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A new Claus catalyst to reduce atmospheric pollution

Christophe Nédez [a,*], Jean-Louis Ray [b]

[a] Rhône-Poulenc Recherches, 52 rue de la Haie-Coq, 93308 Aubervilliers Cedex, France
[b] Procatalyse, 212-216 avenue Paul Doumer, 92500 Rueil-Malmaison, France

Abstract

The discovery of two new concepts have made it possible to draw the physico-chemical map of the best alumina Claus catalyst. An optimized profile of the ultramacroporosity, between 0.1 and 1 μm, reduces diffusional constraints. A low sodium (Na_2O) content (< 2500 ppm) reduces the sulphation, thus slowing down the deactivation of the catalyst.

Keywords: Claus catalyst; Atmospheric pollution

1. Introduction

Claus catalysis consists in transforming into elementary sulphur the hydrogen sulphide present in gases of different origins (natural gas, refinery gas or coal gasification gas) [1]. Exploitation of H_2S-rich oil fields and development of hydrotreatments such as hydrodesulphurization (in refineries) produce greater quantities of H_2S, which have to be treated.

Invented at the end of the last century, Claus catalysis consisted first of a direct oxidation of H_2S in sulphur according to the following equation:

$$H_2S + 1/2O_2 \rightarrow 1/x\, S_x + H_2O \qquad (1)$$

Since important thermodynamic limitations considerably reduced the efficiency of this reaction, the H_2S treatment was separated into two steps during the 1930s. The first step is thermal and consists of the oxidation of one third of the H_2S in SO_2 (Eq. (2)); almost 70% of the sulphur compound is already been recovered as elementary sulphur. The second step enters the world of catalysis (Eq. (3)).

$$1/3H_2S + 1/2O_2 \rightarrow 1/3SO_2 + 1/3H_2O \qquad (2)$$

$$2H_2S + SO_2 \rightarrow 3/xS_x + 2H_2O \qquad (3)$$

Several (generally three) reactors are hooked up in cascade (Fig. 1). They operate at decreasing temperatures in order to obtain a high yield in sulphur recovery.

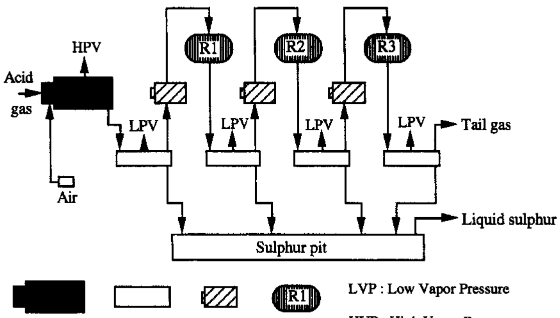

Fig. 1. Conventional modern Claus process configuration.

* Corresponding author.

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All sulphur compounds which are not transformed into elementary sulphur during the catalytic stages are oxidized into sulphur dioxide in either a thermal or a catalytic incinerator and then vented to the atmosphere. But sulphur dioxide represents a genuine threat to the environment because it can react with atmospheric moisture and oxygen to form sulphuric acid, which is partially responsible for acid rain [2].

Effective protection of the environment depends on the optimization of the sulphur recovery yields. Governments have understood this problem and have constantly tightened regulations limiting the SO_2 tonnage emitted by each unit. Regulations to protect nature will continue to drive us to enhance the level of sulphur recovery [3]. The best possible sulphur yields must be obtained before incineration.

The improvements made in tail gas treatments (like the Sulfreen process, for example) are thus a positive development [4,5]. Another path to ensure good performances in a modern sulphur plant involves improving the catalysts to be used in Claus reactors. Therefore, improving the catalysts will always be a priority.

In addition to a high level of performance in the conventional Claus reaction (Eq. (3)), a good catalyst must perform as well as possible in COS hydrolysis (Eq. (4)) and CS_2 hydrolysis (Eq. (5)). COS and CS_2, formed during the thermal stage, are two important by-products present in the gases to be treated. Their presence is not a minor problem, given that in a modern sulphur plant 50% of the yield losses in sulphur recovery may be due to an insufficient hydrolysis of these two components.

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad (4)$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \qquad (5)$$

While a decrease in temperature will favor the displacement of the reaction (3) towards the right, it will handicap hydrolysis reactions. The presence of oxygen, due to the use of a burner and heat exchangers, also plays an important role because even low levels of oxygen will induce a sulphation, leading to a relatively significant deactivation of the catalyst.

The most efficient catalyst on the market: the Procatalyse's CRS 31, is made from titanium dioxide. Titanium dioxide is very active in the Claus reaction as well as in hydrolysis reactions. Furthermore its ability to forestall sulphation makes it an extraordinarily stable catalyst [6,7].

Economic considerations, however, often impose the use of a basic Claus catalyst: alumina. Alumina is the most common catalyst used in the Claus process. The purpose of this paper is to present the precise influence of all physical and chemical parameters that can be of paramount importance for the effective performance of the alumina.

2. Experimental part

The quality of a Claus catalyst is most important under first reactor conditions (R_1) where the objective is to hydrolyse COS and particularly CS_2, but it is also significant under second (R_2) or even third (R_3) reactor conditions, where the Claus reaction (Eq. (3)) is more discriminating. Considering the problem caused by the hydrolysis of CS_2, this is the crucial reaction we chose, in first reactor conditions, as a key reaction to classify catalysts according to their performances.

Our test procedures developed to study the performance of sulphur recovery catalysts are genuine scale models of modern sulphur plants. This is essential to track down the factors that determine the quality of a catalyst.

2.1. Procedure

A previous work showed that macroporosity and sodium level of the surface are essential for the catalytic performances of the aluminas [8]. Thus, alumina has been synthesized in order to clarify the real consequences of all physical and chemical factors. This synthesis consisted of fast dehydration of an aluminum hydroxide, followed by optimized bead formation.

Experimental conditions for the catalytic tests were representative of the conventional first reactor conditions: 6% H_2S, 4% SO_2, 1% CS_2, 30% H_2O, N_2 (the 'true' ratio $H_2S/SO_2=2$ is respected because the hydrolysis of CS_2 gives 2 moles of H_2S (Eq. (5)). H_2S and SO_2 must be present, since these two molecules directly influence the conversion of CS_2. It is well known that, for example, an excess of SO_2 will inhibit the hydrolysis of CS_2 [9]. The precise quantity of water in contact with the catalyst is also very important, as reactivities are completely altered in the absence of water. Oxygen strongly affects the performance of an alumina-based catalyst, since it favors its sulphation [10]; it is thus another key-factor to be controlled. So we tested the performances of the aluminas between 10 and 2000 ppm of oxygen. The conditions used for the test were: 2 or 3 s (TPN) of contact time, 120 cm^3 of catalysts and a temperature of 320°C (in an isothermal reactor). These conditions are close to actual industrial conditions.

The experiments are carried out until a stable level of CS_2 conversion is reached. It is meaningless to speak of initial conversion for a Claus catalyst, given that balancing the system (SO_2 adsorption and initial sulphation) lowers the CS_2 conversion by 30% after about 24 h.

After the elimination of water in the reaction, the conversion of the gases is analyzed by gas phase chromatography.

2.2. *Artificial ageing of alumina*

Under real conditions alumina undergoes different kinds of ageing (sulphation, reduced surface area), due either to normal running conditions or to some accidental causes. To get a better idea of the catalyst's performance, it is necessary to look at the ageing process. We have therefore developed the following procedure that simulates ageing: a treatment at 630°C during 14 h, in a nitrogen flow, with 80% water vapor.

The main consequence is that the surface area of the catalyst is reduced to 120 m^2/g, close to the level at which users recharge the alumina in their units. This reduction is caused by the collapse of the micropores smaller than 40 Å in diameter, as seen with porous distribution measured by mercury porosimetry. No modification of macropores is observed.

3. Results and discussion

Macroporosity of an alumina is important because it reduces diffusional constraints, which gives then higher conversions for Claus reaction (Eq. (3)) as well as for hydrolysis reactions of COS and CS_2 (Eqs. (4)–(5)). But what level of macroporosity is necessary to obtain the best performances? Literature data often speak about pore diameters above 600 or 750 Å [11]. In fact, the reference to a volume of pores having diameters of 750 Å is not correct. We establish the following new concept: the decisive zone is localized between 0.1 and 1 μm. So we have to speak about ultramacroporosity with a ratio: the volume of pore diameters greater than 1 μm over the volume of pore diameters greater than 0.1 μm ($V_1/V_{0.1}$). Fig. 2 illustrates this. According to these results, a ratio $V_1/V_{0.1}$ larger than 0.7 will be useful, for a $V_{0.1}$ value around 20 ml/100 g, to obtain a Superior catalyst for Sulphur recovery.

Similarly, we have looked into the influence of the granulometry of the alumina beads on their performances. We have determined that the best

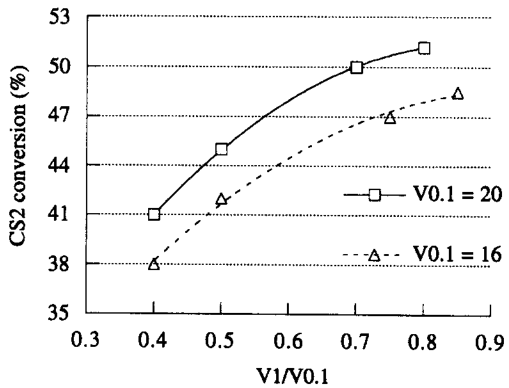

Fig. 2. CS_2 conversions, at equilibrium, obtained with fresh aluminas, as a function of their volume at 0,1 μm and their ratio $V_1/V_{0.1}$, under 10 ppm O_2, for a 2 s contact time (sodium level of the samples: 2000 ppm (Na_2O), bead granulometry: 3.1–6.3 mm).

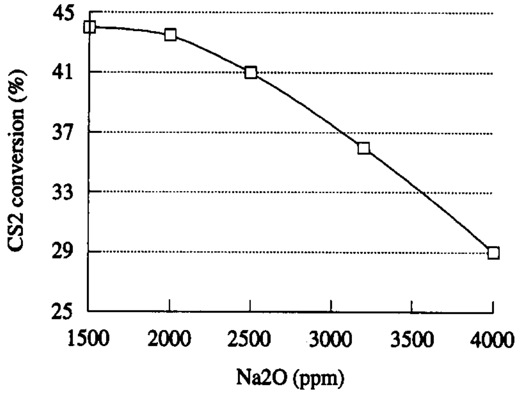

Fig. 3. CS_2 conversions, at equilibrium, obtained with fresh aluminas, as a function of their sodium content, under 1500 ppm O_2, for a 2 s contact time (with $V_{0.1}$ = 16 ml/100 g, $V_1/V_{0.1}$ = 0.75, bead granulometry: 3.1–6.3 mm).

Table 1
Physico-chemical characteristics of fresh aluminas

Characteristics	CR-3S	Alumina X
Granulometry (mm)	3.1–6.3	3.4–6.4
Na_2O level (ppm)	2100	3235
Surface (m^2/g)	380	380
Total pore volume (ml/100 g)	55	56
$V_{750Å}$ (ml/100 g)	19.6	20
$V_{0.1\mu m}$ (ml/100 g)	19.3	19.5
$V_{1\mu m}$ (ml/100 g)	16.1	10
$V_1/V_{0.1}$	0.83	0.51

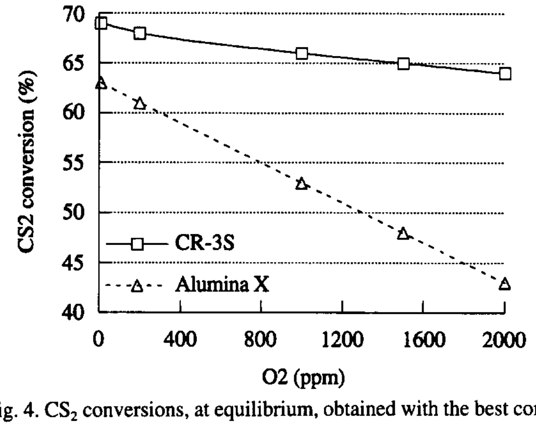

Fig. 4. CS_2 conversions, at equilibrium, obtained with the best competitive alumina (alumina X) and CR-3S (fresh catalysts), as a function of the oxygen level applied, for a 3 s contact time.

compromise is a particle size distribution from 3.1 to 6.3 mm. Diffusional constraints are well reduced for beads of smaller size, without problems linked to pressure drops.

But catalysis is not only a question of physical optimization of the alumina texture: the chemical state of the surface is as important as physical aspects. The sodium level of the alumina will distinguish a Superior Claus alumina from a standard product. A minimal level of sodium (> 1000 ppm of Na_2O) is necessary to have a correct active catalyst. But if this level is larger than 2500 ppm of Na_2O, harmful sulphation reactions appear and cause a drastic deactivation of the alumina (Fig. 3). This is the second concept to emerge from our study.

With all these indications, Procatalyse together with Rhône-Poulenc has developed a new Claus alumina: CR-3S. CR-3S presents a size distribution of beads from 3.1 to 6.3 mm with around 20 ml/100 g of 0.1 μm pores by volume with a ratio $V_1/V_{0.1}$ over 0.7, and a sodium level (Na_2O) between 1700 and 2300 ppm. The concepts determined here have been verified by testing this new specialty catalyst, CR-3S, against a competitive product: X (Table 1).

The oxygen concentration present in Claus reactors has very crucial effects on performances. In first reactor, it is conventional in Claus industrial plants to analyze the presence of oxygen levels between 100 and 2000 ppm.

In all cases, CR-3S proves to be superior to X: the more severe the experimental conditions are, the larger is the benefit obtained with CR-3S (Fig. 4). The stability performances of the new Procatalyse Claus alumina are extraordinary, even in the most extreme conditions. For a 3 s contact time, under 2000 ppm of oxygen, CR-3S increases conversion of CS_2 by 23%, at equilibrium, as compared to X. In a Claus plant, a temporary flow of oxygen will have fewer consequences on the results (on the yield of Sulphur as well as on the ageing of the catalyst) of the unit, if CR-3S is used.

A similar classification can be made after hydrothermal ageing treatment of the catalysts, under all experimental conditions (oxygen level, contact time) (Fig. 5).

The physical and chemical characteristics of CR-3S will show its real superiority when the constraints linked to sulphation are more severe, i.e., in second or third Claus reactors conditions.

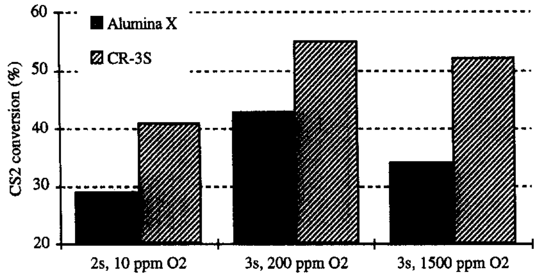

Fig. 5. CS_2 conversions, at equilibrium, obtained with the best competitive alumina (alumina X) and CR-3S (aged catalysts), as a function of the oxygen level and the contact time applied.

While CR-3S's well regulated macroporosity already increases diffusion, a greater stability due to the minimization of sulphate formation on its surface is guaranteed by its low sodium level.

4. Conclusion

Using rigorous methodology, we have succeeded in defining of the world's best Claus alumina. The discovery of several new concepts has turned alumina into a specialty catalyst. To obtain the best yields for the improvement of the protection of the environment, the alumina will have to possess the following physical and chemical characteristics:

- a specific surface over 330 m^2/g;
- a particle size distribution of beads from 3.1–6.3 mm;
- a porous volume $V_{0.1}$ (volume for pore diameters larger than 0.1 μm) over 12 ml/100 g;
- a volume ratio $V_1/V_{0.1}$ over 0.7;
- a sodium level (Na_2O) between 1700 and 2300 ppm.

The industrial development stage of this new product has already been achieved, and this product of the future is already available. Its name is CR-3S, because it is Superior in Sulphur recovery, with Stable performances over time.

From specifically focused research, in conjunction with industrial realities, Rhône-Poulenc and its subsidiary Procatalyse are tirelessly working to improve the quality of their catalysts. In this way they are maintaining their rank as world leader in this field.

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