg) was heated at 10 °C min^{-1} up to 800 °C (620 °C for TPD-NO_x tests) under a N_2 flow (30 SL h^{-1}); TPO tests were performed under a flow of air or O_2 (5000 ppmv) in N_2. Gas analysis was performed by means of two continuous analyzers with cross sensitivity corrections: i) an ABB Optima Advance Limas 11 UV for NO and NO_2; ii) an ABB Optima Advance Limas 11 UV for the simultaneous measurement of H_2S (0–300 ppmv) and SO_2 (0–100 ppmv) concentrations.

DRIFT experiments were performed on a Perkin Elmer Spectrum GX spectrometer equipped with a liquid-N_2 cooled MCT detector with a spectral resolution of 4 cm^{-1} averaging each spectrum over 50 scans. Samples were diluted in KBr (2%) and about 100 mg finely grounded powder was placed in the DRIFT cell equipped with a ZnSe window and connected to gas lines. Samples were pre-treated for 40 min at 120 °C under Ar flow and then cooled down to 40 °C.

3. Results and discussion

The elemental analysis performed on functionalized sorbents showed that the total metal content (Cu + Zn) was in the range 8.2 ± 0.15% wt., in line with the target loading. SEM-EDX analysis carried out on the sorbent containing an equimolar Cu:Zn ratio (Fig. 1) highlighted a homogeneous distribution of both the elements across the section of the spherical alumina particles.

BET surface area values obtained for the tested sorbents are listed in Table 1. Results indicate that the deposition of the active phases determines a nearly 10% reduction of the surface area for functionalized sorbents with respect to the bare substrate, whereas BET values for Cu_xZn_{1-x}/Als sorbents (157 ± 1 m^2 g^{-1}) are not influenced by the Cu:Zn ratio.

Fig. 2 shows the PSD for both raw alumina and $Cu_{0.5}Zn_{0.5}$/Als sorbents. Data highlight that the functionalization treatment does not affect the PSD of the parent support and induces a minor reduction of its pore volume, thus confirming a homogenous dispersion of the active phases onto the mesoporous alumina.

Fig. 3 depicts the XRD patterns of the raw and functionalized alumina sorbents together with the diffraction spectrum of the $Cu_{0.5}Zn_{0.5}$/Als sample after saturation with H_2S at 3000 ppmv and 30 °C.

The support spheres show the typical diffraction peaks of γ-alumina. The XRD patterns for $Cu_0Zn_{1.0}$/Als and $Cu_{0.1}Zn_{0.9}$/Als are equivalent to the one of the parent substrate, probably due to the low content of the active phases associated to a high dispersion and/or poor crystallinity.

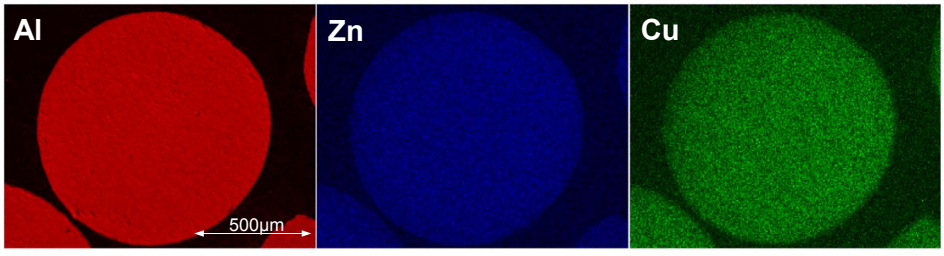

Fig. 1. SEM-EDX maps in false colours showing the distribution of the elements (Al, Zn and Cu) across the section of a spherical particle of $Cu_{0.5}Zn_{0.5}$/Als sorbent.