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Novel Fe–Mn–Zn–Ti–O mixed-metal oxides for the low-temperature removal of H_2S from gas streams in the presence of H_2, CO_2, and H_2O

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Abstract

The efficiency of Fe–Mn–Zn–Ti–O mixed-metal oxides of varying composition prepared by sol–gel methods toward removal of H_2S from a gas mixture containing 0.06 vol% H_2S, 25 vol% H_2, 7.5 vol% CO_2, and 1–3 vol% H_2O was studied in the 25–100 °C range. In particular, the effects of the Fe/Mn molar ratio in the Fe–Mn–Zn–Ti–O solids on the H_2S uptake and regeneration performance of the solids were studied. The nominal chemical composition (metal mol%) of the Fe–Mn–Zn–Ti–O solids was found to strongly influence the chemical composition, particle size, and morphology of the crystal phases formed. It was found that the 5 Fe–15 Mn–40 Zn–40 Ti–O mixed-metal oxide provides the highest H_2S uptake as fresh and after regeneration in 20% O_2/He gas mixture in the 500–750 °C range compared with the other solids investigated. It was also found that 5 Fe–15 Mn–40 Zn–40 Ti–O exhibits higher H_2S uptake than a commercial Ni-based H_2S adsorbent in the 25–50 °C range. In particular, a three times greater H_2S uptake at 25 °C compared with that on the commercial adsorbent was found. The effectiveness of the regeneration procedure of 5 Fe–15 Mn–40 Zn–40 Ti–O solid after complete sulfidation was found to be in the 48–82% range, depending on the sulfidation temperature and regeneration conditions applied. A detailed characterization of the fresh, sulfided, and regenerated 5 Fe–15 Mn–40 Zn–40 Ti–O and 20 Fe–40 Zn–40 Ti–O solids, which exhibited the best and worst H_2S uptake performance, respectively, using BET, XRD, Raman, XPS, and Mössbauer techniques revealed important information on the sulfidation mechanism. The present work provides new fundamental knowledge that could trigger further research efforts toward the development of alternative mixed metal oxides not based on toxic chromia (Cr_2O_3–Fe_2O_3/α-Al_2O_3), which is used today in several industrial plants for the catalytic oxidation of H_2S (Claus process).

Keywords: H_2S removal; Fe-based H_2S adsorbents; Mixed metal oxides; Zinc ferrite spinels; Sulfidation; Adsorbent regeneration; H_2-TPR; Mössbauer; Raman; XPS

1. Introduction

The removal of H_2S from a gas stream can be accomplished by adsorption onto a solid surface [1,2], catalytic oxidation [3–5], and absorption by a liquid solution (amine/alkaloamine) [5]. Various solid materials have been developed to remove H_2S from a number of industrial gas effluent streams. Most of the work carried out to date on the development of H_2S solid adsorbents has been focused on materials suitable at temperatures >300 °C. Among the most studied solid materials for the removal of H_2S from a "coal-gas" are Fe- and Ca-containing materials, because of their high reactivity and low cost [6,7]. However, due to the fact that "coal-gas" contains a large fraction of H_2 and a high CO/CO_2 ratio, these materials have some drawbacks. For example, Fe_3O_4 is reduced to FeO and Fe, whereas the formation of Fe_3C reduces the sulfur uptake of the solid [6–8]. Moreover, regenerating the sulfided Ca-containing solids is very difficult. Lew et al. [9] have shown that ZnO is more attractive than iron oxide because of its more favorable sulfidation thermodynamics. On the other hand, ZnO has much slower sulfidation kinetics than iron oxide. A major limitation

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of ZnO-based adsorbents for hot-gas cleaning is their loss due to reduction of ZnO to volatile elemental zinc.

Mixed metal oxides, such as Cu–Mn–O, Cu–Fe–O, Cu–Mo–O, Zn–V–O, Zn–Ti–O, Zn–Fe–Ti–O, and Zn–Fe–V–O, have been studied as H_2S adsorbent materials [10–13]. Their reactivity and regeneration ability are improved when deposited on a suitable support. $ZnFe_2O_4$ mixed-metal oxide was also found to be a good H_2S adsorbent in the 500–700 °C range [14,15]. Kobayashi et al. [16,17] studied zinc ferrite–silicon dioxide composites as high-temperature fuel gas desulfurization adsorbents. Sulfidation of zinc ferrite in the reducing environment yielded wurtzite, zinc blende, and iron sulfides in the presence of 500 ppm of H_2S.

Little research work has been carried out on the development and characterization of solid materials for low-temperature removal of H_2S [18–28]. Carnes and Klabunde [22] studied nanocrystalline metal oxides prepared by sol–gel methods. At low temperatures (25–100 °C), the activity order was $ZnO > CaO > Al_2O_3 \gg MgO$. Davidson et al. [19] reported on the adsorption of H_2S on ZnO in the 25–45 °C range, where about 40% conversion of H_2S was observed. Sasaoka et al. [23] studied the adsorption of H_2S on ZnO in the presence of CO, CO_2, and H_2O and found that CO inhibits sulfidation reaction due to its competitive adsorption with H_2S for the same active sites, whereas H_2O inhibits the reaction due to promotion of the reaction with ZnS to form H_2S and ZnO. Baird et al. [24] have found that mineral feroxyhyte is an efficient adsorbent of H_2S at room temperature due to its high surface area and the presence of the Fe^{3+}/Fe^{2+} redox couple. In another study, Baird et al. [18] found that reaction of H_2S with ZnO doped with first-row transition metals was restricted to about 0.6 surface monolayers. The main role of the transition metal oxide was to increase the total surface area available for reaction with H_2S. Baird et al. [25] studied Co–Zn–Al–O mixed-metal oxides as H_2S adsorbents at 28 °C. A comparison of H_2S uptake with Co–Zn–O uptake suggested that the presence of aluminum ions in the mixed-oxide matrix gave rise to an increased surface area, but not to H_2S uptake. Other H_2S adsorbent materials that have been investigated include activated carbons [26,27], the surface acid chemistry of which has been shown to play an important role.

The present work concerns the development of novel Fe–Mn–Zn–Ti–O mixed-metal oxides prepared by sol–gel methods and tested for the first time toward low-temperature removal of H_2S from a gas mixture containing H_2, CO_2, and H_2O. The following parameters have been investigated with respect to their effects on the H_2S uptake performance of the solids investigated: mixed-metal oxide composition, adsorption temperature, temperature of adsorbent regeneration in 20% O_2/He, time of regeneration in 20% O_2/He, and presence of water in the feed stream. A commercial Ni-based catalyst was also investigated for a critical comparison. A detailed characterization of some of the fresh, sulfided, and regenerated Fe–Mn–Zn–Ti–O solids using BET, XRD, Raman, XPS, and Mössbauer techniques has revealed important information on the sulfidation mechanism.

The selective catalytic oxidation of H_2S to elemental sulfur (Claus reaction) is an industrial practice that makes use of α-Al_2O_3-supported iron and chromium oxides [29,30]. Continuing research is being conducted into the development of new materials for this important catalytic reaction, excluding the use of Cr_2O_3 because of its severe toxicity. Despite numerous investigations into the mechanism of this reaction over different metal oxides [31,32], a detailed mechanism based on which further significant catalyst developments would be expected has not yet been established. The selection of a better catalyst for the Claus reaction is still based on a modification of the surface acid/base properties of mixed-metal oxides [32,33]. Li et al. [34] reported that Fe–Sb–O and Fe–Sn–O mixed-metal oxides are good H_2S oxidation to sulfur catalysts. The catalytic properties of these materials change significantly with their composition.

Based on the work mentioned in the previous paragraph, the results of the present work, which relate to the chemisorption and bulk chemical reaction of H_2S with new Fe–Mn–Zn–Ti–O mixed metal oxides and also to the oxidation (use of air) of the latter sulfated solids, could trigger further research into Fe–Mn–Zn–Ti–O mixed-metal oxides as important catalytic materials for the oxidation of H_2S to elemental sulfur. The present work was motivated by a European project [35] in which the gas effluent stream from a bioreactor used to reduce toxic Cr^{6+} present in waters into Cr^{3+} after using the sulfate metal-reducing bacteria (SMRB) had to be treated to remove the nondesirable H_2S gas evolved.

2. Experimental

2.1. Synthesis of H_2S solid adsorbent materials

A series of Fe–Mn–Zn–Ti–O mixed-metal oxides were prepared by the sol–gel method [36] using $Fe(NO_3)_3$, $(CH_3COO)_2Mn$, $(CH_3COO)_2Zn$, and $Ti(i\text{-}OPr)_4$ (Aldrich) as precursors of Fe, Mn, Zn and Ti, respectively. Appropriate amounts of each reagent were used to obtain a $(Fe + Mn)/(Fe + Mn + Zn + Ti)$ molar ratio of 0.2 and Fe/Mn molar ratios of 15/5, 10/10, and 5/15 in the final product. An 20 Fe–40 Zn–40 Ti–O solid composition was also prepared. An appropriate amount of $(CH_3COO)_2Zn$ was dissolved in H_2O, and the pH of the resulting solution was adjusted in the 8.5–9.4 range by dropwise addition of ammonia solution (25% v/v). Appropriate amounts of iron nitrate, manganese acetate, and titanium isopropoxide solutions were then added, with the pH kept within the same range, until the formation of a brown gel-like product was noted. This product was then dried at 70 °C overnight in the presence of air. The dried powders were finally calcined in air at 100 °C for 1.5 h, at 150 °C for 1.5 h, at 200 °C for 2.5 h, and finally at 500 °C for 4 h before storage and further use.

A second series of Fe–Mn–Zn–Ti–O mixed-metal oxides were synthesized by means of co-hydrolysis of iron nitrate, manganese acetate, zinc acetate, and titanium isopropoxide. Appropriate amounts of each reagent were used so as to yield a $(Fe + Mn)/(Fe + Mn + Zn + Ti)$ molar ratio of 0.1 in the final product, with Fe/Mn molar ratios of 7/3 and 5/5.