Solar-assisted development of nanoadsorbents for the H_2S/SO_2 capture from biogas

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Keywords: H_2S, SO_2, adsorption, biogas, solid wastes, $CaCO_3$, nanoparticles
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Introduction

Calcium carbonate is a versatile material with high importance for industrial and building applications. In nature, $CaCO_3$ is highly available in dolomites, limestones and marbles depending on the conditions and the environment of sedimentation process. It can also be obtained as a fine product from chemical precipitation methods with better control of purity and granulation. However, there are cases where $CaCO_3$ is considered a solid waste requiring some form of treatment or stabilization to avoid deposition in the environment. Suggestively, marble processing produces extremely large quantities of residual marble dust in the form of aqueous dispersion while mussels or oyster shells and eggshells are another significant source of $CaCO_3$ wastes. The recovery and utilization of such by-products is usually attempted by their incorporation in cements, road asphalts and plastics as replacements of other inert powders Another set of applications considers the alkaline character of $CaCO_3$, as well as its product CaO, as a way to neutralize acidic sources.

Particularly, the desulfurization of gas streams through fixed-bed columns filled with $CaCO_3$ has been applied for the elimination of H_2S or SO_2 from flue gases in power stations (Kougias, 2018). The same approach has the potential to remove H_2S from the biogas produced by anaerobic treatment of organic wastes and, therefore, protect the engine and exhaust gas heat recovery equipment from severe corrosion (Husmann, 2016). During contact of hydrogen sulfide with $CaCO_3$ a stabilized solid such as CaS and CO_2 are produced according to the reaction $CaCO_3 + H_2S \rightarrow CaS + H_2O + CO_2$. In spite of the low cost for $CaCO_3$, the removal efficiency is limited by the relatively slow kinetic of the reaction when proceeding at environment temperatures. In addition, the surface activity of the granules when originating from mineral sources is also reduced. For this reason, $CaCO_3$ is usually combined with other phases (FeOOH, MnO_2) able to improve the reaction rate and the overall capture efficiency (Khabazipour, 2019). However, the addition of these materials implies to an increase of desulfurization cost due to required mixing process and the cost to obtain such additives.

To this end, succeeding the preparation of surface-activated $CaCO_3$ would be an advantageous approach to establish a more efficient desulfurization of biogas especially if combined with the proper processing and upgrade of secondary $CaCO_3$-rich sources such as mussels, eggshells or marble by-products. This study aims to the development of novel adsorbents with high desulfurization potential through the production of calcium carbonate-based nanoparticles using the solar physical vapor deposition (SPVD) technique, and their evaluation in a laboratory-scale setup.

Experimental

Studied nanopowders were prepared using the simple and low-cost method of SPVD in a Heliotron 2 kW glass chamber (Figure 1a). Experiments were carried out at the CNRS-PROMES laboratory, UPR 8521, belonging to the French National Centre for Scientific Research (CNRS). Briefly, the solar beam (about 1 kW/m^2) was reflected by a plane mirror that tracks the sun, and then focused on the target by a parabolic (2 m diameter) concentrator placed above the chamber. Evaporation occurred under a pressure of 10 mbar controlled by a continuous flow of Ar gas. Particles were collected on a nanoporous metallic filter located in the direction of pumping flow. The used targets were prepared by pressurizing fine powder received from different sources of $CaCO_3$ by-products such as mussel shells, eggshells and mining dusts (marble and dolomite).

Structural characterization of the obtained samples was performed by X-ray diffraction (XRD) using a Rigaku Ultima+ powder diffractometer with Cu-K_α radiation. In order to image the morphology of nanopowders, scanning electron microscopy (SEM) micrographs of numerous samples were taken in a Quanta 200 ESEM FEG FEI microscope. The uptake efficiency of nanoadsorbents for H_2S and SO_2 was evaluated by flowing a gas stream (<3500 ppm in nitrogen) through a vertical fixed-bed reactor packed with a quantity of the material (Figure 1b). The concentrations of H_2S or SO_2 in the outflow stream was monitored in line by a continuous gas analyser.

Saturated adsorbents were analysed by X-ray photoelectron spectroscopy (XPS) to identify the occurring adsorption mechanism on the solid's surface. Spectra were acquired in an Axis Ultra DLD system by KRATOS.

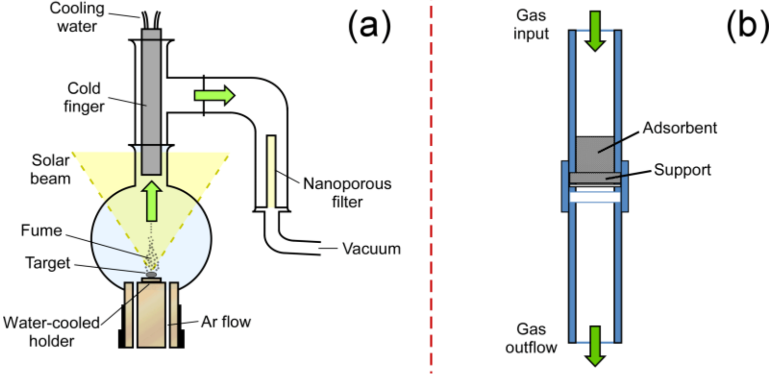

Figure 1. Production of nanopowders by SPVD system (a). Vertical fixed-bed reactor for gas desulfurization (b).

Results

Structural characterization of the produced nanopowders indicate high-crystalline CaO as the major phase appearing in all samples (Figure 2a). However, when eggshells and mussels where used as $CaCO_3$ sources, a significant presence (>50 %wt.) of low-crystalline $Ca(OH)_2$ was also detected. On the other hand, the presence of $MgCO_3$ in dolomite and marble targets is responsible for the presence of MgO in the corresponding nanopowders. SEM images of the collected samples indicate the nanopowders consist of small nanoparticles with typical dimensions below 40 nm.

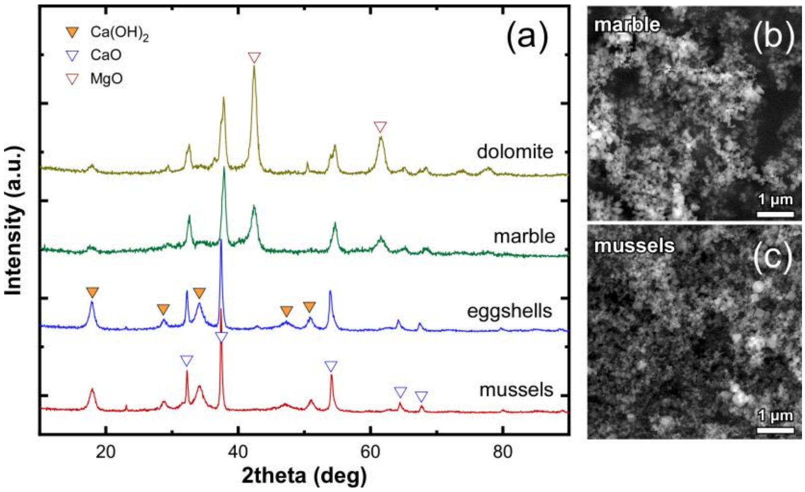

Figure 2. XRD diagrams (a) and SEM images of developed nanopowders from marble (b) and mussels (c).

The preliminary evaluation of nanopowders in the fixed bed reactor indicated an enhancement of adsorption efficiency in comparison to corresponding raw materials. This is mainly attributed to the dramatic increase of specific surface area in the studied nanopowders which enables higher contact times and reaction kinetics. XPS analysis suggests that sulfur capture can be performed through elemental sulfur or HS^- species for H_2S and SO_3^{2-} and SO_4^{2-} when SO_2 was tested.

Acknowledgements

Authors would like to thank the CNRS-PROMES laboratory, UPR 8521, belonging to the French National Centre for Scientific Research (CNRS) for providing access to its installations, the support of its scientific and technical staff (N. Boullet, E. Guillot, A. Badziaka), and the financial support of the SFERA-III project (Grant Agreement No 823802).

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