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Editorial

Catalysts and Processes for H_2S Conversion to Sulfur

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1. Definitions, State of the Art, Challenges

Hydrogen sulfide is one of the main waste products of the petrochemical industry; it is produced by the catalytic hydrodesulfurization processes (HDS) of the hydrocarbon feedstocks, and it is a byproduct from the sweetening of sour natural gas and from the upgrading of heavy oils, bitumen, and coals. It is a toxic gas and is classified as hazardous industrial waste. The exploitation of hydrogen sulfide as fuel using conventional combustion technologies is forbidden and criminalized by the more stringent environmental policies due to its deleterious effect like SO_2 formation, which is the main factor responsible for acidic precipitation.

There are different technologies for the removal of hydrogen sulfide, but they are characterized by high costs and limited H_2S conversion efficiency. The main purification treatments for H_2S removal comprise absorption, adsorption, membrane separation, and catalytic processes. Among these, adsorption and catalytic oxidation could be considered interesting methods to carry out the desulfurization thanks to their simplicity, efficiency, and low cost. Materials with high surface area and large pore volume, such as activated carbons, zeolites, mesoporous silica, and metal-organic frameworks, are generally used for the adsorption process [1].

The catalytic methods are among the most attractive as they allow the conversion of highly hazardous hydrogen sulfide into a nontoxic, marketable product, elementary sulfur. Basic processes for hydrogen sulfide-to-sulfur conversion are the direct oxidation of H_2S into elementary sulfur and the low-temperature reduction of sulfur dioxide [2].

Today, hydrogen sulfide is usually removed by the well-known Claus process, which is mainly used in refineries and natural gas processing plants for the treatment of rich-H_2S gas streams. The Claus process is the dominant technology to produce sulfur but it is not economically profitable because the hydrogen is lost as water. It is worth noting that the vast majority (about 94%) of the 8.1 million metric tons of sulfur produced in the United States in 2020 was synthesized using the Claus process [2,3].

Recently, there has been a growing interest in the utilization of H_2S as feedstock for hydrogen generation. Thermochemical cycles have been proposed by many researchers in order to obtain hydrogen and sulfur from hydrogen sulfide such as electrolysis, photolysis, plasmolysis, and their many variants [4]. An interesting alternative could be to produce sulfur and hydrogen simultaneously by the thermal catalytic decomposition of H_2S, even if the amount of energy requested to achieve extremely high temperatures, a low hydrogen yield, and the need for subsequent separation stages represent the main drawbacks to an industrial application.

Therefore, the challenge is to realize the H_2S removal in a one-reaction step in the presence of an active catalyst very selective to sulfur. The choice of the catalyst plays a fundamental role in assuring a high grade of H_2S removal with a lower selectivity to SO_2. In this regard, many efforts are addressed to the identification of active materials at the lower admissible temperature, in order to improve the H_2S abatement by reducing operational costs and so optimizing the desulfurization technology.

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2. Special Issue

I would particularly like to thank all the authors who contributed their excellent papers to this Special Issue covering significant aspects of this topic accompanied by a variety of novel approaches. The contributions represent interesting and innovative examples of the current research trends in the field of H_2S removal from liquid and gas streams.

I also wish to thank the Editorial Staff of *Catalysts* for their help to organize this issue and in particular Vivian Niu for the support, assistance, and encouragement.

This Special Issue is particularly devoted to the preparation of novel powdered/structured supported catalysts and their physical–chemical characterization, the study of the aspects concerning stability and reusability, as well as the phenomena that could underlie the deactivation of the catalyst.

This Special Issue comprises 7 articles, 1 communication, and 1 review regarding the desulfurization of sour gases and fuel oil, as well as the synthesis of novel adsorbents and catalysts for H_2S abatement. In the following, a brief description of the papers included in this issue is provided to serve as an outline to encourage further reading.

Chen et al. investigated porous carbonaceous materials for the reduction of H_2S emission during swine manure agitation. Two biochars, highly alkaline and porous, made from corn stover and red oak were tested. The authors verified the possibility of using surficial biochar treatment for short-term mitigation of H_2S emissions during and shortly after manure agitation [5].

Bao et al. used the waste solid as a wet absorbent to purify the H_2S and phosphine from industrial tail gas. The reaction mechanism of the simultaneous removal of H_2S and phosphine by manganese slag slurry was investigated. The best efficiency removal of both H_2S and phosphine was obtained by the modified manganese slag slurry [6].

The desulfurization of sour gases was studied by Duong-Viet et al. in carbon-based nanomaterials in the form of N-doped networks by the coating of a ceramic SiC. The chemical and morphological properties of the nano-doped carbon phase/SiC-based composite were controlled to get more effective and robust catalysts able to remove H_2S from sour gases under severe desulfurization conditions such as high GHSVs and concentrations of aromatics as sour gas stream contaminants [7].

Li et al. carried out the oxidative desulfurization of fuel oil for the removal of dibenzothiophene by using imidazole-based polyoxometalate dicationic ionic liquids. Three kinds of catalyst were synthesized and tested under different conditions [8]. The catalytic performance of the catalysts was studied under different conditions by removing the dibenzothiophene from model oil. The authors identified a catalyst with an excellent DBT removal efficiency under optimal operating conditions.

The removal of H_2S and SO_2 at low temperatures was investigated by Ahmad et al. in eco-friendly sorbents from raw and calcined eggshells. They studied the effect of relative humidity and reaction temperatures. The best adsorption capacities for H_2S and SO_2 were obtained at a high calcination temperature of eggshell [9].

Zulkefli et al. prepared a zinc acetate supported with commercial activated carbon for the capture of H_2S by adsorption. The optimization conditions for the adsorbent synthesis were carried out using RSM and the Box–Behnken experimental design. Several factors and levels were evaluated, including the zinc acetate molarity, soaking period, and soaking temperature, along with the response of the H_2S adsorption capacity and the surface area [10].

Vanadium-sulfide-based catalysts supported on ceria were used for the direct and selective oxidation of H_2S to sulfur and water at a low temperature. Barba et al. performed a screening of catalysts with different vanadium loadings in order to study the catalytic performance in terms of H_2S conversion and SO_2 selectivity. The effect of the temperature, contact time, and H_2S inlet concentration was studied in relation to the catalyst that has exhibited the highest H_2S removal efficiency and the lowest SO_2 selectivity [11].

H_2S adsorption was studied in relation to a novel kind of hydrochar adsorbent derived from chitosan or starch and modified by CuO-ZnO. Zang et al. investigated the formation

of CuO-ZnO on hydrochar, the effect of the hydrochar species, the adsorption temperature, and the adsorption mechanism [12]. A review concerning the different technologies of the gas-based phase for the direct catalytic oxidation of H_2S to sulfur was the object of study by Khairulin et al. [2]. The development of catalysts for the direct oxidation reaction (e.g., metal oxides, nanocarbon materials) and the discussion of the data concerning the Claus process and its recent adaptations were widely analyzed. Furthermore, the authors presented the results of basilar investigations obtained at the Institute of Catalysis where an industrial installation for H_2S removal from gas streams was located.

I hope that the topics presented in this issue will inspire readers to further investigate new materials and solutions to significantly reduce the presence of pollutants such as H_2S, SO_2 and other sulfur-based compounds, thereby pursuing the objective of "zero emissions" in the atmosphere.

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