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New concepts for a new generation Claus alumina

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Abstract

We have developed a new Claus alumina which presents a particular ultramacroporosity, between 0.1 and 1 μm (to reduce diffusional constraints) and a well-defined soda content (below 2500 ppm Na_2O) to reduce the sulfation of the surface and, thus, prolong the life of the catalyst.

Keywords: Claus catalysis

1. Introduction

Claus catalysis makes it possible to transform hydrogen sulfide from different origins, such as natural gas, refinery gas or coal gasification gas into elementary sulfur [1].

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

Legislation to protect nature will drive us continuously to enhance the level of sulfur recovery [2]. So, the best possible sulfur yields must be obtained before incineration. The development of tail gas treatments (such as the Sulfreen process) is helpful [3], but improving the catalysts will always be necessary.

In addition to a high level of performance in the conventional Claus reaction (1), a good catalyst must perform as well as possible in COS hydrolysis (2) and especially CS_2 hydrolysis (3). Indeed, 50% of sulfur recovery yield losses can be observed in Claus plants when the hydrolysis level is insufficient.

$$2\,H_2S + SO_2 \rightarrow \tfrac{3}{x}S_x + 2\,H_2O \qquad (1)$$

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad (2)$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \qquad (3)$$

So, CS_2 hydrolysis in first reactor conditions is a key reaction used to classify catalysts according to their performances.

Alumina is the most common catalyst used in the Claus process. The objective of this paper is to present the precise influence of all physical and chemical parameters which can be of prime importance for the effective performances of the catalyst.

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2. Experimental part

The preparation of the different aluminas A_i ($i \in [1;5]$) and B presented in this paper was carried out at the Rhône–Poulenc Salindres plant. Alumina X_1 is the best competitive alumina and X_2 a conventional one.

The performances of the different aluminas were classified according to their performances in hydrolysis of CS_2, under first reactor conditions (R_1). Experimental conditions were the following: 6% H_2S, 4% SO_2, 1% CS_2, 30% H_2O and N_2, with an oxygen level precisely defined (between 10 and 1500 ppm). Indeed, O_2 is a very important factor in sulfation (and, thus, of deactivation) of the alumina. The conditions used were: an isothermal temperature of 320°C, with a contact time equal to 2 or 3 s (TPN), with 120 cm^3 of catalyst. These correspond to actual industrial conditions.

The catalytic performances of the aluminas were given after attaining a stable level of CS_2 conversion (after ca. 70 h). The conversion of the gases was analyzed by gas phase chromatography, after elimination of water.

An artificial ageing procedure of alumina was defined: a treatment at 630°C for 14 h, under nitrogen flow, with 80% water vapor. The conditions involve a reduction of the specific area to 120 m^2/g, close to the level at which users recharge the alumina in their units.

The sodium concentration of the samples were determined by X-ray fluorescence. The porous distribution of the aluminas were measured by mercury porosimetry.

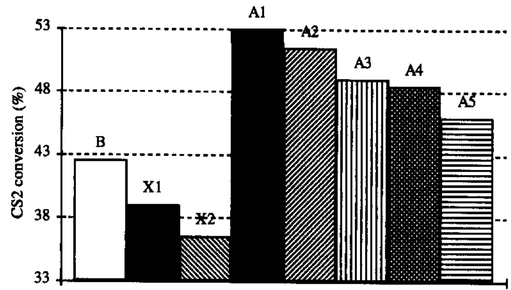

Fig. 1. CS_2 conversions, at equilibrium, obtained with fresh aluminas, under 10 ppm O_2, for a 2 s contact time.

3. Results and discussion

3.1. Aluminas

Principal characteristics of the aluminas are given in Table 1.

3.2. Catalytic performances of the aluminas under 10 ppm O_2

For fresh catalysts, the five A_i samples present a CS_2 conversion, at equilibrium, greater than that obtained with B, and a fortiori with X_1 and X_2 (Fig. 1).

Diffusional constraints can greatly limit Claus and hydrolysis performances of the catalysts. The representation of the same results, versus

Table 1
Physico-chemical characteristics of aluminas studied

	A_1	A_2	A_3	A_4	A_5	B	X_1	X_2
Granulometry (mm)	3.1–6.3	3.1–6.3	3.1–6.3	3.1–6.3	3.1–6.3	4–8	3.4–6.4	3.4–6.4
Surface (m^2/g)	375	381	384	393	394	359	380	256
Na_2O (ppm)	2100	2090	2360	2090	2225	2100	3235	3500
TPV [a] (ml/100 g)	55	55	58	55	55	52	56	46
$V_{0.1}$ (ml/100 g)	19.3	18.0	15.9	15.1	11.4	12.0	19.5	8.6
V_1 (ml/100 g)	16.1	14.7	12.0	11.3	7.2	8.0	10.0	1.8
$V_1/V_{0.1}$	0.83	0.82	0.75	0.75	0.63	0.67	0.51	0.21

[a] Total pore volume.
$V_{0.1}$ and V_1 correspond to the volume of pores with a diameter respectively above 0.1 and 1 μm.

the volume of pores with diameter above 0.1 μm (Fig. 2) is interesting because it well explains the importance of the macroporosity of the alumina in its catalytic properties (A_i series).

Both comparisons A_5–B (similar macroporosity) and A_1–A_5 reveal the consequence of a modification of the bead size versus that of the macroporosity level. So, a small granulometry is favorable to catalysis. In first Claus reactor conditions, between B and A_1, a third of the advantage comes from the granulometric difference and the other two-thirds from a greater macroporosity.

But comparison between the performances of aluminas A_5 and X_1 proves that the reference to a macroporous volume at 0.1 μm (or at 750 Å), described in the literature [4], is really insufficient: the volumes $V_{0.1}$ and V_1 of A_5 are smaller than those of X_1, but A_5 is more effective in CS_2 hydrolysis. Sodium content of the alumina plays a decisive role in a stable catalytic performance [5]: although it can furnish better initial activity, sodium soon becomes a chemical poison and fosters sulfation and therefore the deactivation of the catalyst.

The sodium aspect is nevertheless insufficient to explain all the experimental phenomena observed: the porosity distribution, between 0.1 and 1 μm, as well as the ratio $V_1/V_{0.1}$ are crucial (compare A_i and X_i samples). In other words, a ratio $V_1/V_{0.1}$ greater than 0.7 will lead to a more effective product.

Several experiments have been carried out on

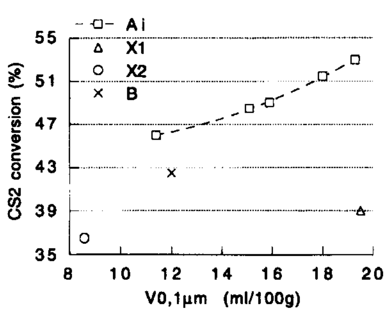

Fig. 2. CS_2 conversions, at equilibrium, obtained with fresh aluminas, versus their $V_{0.1}$ volume, under 10 ppm O_2, for a 2 s contact time.

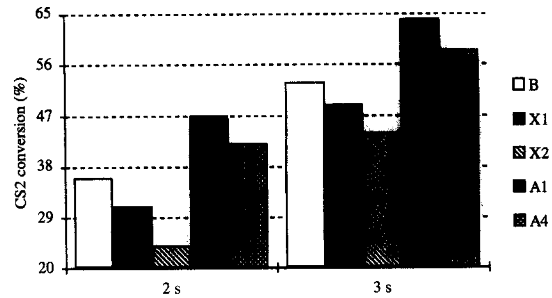

Fig. 3. CS_2 conversions, at equilibrium, obtained with fresh aluminas, under 1500 ppm O_2, for a 2 or 3 s contact time.

aged aluminas and similar performance classification is found: in the same experimental conditions (oxygen, contact time), for example, X_1 hydrolyzes 29% of CS_2 at equilibrium, as opposed to 37% for A_2.

3.3. *Influence of the oxygen concentration*

The oxygen concentration can have dramatic consequences on the sulfation of the aluminas [6] and thus on their performances (compare Fig. 3 with Fig. 2): the greater this concentration is, the greater is the handicap of a rich-sodium alumina (Na_2O > 2500 ppm).

4. Conclusion

Using rigorous methodology, we have succeeded in defining the world's best Claus alu-

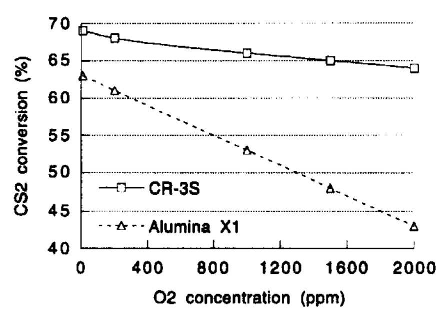

Fig. 4. CS_2 conversions, at equilibrium, on fresh aluminas, versus oxygen concentration, for a 3 s contact time (CR-3S: new Procatalyse Claus alumina; alumina X_1: best competitive Claus alumina).

mina: A_1, called CR-3S commercially. Two new concepts have been proved:

- the literature often mentions how important macroporosity is in reducing diffusional constraints. But the reference to a value of porosity at 750 Å is not relevant. Indeed, we have shown that it is the ultraporosity area, between 0.1 and 1 μm, which is crucial: the best results have been observed on an alumina with a volume at 0.1 μm of around 20 ml/100 g and a ratio: volume at 1 μm/volume at 0.1 μm over 0.7;

- the sodium content of the alumina is very important: we have shown that below 1000 ppm (Na_2O) [7], the activity of the catalyst is insufficient, but that above 2500 ppm, sulfation reactions cause negative deactivation of the alumina, especially when the conditions are more severe, i.e., when the oxygen concentration in the reactor is high.

A good illustration of all these aspects can be seen in Fig. 4: the new Procatalyse CR-3S alumina, designed from our two new concepts, gives very good catalytic performance, quite a bit better than those obtained from the best competitive Claus alumina.

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