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# Selective catalytic oxidation of H<sub>2</sub>S to elemental sulfur over titanium based Ti–Fe, Ti–Cr and Ti–Zr catalysts

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## ABSTRACT

In this study, titanium oxide catalyst was incorporated with iron, chromium and zirconium to improve catalytic activity for selective catalytic oxidation of H<sub>2</sub>S to elemental sulfur. Equimolar titanium based iron (Ti–Fe), chromium (Ti–Cr) and zirconium (Ti–Zr) catalysts were synthesized by the complexation method and tested in oxidation between the temperature range of 200–300 °C and using different O<sub>2</sub>/H<sub>2</sub>S ratios. Ti–Fe catalyst with Fe<sub>2</sub>TiO<sub>5</sub> crystalline phase and Ti–Cr catalyst with mainly Cr<sub>2</sub>O<sub>3</sub> crystalline phase showed complete conversion of H<sub>2</sub>S and high sulfur selectivity (close to one) at 250 °C. Ti–Zr catalyst having relatively high surface and small pore diameter could not prevent sulfur deposition on the surface and lost in catalytic activity at the same temperature. Ti–Fe catalyst had high activity with 100% conversion and sulfur selectivity in the reaction period of an experimental run (150 min) even at lower oxidation temperature (200 °C). It was concluded that incorporation of iron into Ti–Fe catalyst structure improved the redox ability and surface acidity of the catalyst. Fe<sub>2</sub>TiO<sub>5</sub> mixed metal oxide in the Ti–Fe catalyst was responsible and active phase resulting in complete conversion of H<sub>2</sub>S and high sulfur selectivity in the selective oxidation of H<sub>2</sub>S to elemental sulfur.

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## Introduction

Due to environmental concerns and economic considerations, sulfur recovery from hydrogen sulfide has attracted significant attention by researchers and fuel producers. High amount of H<sub>2</sub>S is produced as a side product, in the operation of an integrated gasification combined cycle system (IGCC) power plant as well as during gasification of fossil fuels and also in petroleum refinery. The integrated gasification combined cycle, which is an environmentally clean sustainable technology, involves coal gasifier, acid gas cleanup unit, and

power generation facilities. Sulfur in fuel can be converted to H<sub>2</sub>S due to reducing atmosphere during coal gasification. Hydrogen sulfide is usually removed from the sour gas by absorption in ammonia, alkanolamine or alkaline salts. The main disadvantages of the removal of H<sub>2</sub>S by absorption are its relatively high cost and the use of solvent/sorbent [1–3]. Claus process is a well-known process to convert H<sub>2</sub>S from tail gases to elemental sulfur. There are a number of publications in the literature on the modeling of the Claus process [4,5]. In the study of Jones et al., the modified Claus Process, when part of IGCC power plant, was proposed to destroy ammonia completely and recover sulfur thoroughly from a relatively

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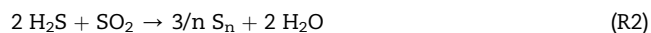
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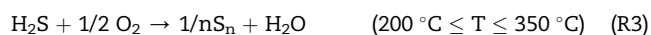
low purity acid gas stream [6]. In the conventional Claus process, 1/3 of the H<sub>2</sub>S in the feed gas is burned to SO<sub>2</sub> (R1 denoted as thermal oxidation) at high temperatures,



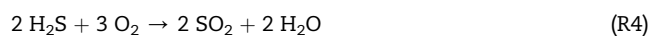
SO<sub>2</sub> is then reacted with the unburned H<sub>2</sub>S to produce elemental sulfur at lower temperatures (R2 denoted as catalytic step or Claus reaction)



The main disadvantage of Claus process is thermodynamic restriction (97–98%) in the catalytic step (R2). Catalytic selective oxidation of H<sub>2</sub>S is an attractive alternate to conventional Claus process, to produce elemental sulfur in a single step (R3).



Direct oxidation of H<sub>2</sub>S (R3) does not have any equilibrium limitations and it is essentially irreversible. Some side reactions may reduce elemental sulfur yield; such as deep oxidation of H<sub>2</sub>S (R4) and oxidation of produced sulfur (R5).



Therefore, development of a selective catalyst for selective oxidation of H<sub>2</sub>S to elemental sulfur is crucial in producing elemental sulfur with a high yield.

A number of investigations have been focused in the literature on the development of active, selective and stable catalysts for catalytic selective oxidation of H<sub>2</sub>S. Iron-, titanium-, chromium-, and vanadium based catalysts have been reported to have high potential in catalytic oxidation of H<sub>2</sub>S to produce elemental sulfur [7–10]. Also, catalysts with different types of supports (for example, MCM-41, SBA-15, alumina, activated carbon, alumina intercalated laponite etc.) have been tried to improve catalytic activity in a single step catalytic oxidation of H<sub>2</sub>S [11–15]. Iron oxide, which is Super-Claus catalyst, is known one of the oldest catalysts tested in oxidation of H<sub>2</sub>S. Also, its lower cost and availability are advantages of iron oxide catalyst. Additionally, relatively high activity of iron based catalyst for oxidation of H<sub>2</sub>S was reported in the literature. However, iron oxide catalyst requires excess amount of oxygen in order to obtain elemental sulfur [16]. Number investigations were tried to modify iron oxide catalyst to achieve high sulfur selectivity. Nguyen et al. studied on thermal conductivity of silicon carbide (β-SiC) supported Fe<sub>2</sub>O<sub>3</sub> catalyst. They have also reported silica supported Fe-containing catalysts [17,18]. Our previous study showed that sulfur selectivity and stability of iron oxide catalyst could be significantly enhanced by the incorporation of cerium into the catalyst structure [16]. Vanadium based catalysts with good

redox properties are also known to be highly active in partial oxidation of hydrocarbon and selective oxidation of hydrogen sulfide. Our earlier studies indicated that oxidation state of vanadium in the catalyst structure had a major role to achieve high sulfur yield. Bimetallic Cu–V catalysts (Cu/V ratio of 1/1) containing partially reduced vanadium in V<sup>+4</sup> state were highly selective to elemental sulfur. However, elemental sulfur yield was significantly decreased when catalyst was in V<sup>+5</sup> state [19,20]. In the study performed by Barba et al., catalytic performances of vanadium-based materials, supported on mixed metal oxides (CeO<sub>2</sub>, TiO<sub>2</sub>, CuFe<sub>2</sub>O<sub>4</sub>) were investigated for partial selective oxidation of H<sub>2</sub>S, at low temperatures (50–250 °C). In that study, high H<sub>2</sub>S conversion was obtained with V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>/CuFe<sub>2</sub>O<sub>4</sub> catalysts [21]. In the recent work of Palma and Barba, V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub> catalysts were investigated for low temperature catalytic oxidation of H<sub>2</sub>S. They proposed possible surface reaction mechanism for H<sub>2</sub>S oxidation to sulfur [22]. In another work of Tan et al., a series of Mn-substituted LaCrO<sub>3</sub> were prepared by self combustion technique and tested as sulfur tolerant anode catalysts in solid oxide fuel cell using fuel gas containing H<sub>2</sub>S [23].

It was reported by Mobil Oil researchers that TiO<sub>2</sub>-based catalysts can be used to oxidize H<sub>2</sub>S to elemental sulfur using stoichiometric amount of O<sub>2</sub> in the MODOP (Mobil Direct Oxidation Process). However, this type catalyst was reported to deactivate in the presence of water [17]. In addition to the catalysts mentioned above, chromium oxide based catalysts which were industrially used in dehydrogenation reaction [24,25], may also have some potential in this reaction. In the literature, studies with the titanium based catalysts are quite limited, as compared to iron and vanadium based catalysts, for selective oxidation of H<sub>2</sub>S to elemental sulfur [8,10].

The objective of the present study is to improve the selectivity and catalytic performance of titanium dioxide based catalysts with the aid of the synergistic effects of bimetallic titanium/iron, titanium/chromium and titanium/zirconium. New bimetallic catalysts, namely Ti–Fe, Ti–Cr, and Ti–Zr were synthesized by the complexation method and their catalytic performances were investigated in selective catalytic oxidation of H<sub>2</sub>S to elemental sulfur, in the temperature range of 200–300 °C and at different O<sub>2</sub>/H<sub>2</sub>S ratios.

## Experimental method

### Catalyst preparation and characterization

In this study, titanium based iron (Ti–Fe), chromium (Ti–Cr) and zirconium (Ti–Zr) catalysts, having equimolar ratios were synthesized by the modification of complexation method, which was originally described by Marcilly et al. [26]. In this synthesis method, equimolar ratio of citric acid and metal salt were mixed in a solution, where ethanol (Merck) was used as solvent. Then, this solution was evaporated at 65 °C for about 3 h, with continuously stirring, until its viscosity had noticeable increased. Evaporation time of solution is markedly decreased due to the use of ethanol. In the second step of synthesis, dehydration was completed in an oven at 65 °C, by placing the viscous solution as a thin layer in a glass dish. The solid foam formed in this step was then calcined at

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