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Simultaneous Production of H₂ and Sulphur by catalytic oxidative decomposition of H₂S

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Abstract

The recovery of hydrogen from H₂S has recently attracted attention because of the economic and environmental advantages: hydrogen is an energy source, a raw material for chemical industry and in the near future it could become a significant fuel.

A great amount of H₂S is obtained as a by-product during the H₂ reduction processes and the hydrodesulphurization of petroleum and, due to the stringent environmental regulations, H₂S has to be removed before its release in the environment. Hydrogen Sulphide is usually removed by the well-known Claus process, where H₂S is oxidized to water and elemental Sulphur by two-step reactions. This process is not profitable from an economic point of view because the price of the Sulphur (the primary product) is depressed and the hydrogen is lost as water. Furthermore, due to the thermodynamic limitations, H₂S conversion in the catalytic stage is limited to ~95-97%, as a consequence further treatments of the residual tail gas are necessary.

So, an attractive alternative could be to produce simultaneously Sulphur and hydrogen by thermal decomposition of H₂S ($\text{H}_2\text{S} = \text{H}_2 + 1/2 \text{S}_2$). Unfortunately, this reaction is very endothermic and it is thermodynamically favored only for extremely high temperatures, thus requiring large amounts of energy and subsequent separation stages with high fixed and operating costs.

A possible solution could be to couple the decomposition reaction with an exothermic reaction, making the system auto-thermal.

For this purpose, the reaction of H₂S oxidative decomposition at high temperature was studied; the main objective of this work was to find a catalyst active and selective to Sulphur and H₂, depressing the possible SO₂ formation related to the presence of the oxygen in the reaction system.

First of all, this reaction was studied in homogeneous phase, by varying the main operating conditions such as temperature, O₂/H₂S, residence time. The results have shown an approach of H₂S conversion and H₂ yield to equilibrium values only at high temperature (1273–1373 K) but with a SO₂ selectivity higher than one expected from equilibrium calculations.

Different sulphide-based catalysts supported on Al_2O_3 , both monometallic and bimetallic, were prepared, characterized and tested under different operating conditions.

MoS_2 -based catalysts have shown good results at 1273 K, even at very low contact times (20-40 ms) and at high H_2S inlet concentration (40 vol%) in terms of H_2S conversion, H_2 yield and SO_2 selectivity, exhibiting values very close to those expected from the thermodynamic equilibrium.

Based on the experimental collected data, a kinetic macroscopic model able to describe the main reactions was also developed and compared with the homogeneous phase reaction system. The results have evidenced that $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst (at 10 wt % MoS_2), was able to promote the Claus reaction, besides the H_2S decomposition reaction and the partial oxidation to Sulphur, determining a decrease of the SO_2 formation.

The system was also studied in the presence of CH_4 in the feed stream. The results showed that the MoS_2 -based catalysts has favored the formation of undesired by-products as COS and CS_2 . Different mono and bimetallic catalysts were also tested and compared. The best results in terms of H_2S conversion, H_2 yield, and SO_2 , COS and CS_2 selectivity were obtained in the case of the Mo-Fe bimetallic samples.

As a consequence, the bimetallic 10 wt% MoS_2 - 5 wt% $\text{FeS}_2/\text{Al}_2\text{O}_3$ sample was tested also in presence of ammonia, ensuring a complete NH_3 conversion at 1333 K with a contact time of 1 s.

Finally, the active phases were supported on cordierite honeycombs monolith, which were tested for 25 hours at $T=1333$ K in presence of a feed stream with a defined composition, representative of a typical refinery stream.

The catalytic activity of the structured catalyst was also tested for 30 h of TOS at very high temperatures and very stressing conditions in terms of H_2S , NH_3 , CH_4 and Oxygen concentrations. The results showed that also in these conditions, an almost total NH_3 conversion is possible without any significative apparent deactivation phenomena, making this catalyst a suitable system for H_2S oxidative decomposition in presence of other compounds, such as methane and ammonia.

