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Catalytic Oxidative Decomposition of H_2S for Hydrogen Production

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A supported metal sulphide - based catalyst was prepared and studied for the reaction of H_2S oxidative decomposition to produce simultaneously H_2 and sulphur. The study was carried out by investigating different operating conditions such as H_2S inlet concentration (10 - 40 vol%), O_2/H_2S feeding molar ratio (0.2 - 0.35) and reaction temperature (700 – 1,100 °C) with the aim to minimize SO_2 selectivity and maximize the H_2 yield together with a good H_2S conversion. From the preliminary experimental tests, it was possible to identify the optimal operating conditions (T = 1,100 °C, H_2S = 10 vol%, O_2/H_2S = 0.2), suitable to obtain a high H_2S conversion (59 %), a good H_2 yield (20 %) and depressing the SO_2 selectivity (< 0.05 %). The catalyst showed a good activity and stability during 10 h of time on stream without any deactivation phenomena. The presence of the catalyst resulted in an improvement of both H_2S decomposition reaction to produce H_2 and partial oxidation reaction to sulphur, realizing simultaneously the abatement of SO_2 by the Claus reaction.

1. Introduction

H_2 can be produced from a variety of feedstock. These include fossil resources, such as natural gas and coal, as well as renewable resources. A very interesting alternative could be the recovery of H_2 from chemical substances identified as pollutants, such as H_2S. H_2S is a by-product from sweetening of sour natural gas, hydrodesulphurization of light hydrocarbons, and from upgrading of heavy oils, bitumen and coals. H_2S is usually removed by the well-known Claus process in which H_2S is oxidized to water and elemental sulphur by a two-step reaction (Clark et al., 2004).

Because of the significant amounts of H_2S available worldwide, efforts have been made in recent years to obtain H_2 and sulphur from H_2S through different approaches. It is widely recognized that the most direct process to convert H_2S into H_2 and sulphur is the catalytic or non-catalytic thermal decomposition. The decomposition of H_2S can be enhanced with respect to the homogeneous reaction by using highly active heterogeneous catalysts (Reshetenko et al., 2002). Sulphides transition metals oxides supported on Al_2O_3 (Bishara et al., 1987) have been studied in heterogeneous high-temperature decomposition of hydrogen sulphide in the absence of O_2.

Despite the presence of several studies, no method for H_2S decomposition can be considered commercially feasible today. In fact, on the basis of thermodynamic and energetic considerations on this reaction, this approach has been considered impractical from an industrial point of view (Norman et al., 1984).

Partial oxidation of H_2S at high temperature could be a cost-effective process that may overcome thermodynamic limitations of the H_2S thermal decomposition, but the formulation of a selective catalyst must be improved in order to further decrease the SO_2 formation (Palo et al., 2014).

It must be underlined that the environmental regulations will become more and more stringent towards the SO_2 emissions to the atmosphere, which actually should be much lower than 150 mg/Nm^3 (lower than 50 ppm) (Colozzi et al., 2016). New process schemes of the sulphur recovery plants are required in order to be in compliance with such strictest future regulations (Colozzi et al., 2016).

Then, the objective of this work is to study an innovative process based on the H_2S oxidative decomposition for the concurrent production of sulphur and H_2, with SO_2 zero emission.

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In a previous work, the thermal H_2S decomposition reaction in presence of oxygen was studied in homogeneous phase in a wide temperature range (700 – 1,100 °C); an approach of the H_2S conversion and H_2 yield to the equilibrium values was observed only at high temperature (1,000 – 1,100 °C), obtaining unfortunately a SO_2 selectivity significantly higher than that one expected from equilibrium calculations (Palma et al., 2016). On the other hand, preliminary interesting results were obtained using an alumina-based catalyst that allowed to minimize the SO_2 formation at very low contact times (~20 ms), with together H_2S conversion and the H_2 yield very close to the thermodynamic values (Palma et al., 2017).

To our knowledge no papers regarding the use of a catalyst different than alumina in the oxidative H_2S decomposition for the simultaneous production of H_2 and sulphur have been published.

For this reason, in this work, the oxidative decomposition of H_2S has been assessed for the first time using a metal sulphide - based catalyst supported on Al_2O_3. The influence of the main operating conditions on H_2S conversion, H_2 yield and SO_2 selectivity has been investigated in order to improve the process selectivity towards H_2 and sulphur.

2. Experimental

A molybdenum sulphide-based catalyst was prepared by wet impregnation of alumina using a precursor salt of molybdenum species. Catalytic experiments were carried out in a fixed bed quartz reactor consisting of a tube with 300 mm length and internal diameter of 12 mm.

Sulphur and other solid species produced by the reaction were trapped by using a quartz-wool filter placed at the outlet of the reactor in the quenching zone. The schematic picture of the experimental apparatus is reported in our previous paper (Palma et al., 2017).

In order to avoid the SO_2 absorption in the water produced from the reaction, a cold trap was placed after the quenching zone allowing to remove selectively sulphur and water without SO_2 absorption (Palma et al., 2015). The exhaust stream was analysed by a quadrupole filter mass spectrometer (Hiden HPR 20).

The operating conditions are reported in Table 1:

Table 1: Operating conditions for the activity tests

Temperature, °C	H_2S concentration, vol%	O_2/H_2S molar ratio, [-]	Contact time, ms
700 – 1,100	10 - 40	0.2 - 0.35	30

The evaluation of the catalytic performance in terms of H_2S conversion (x H_2S), SO_2 selectivity (s SO_2) and H_2 yield (y H_2) were calculated by using the following equations:

$$x\,H_2S(\%) = \frac{(zH_2S_{IN} - zH_2S_{OUT})}{zH_2S_{IN}} \cdot 100 \tag{1}$$

$$s\,SO_2(\%) = \frac{zSO_{2\,OUT}}{(zH_2S_{IN} - zH_2S_{OUT})} \cdot 100 \tag{2}$$

$$y\,H_2(\%) = \frac{zH_{2\,OUT}}{zH_2S_{IN}} \cdot 100 \tag{3}$$

where:
zH_2S_{IN}: Inlet H_2S volumetric fraction [-],
zH_2S_{OUT}: Outlet H_2S volumetric fraction [-],
zSO_{2OUT}: Outlet SO_2 volumetric fraction [-],
zH_{2OUT}: Outlet H_2 volumetric fraction [-].

3. Results

3.1. Effect of the H2S inlet Concentration and O_2/H_2S Feeding Molar Ratio

The results related to molybdenum sulfide - based catalyst obtained at different H_2S inlet concentration, between 10 and 40 vol%, are reported in terms of H_2S conversion, H_2 yield and SO_2 selectivity at 1,000 °C with O_2/H_2S equal to 0.2 (Figure 1).

By increasing the H_2S inlet concentration, the decrease of H_2S conversion and H_2 yield were obtained and unfortunately a slight increase of the SO_2 selectivity was observed.

The best results were obtained by feeding a H_2S concentration of 10 vol%, which allowed to achieve a H_2S conversion of about 55 %, the H_2 yield close to the equilibrium value (15 %) and SO_2 selectivity lower than 1 %. Based on these results the other tests were carried out with a H_2S inlet concentration equal to 10 vol%.

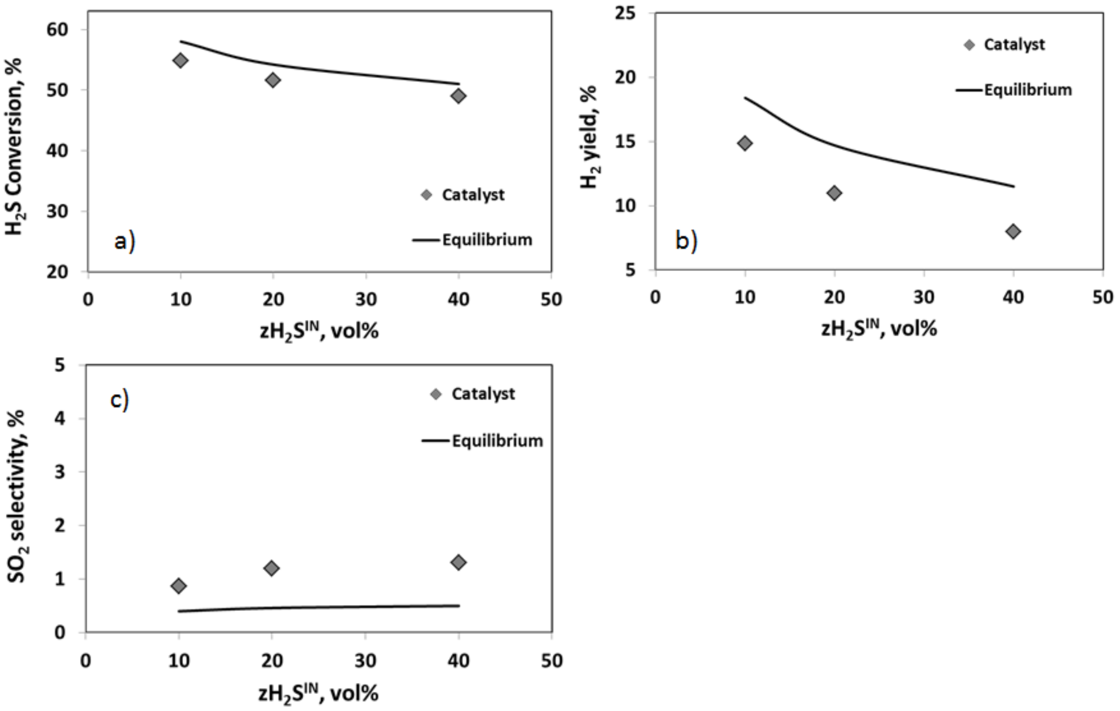

Figure 1: Influence of the H_2S inlet concentration on the H_2S conversion (a), H_2 yield (b) and SO_2 selectivity (c) in comparison with the equilibrium data (T = 1,000°C, O_2/H_2S = 0.2).

The results of the catalytic tests with different feeding molar ratio (O_2/H_2S) are reported in Figure 2.

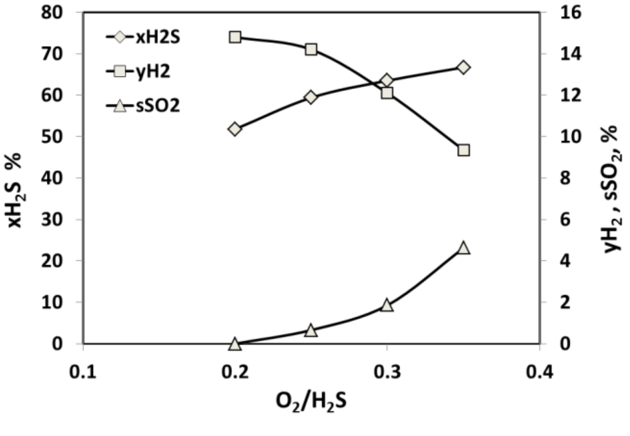

Figure 2: Catalytic performances at different O_2/H_2S feeding molar ratio (T = 1,000 °C).

As it is expected, the increase of feeding molar ratio from 0.2 to 0.35 determined an increase of H_2S conversion and SO_2 selectivity and a slight decrease of H_2 yield. These results can be explained considering that the total H_2S oxidation reaction (producing SO_2 and H_2O) may occur together with the H_2S oxidative decomposition reaction, thus leading to an increase of the H_2S conversion but reducing the H_2 production due to the SO_2 formation.

Based on the obtained results, the optimal O_2/H_2S feeding molar ratio that allows to minimise the SO_2 selectivity and maximize the H_2 yield together with a high H_2S conversion, is equal to 0.2.

3.2 Influence of the Reaction Temperature

The influence of the reaction temperature, between 700 – 1,100 °C was investigated on Al_2O_3 support and on the final catalyst (Figure 3). The thermodynamic equilibrium data and the results of the homogenous phase reaction are also reported in the same Figure.

In general, by increasing the reaction temperature, an increase of H_2S conversion and H_2 yield was observed; in particular their values were close to the thermodynamic equilibrium data in almost all the investigated reaction temperatures.

Only at T = 1,100 °C, the H_2S conversion has started to deviate from the equilibrium thermodynamic trend, likely due to the contribution of the homogeneous reactions that becomes very important. In fact, the H_2S conversion obtained in the presence of catalyst is the same of that one observed in the homogenous case (Figure3a).

The decrease of H_2S conversion at 1,100 °C caused consequently a decrease of H_2 yield (Figure 3b).

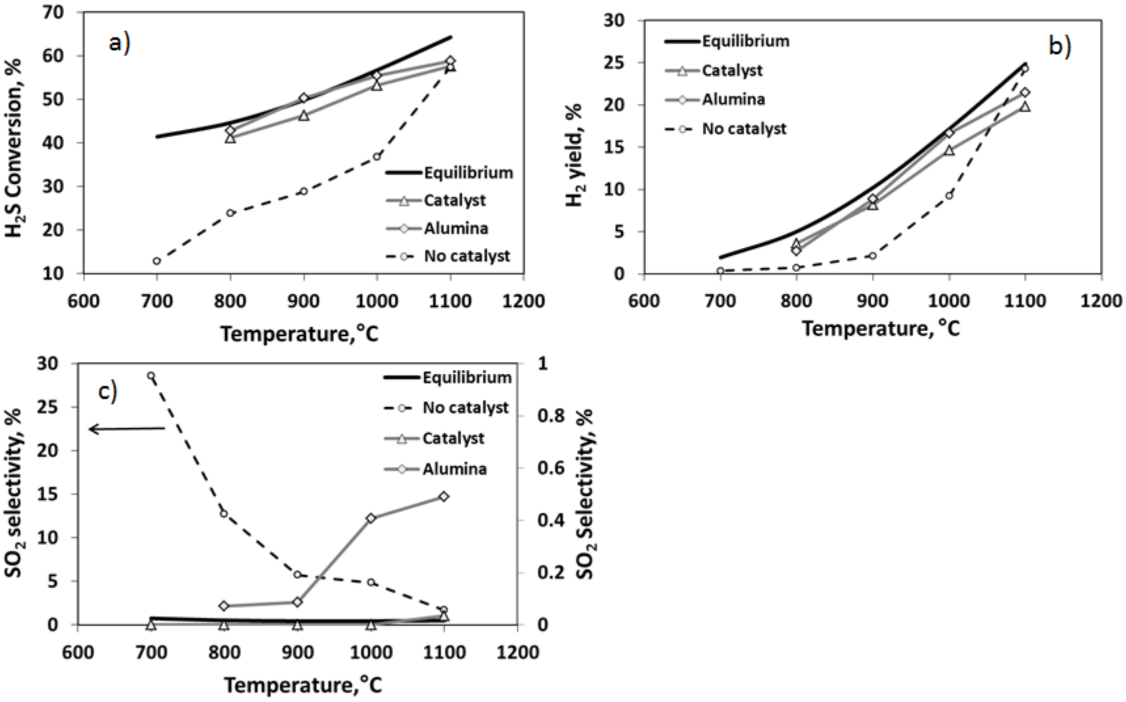

Figure 3: Effect of the reaction temperature on the H_2S conversion (a), H_2 yield (b) and SO_2 selectivity (c) in comparison with the equilibrium data (zH_2S_{IN} =10 vol%, O_2/H_2S = 0.2).

It is worthwhile to note that the SO_2 selectivity obtained in homogenous phase showed values higher than the thermodynamic equilibrium data in all the temperature range investigated, because in these conditions, the kinetic effect is very significant, and the reaction system is very far from equilibrium (Figure 3c). In fact, for temperatures lower than 1,100 °C, the difference between the equilibrium values and the experimental data is even more dramatic. This result could be explained considering that, the total oxidation reaction of H_2S to SO_2 is more favoured from a kinetic point of view with respect to the other reactions (H_2S partial oxidation, H_2S decomposition, Claus reaction), and as a consequence, the SO_2 concentration in the gas phase is higher.

The influence of the catalyst on the SO_2 selectivity with respect to the Al_2O_3 support and equilibrium values is better evidenced in Figure 4.

In presence of the only support, the experimental SO_2 selectivity was even lower than the equilibrium data up to 900 °C, while for higher temperatures it is possible to observe an approach to the equilibrium, maybe because it begins to be significant also the contribution of the homogeneous reactions.

The SO_2 selectivity at temperature of 1,100°C was <0.05 % corresponding to ~30 ppm in presence of catalyst. On the contrary, in presence of Al_2O_3 the SO_2 selectivity was ~0.5 % (~300 ppm).

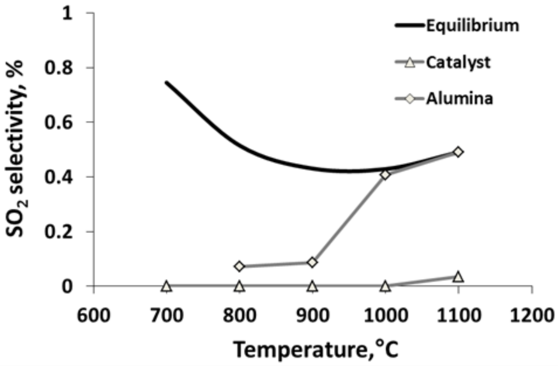

Figure 4: Effect of the temperature in terms of SO_2 selectivity in presence of the support and the catalyst in comparison with the equilibrium data (zH_2S_{IN} =10 vol%, O_2/H_2S = 0.2).

3.3 Stability Test

The behaviour of a typical catalytic test performed at the temperature of 1000 °C is reported in Figure 5.
The results show the concentration profile of the species involved in the reaction such as H_2S, O_2, H_2, SO_2. After the stabilization of H_2S and O_2 inlet concentration values (H_2S =10 vol%, O_2 = 2 vol%) in by-pass position, the feed stream is sent to the reactor and the H_2S and O_2 outlet concentrations immediately decrease whereas the products concentration increases reaching a steady state value.

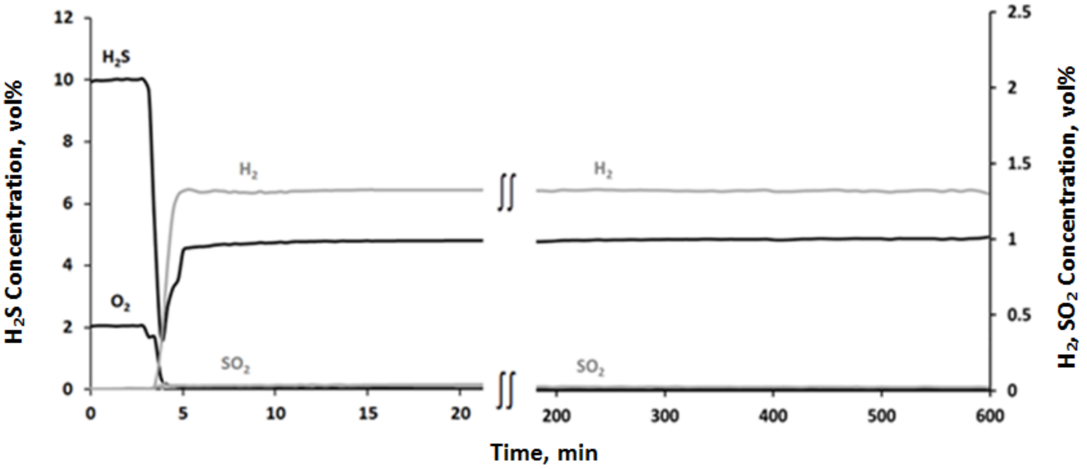

Figure 5: Stability test (T = 1,000 °C, zH_2S_{IN} = 10 vol%, O_2/H_2S = 0.2, contact time = 30 ms).

The final value of H_2S conversion was about 51 % with a total consumption of oxygen; the H_2 yield was equal to 13 % and no formation of SO_2 was observed in the overall test time.
Moreover, any evident deactivation phenomena were observed evidencing the good stability of the catalyst.

4. Conclusions

The reaction of the H_2S oxidative decomposition for the simultaneous production of H_2 and sulphur at high temperature was studied in presence of a molybdenum-based catalyst supported on Al_2O_3.
The influence of the main operating conditions, such as H_2S concentration (10 - 40 vol%), O_2/H_2S feeding molar ratio (0.2 - 0.35) and reaction temperature (T = 700 – 1,100 °C) were studied in order to minimize as much as possible the SO_2 selectivity, assuring a good H_2S conversion and H_2 yield.
The increase of the H_2S inlet concentration from 10 up to 40 vol% has determined a decrease of H_2 yield and a slight increase of the SO_2 selectivity; the same behaviour was observed by increasing the feeding molar ratio O_2/H_2S, evidencing that the SO_2 formation is strictly related to the presence of the oxygen in the reaction system.
The tests at different reaction temperatures evidenced that, with respect to the Al_2O_3 support and to the

homogeneous reaction, the catalyst was able to minimize the SO_2 selectivity allowing to obtain H_2S conversion and H_2 yield values very close to those ones expected by the thermodynamic equilibrium.

Based on the obtained results, the optimal operating conditions suitable to obtain a high H_2S conversion (59 %), a good H_2 yield (20 %) with a very low SO_2 selectivity (< 0.05 %) were identified (T=1,100 °C, $O_2/H_2S = 0.2$, H_2S =10 vol%).

The preliminary stability test (10 h) performed on the catalyst has not evidenced deactivation phenomena.

In particular, after 10 h of run time, the H_2S conversion and H_2 yield were about 50 % and 13 %, and only a negligible SO_2 formation was observed.

In summary, the molybdenum-based catalyst has favoured both the H_2S thermal decomposition reaction to produce H_2 and sulphur and the H_2S partial oxidation reaction to sulphur and water, promoting also the consumption of SO_2 by the Claus reaction. Therefore, these results may be the starting point to investigate a feed stream more complex, containing simultaneously a high H_2S concentration (up to 70 vol%), hydrocarbons, and ammonia, in order to verify the effectiveness of the formulated catalyst in presence of a representative refinery stream. The catalyst performance may assure to achieve simultaneously a high conversion of H_2S, hydrocarbons and NH_3, a good H_2 yield and the minimisation of the undesired by-products, such as COS, CS_2, SO_2, NO_X in order to avoid additional treatment stages.

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