Determination of the chemical and hydrothermal stability of the Claus catalyst

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Abstract. The hydrothermal and thermal stability used in the Claus process are important indicators in their workflow. In this work, the stability of two catalyst samples obtained from local raw materials was studied. The samples were processed with SO2 / O2 oxides and water vapor, and their properties were studied. As a result, SO2 adsorption reduced catalyst activation. The process is reductive; the recovery of catalyst activation by reducing SO2 in the system has been determined. The stability of sulfation of MgO / TiO2 catalyst in comparison with CaO / V2O5 samples was also determined.

1 Introduction

The largest sources of air pollution with sulfur compounds are sour gases resulting from the purification of oil and natural gas from hydrogen sulfide and mercaptans and waste gases from non-ferrous metallurgy enterprises. The Claus process is widely used to recover sulfur from such gases. The main disadvantage of modern industrial catalysts for the Claus process based on alumina and titanium dioxide is their deactivation due to the formation of surface sulfates, which leads to a decrease in activity in the Claus reaction and the hydrolysis reaction of COS and CS2.

During operation, industrial catalysts gradually undergo irreversible changes: the specific surface area and total porosity decrease, and the catalytic activity decreases. Of the variety of reasons causing the deactivation of Claus catalysts, the most important are:

- thermal and hydrothermal aging with the transformation of the structure and texture of the catalyst;
- sulfation of the catalyst surface;
- deposition of liquid sulfur on the surface and in the pore volume of the catalyst;
- a decrease in the specific surface area and pore volume of the catalyst due to coke deposits.

The generalization of many years of experience in the industrial operation of alumina catalysts [1-2] shows that the main responsibility for their deactivation is the change in the chemical properties and texture of Al2O3 as a result of the formation and deposition of sulfates. Catalyst

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samples taken from Claus industrial plants contain sulfates in amounts ranging from 1% to 10%.

In real conditions [3], the gas mixture, in addition to H₂S, contains SO₂ up to 30% vol. water vapor. Most oxides of metals of variable valence (for example, Cu, Fe, Co, Bi, Mo, Ni, Sb), proposed as catalysts for the oxidation of hydrogen sulfide with oxygen and/or sulfur dioxide, under the action of H₂S form sulfides and significantly lose their initial activity in the Claus reaction [4] and direct oxidation reactions [5].

With an increase in the ratio of oxidant/hydrogen sulfide, the sulfation of catalysts can occur. It is known from the literature [6] that the sulfur yield in the catalytic stages decreases rapidly with an increase in the content of sulfates in the catalyst. The main reason for the sulfation of catalysts is oxygen and water in the process gases and the difficulty in controlling the H₂S / SO₂ ratio (excess SO₂). Sulfation especially significantly reduces the activity of catalysts in low-temperature processes used to carry out the reaction at temperatures below the dew point of sulfur ("Sulfrene"). Under conditions when the H₂S / SO₂ molar ratio is close to stoichiometric, and there is no oxygen in the gas mixture, an equilibrium concentration of sulfates occurs on the surface of the alumina catalyst in the reaction medium, which, depending on the process temperature, is 2-3 wt%. [7]. The concentration of sulfates on the surface does not practically change during 60 months of operation [8]. In the presence of an excess of an oxidizing agent (SO₂, O₂) in gas mixtures containing water vapor, the amount of sulfates on the catalyst surface becomes above equilibrium and increases with time. This leads to a gradual loss of catalyst activity, which is restored after regeneration. Thus, the amount of sulfation, and, consequently, the activity of the catalyst, depends on the content of water, sulfur dioxide, and oxygen in the reaction medium.

The presence of water vapor significantly affects the thermodynamics [9] and the kinetics of the process [10]. Water vapor displaces the equilibrium of the reversible Claus reaction; the reaction is inhibited by water vapor due to the competitive adsorption of water on the catalyst's active sites.

In addition, water vapor is the main cause of irreversible catalyst deactivation due to hydrothermal degradation. In most works, when testing catalysts, either deactivation of the catalyst is not taken into account at all [11], or only the sulfation of the catalyst is taken into account by performing an aging test, by treatment with a mixture with different contents of SO₂/O₂ [12,13]. Only several works propose a technique for simulating hydrothermal aging.

2 Methods

The procedure for preparing alumina granule samples is based on the following stages:
- preparation of raw materials and their grinding (disintegration);
- granulation by the pelletizing method;
- physical and chemical processing;
- sieving granules;
- calcination;
- rescreening of granules and packaging of the finished product.

To prepare the catalyst, waste alumina adsorbent is used and in the form of an active component vanadium oxide, calcium hydroxide (1), and magnesium nitrate, titanium dioxide (2). Two different samples were taken: 1. Titanium dioxide and magnesium oxide as active ingredients; 2. Vanadium (V) oxide and calcium oxide as active ingredients. The disintegrated product, which mainly consists of particles less than 100 microns in size, while the fraction of the fraction less than 50 microns must be at least 75%, is dosed onto a
disc granulator at a speed of n = 18 rpm, in which a finely atomized solution is simultaneously fed binder (solution of calcium hydroxide, magnesium nitrate or water).

After the granulator, the resulting intermediate product with a moisture content of 20-25% enters the reactor of physicochemical treatment, where it is kept in saturated water vapor for at least 2 hours at a temperature of 85-90 °C. Then, the granules are sieved and dried at 120 °C for 24 hours, after which they were calcined at 420–550 °C in a stream of dried air (dew point is not higher than −40 °C). The pellets were heated at a rate of 70 °C/h. The duration of calcination after reaching the regime was 4 hours.

Hydrolysis of COS to CO₂ and H₂S was carried out in a flow reactor. Pure oxides or impregnated sulfated samples were first washed in the reactor for 2 hours at 543 K: the temperature was set equal to the reaction temperature. Water was transferred from a thermostated saturator in a controlled flow of helium, and 2.7 mmol·h⁻¹ COS was added to the feed so that the composition of the feed was as follows: 1% COS, 2.2% H₂O, and 96.8% He. It was passed through a temperature-controlled pyrex glass reactor containing a fixed bed of catalyst (0.025 g with a particle size in the 0.4 μm range). All samples were tested under such conditions to avoid diffusion phenomena. This made it possible to directly compare the conversion (% conversion per square meter) after 30 minutes of submission. In another series of experiments, 0.2% SO₂ was continuously added to the feed to monitor its toxic effect. After stabilization of activity, SO₂ was turned off, and the conversion was measured again.

3 Results and Discussion

To determine the resistance of the catalyst to sulfation, the samples were treated with a SO₂/O₂ gas mixture at 200–320 °C for 5 hours.

Figure 1 shows a decrease in the activity of the samples when SO₂ is introduced into the feed, regardless of the metal oxide. Since the effect of SO₂ is relatively less pronounced on TiO₂, the order of activity in the presence of SO₂ becomes as follows: 1>2. Cutting out SO₂ in the feed restores the original activity, showing that SO₂ poisoning is almost completely reversible (Figure 1). These results well explain why the addition of SO₂ to the feed gas partially inhibits COS hydrolysis. SO₂ and COS are competitively adsorbed on the same main Bronsted centers, and the former are adsorbed more strongly than the latter.

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**Fig.1.** Effect of SO₂ (0.2%) on the hydrolysis of COS at 503 K (1. MgO + TiO₂; 2. CaO + V₂O₅).
The loading of pure oxides with sulfates decreases the catalytic activity regardless of the sample (Fig. 2). When the amount of sulfate reaches 0.8 mmol • m⁻², the degree of deactivation changes in the following order: 2>1 so that V₂O₅ becomes more active than TiO₂. Sulfate particles are well characterized by an IR band of 1360 cm⁻¹ on samples activated for 2 hours at 723 K, and their number is proportional to its intensity [14]. We measured the sulfate concentration by this spectroscopic method before and after the reaction. The amounts of sulfate did not appear to change, indicating that they are stable and not reduced by H₂S, one of the reaction products under the reaction conditions used.

The pulse introduction of oxygen into the gas supply during the OH reaction on pure oxides leads to the same effect as presulfation: an irreversible decrease in catalytic activity is observed. For two samples, it was completed after two pulses and is much higher on TiO₂ (68%) than on V₂O₅ (55%). In the IR spectra of the samples after these experiments, there are characteristic bands of the already described sulfate forms. Their number changes in the following order: TiO₂>V₂O₅ and corresponds well to the observed deactivation. It is important to note that pulsed sulfation is more significant on TiO₂ than the less alkaline sample. Under real conditions, alumina undergoes various types of aging (sulfation, reduced surface area), either due to normal use or for some random reason. To better understand the performance of a catalyst, it is necessary to look at the aging process.

Therefore, we have developed the following procedure to simulate aging: treatment at 400-550 °C for 12 hours in a stream of nitrogen with 50% steam.

**Table 1.** Results of hydrothermal aging of the catalyst (depending on time).

| Time, min | 0  | 6  | 8  | 10 | 12 |
|-----------|----|----|----|----|----|
| Surface area, m²/g | 290 | 250 | 200 | 165 | 130 |
| Mechanical strength MPa | 8  | 6.5 | 5  | 4  | 3.5 |
| Total pore volume, cm³/g | 0.55 | 0.48 | 0.42 | 0.38 | 0.33 |
| Density, g/cm³ | 0.69 | 0.70 | 0.72 | 0.73 | 0.75 |
| Macropores, g/cm³ | 0.31 | 0.32 | 0.30 | 0.29 | 0.29 |
| Micropores, g/cm³ | 0.24 | 0.16 | 0.12 | 0.11 | 0.4 |

The main consequence of this is that the catalyst surface area is reduced to 130 m²/g, which is close to the level at which users recharge the alumina in their units. This decrease is
caused by the collapse of micropores with a diameter of less than 40 Å, as seen from the porosity distribution measured by mercury porosimetry. No macropore modification is observed.

**Table 2.** Results of hydrothermal aging of the catalyst (depending on temperature).

| Temperature, °C | 200 | 230 | 260 | 290 | 320 |
|----------------|-----|-----|-----|-----|-----|
| Surface area, m²/g | 290 | 250 | 200 | 165 | 130 |
| Mechanical strength MPa | 8   | 6.5 | 5   | 4   | 3.5 |
| Total pore volume, cm³/g | 0.55 | 0.48 | 0.42 | 0.38 | 0.33 |
| Density, g/cm³ | 0.69 | 0.70 | 0.72 | 0.73 | 0.75 |
| Macropores, g/cm³ | 0.31 | 0.32 | 0.30 | 0.29 | 0.29 |
| Micropores, g/cm³ | 0.24 | 0.16 | 0.12 | 0.11 | 0.4 |

**4 Conclusions**

This study showed that the catalytic activities of the alumina and titanium-based system were decreased due to hydrothermal aging and sulfur poisoning. SO₂ adsorption occurs in the same areas as during COS hydrolysis. These results explain why the addition of SO₂ to the test gas partially inhibits conversion. The reversibility of SO₂ poisoning occurs due to the desorption of hydrosulfite species when SO₂ is turned off and also due to the reaction between residual hydrogen sulfite species and H₂S (Claus reaction) formed during the hydrolysis of COS.

The sulfation of metal oxides poisons the main centers and creates Bronsted acidity, which explains the deactivation of the catalyst (23). The sulfate compounds are quite stable even in the presence of water under the conditions used. It was found that samples based on titanium and magnesium oxide are more resistant to sulfation.

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