Catalysis Letters 13 (1992) 383–387

A new approach on catalytic cracking catalyst deactivation

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Received 9 October 1991; accepted 20 February 1992

The existence of acidic species other than those of vanadic acid is suggested to be responsible for the FCC catalyst deactivation. These species would come from SO_x adsorption on the catalytic surface which would react with the most acid sites of the zeolite, ultimately leading to loss of crystallinity.

Keywords: Catalytic cracking; catalyst deactivation; vanadium effect in FCC; sulfate effect in FCC

1. Introduction

Catalytic cracking [1–3] is one of the most important processes taking place in a refinery. It allows the processing of heavy and residual crudes and transforming them into lighter fractions. As a result, besides the added value involved in this process, it allows the increase of gasoline and intermediate distillate production to meet the demand in the energy market.

Residual and heavy crudes contain sulfur and nitrogen organic compounds as well as organo-metallic compounds mainly consisting of vanadium and nickel. The presence of these compounds poses a series of inconveniences for the catalytic cracking reaction which have already been described in the literature [4]. Of all the above-mentioned compounds, the vanadium effect on the FCC process has been one of the most frequently studied phenomena because it appears to be responsible for the destruction of the zeolite structure in the catalyst with a subsequent activity loss [5–7].

Since Y-type zeolite is the main active agent in the FCC catalyst, a series of studies have been conducted to understand the destruction thereof by vanadium action. When faujasite is in the protonated form, Wormsbecher et al. [5] suggest the volatile species H_3VO_4 to be responsible for the attack by the acid to the solid. The acid could be "neutralized" by adding small amounts of a basic solid such as MgO or CaO. On the other hand, Elvin [6] assumes that vanadic acid is formed in the regenerator from vanadium pentoxide (V_2O_5), two types of deactivation being observed: (a) one derived from zeolite destruction by V_2O_5 and H_3VO_4 attack, and (b) the blocking of zeolite channels by V_2O_5 deposit. When zeolite is in the stabilized form with rare earths (Re-Y), vanadium pentoxide may react with the lanthanum in the sodalitic cage since a temperature of 600°C is reached, thus breaking the La–O–La bonds which give stability to faujasite [7].

Most studies conducted and reported in the literature consider the above-mentioned vanadium compounds to be some of the main factors determining zeolite structure destruction. However, there still remain many unknowns regarding the role played by the metal. This paper is intended to show that another type of acidic species is likely to form in the process and to contribute together with vanadium compounds to the crystallinity losses observed. The compound proposed is an acidic species related to the presence of sulphurous oxides that might destroy the zeolite structure.

2. Experimental

A series of FCC catalysts containing Re-Y zeolite were prepared with different sulfate and vanadium contents. Catalytic activity tests were then performed. Experimental conditions for the MAT test are: West Texas feed, 482°C, contact time 75 s and WHSV 15 h-1. They are presteamed at 760°C with 100% of steam. Experimental results are shown in table 1.

According to table 1, a comparison of results obtained with A-1 and A-2 catalysts shows that the additive (anatase for vanadium metal trap [8]) presence does not have an influence upon the catalytic activity for different vanadium contents. When the sulfate content in the catalyst has been progressively reduced (A-2, A-4, A-5 for 10% of additive and A-1, A-3 without additive), the catalytic activity increases, this effect becoming evident for a 0.08% vanadium content. With catalyst A-5 the percent vanadium increase has not led to a dramatic activity loss similar to that obverved in A-1 and A-2.

Table 1
Different FCC catalyst activities

Catalyst	% additive	% SO_4	Activity with V		
			0% V	0.3% V	0.8% V
A-1	0	1.1	77	65	22
A-2	10	1.3	77	67	24
A-3	0	0.3	75	–	31
A-4	10	0.36	78	71	55
A-5	10	0.08	79	75	68

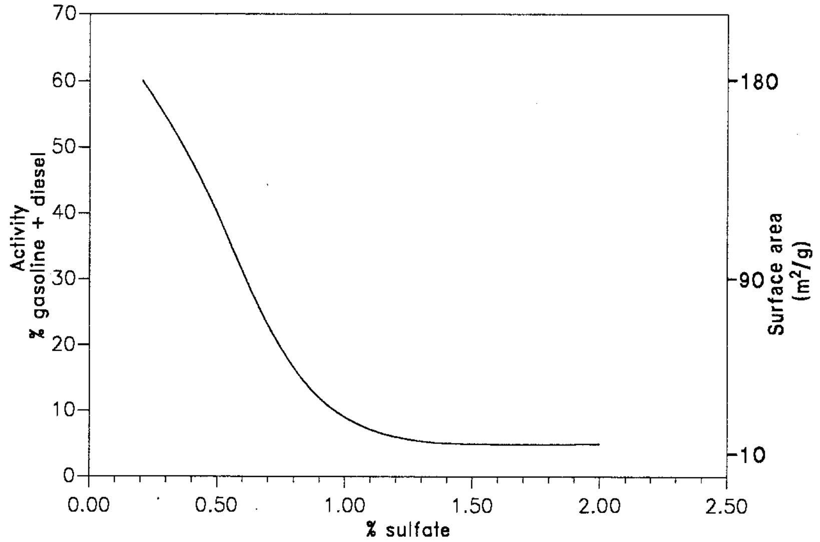

Fig. 1. Effect of percent sulfate in FCC catalyst on activity and surface in the hydrothermal deactivation process.

Likewise, a catalyst with 1% V and with different sulfate contents has been prepared and exposed to a high-temperature deactivation (760°C) in steam atmosphere (100%). Results in fig. 1 show the significant MAT activity drop in gasoline and diesel production as the sulfate percentage in the sample increases, as well as the surface area (BET) reduction thereof.

3. Discussion

The results in section 2 (table 1) show that percent sulfate reduction in the catalyst leads to an increased catalytic activity even in the presence of vanadium. Likewise, activity loss is not so important when the vanadium content varies in the presence of a low sulfate content. All this leads to the conclusion that sulfate derived compounds must be playing a key role in the process. The same conclusion is reached when fig. 1, which illustrates a simulation of the catalyst hydrothermal regeneration stage, is analyzed. Under these temperature (760°C) and steam atmosphere (100%) conditions, sulfate should break down and form different SO_x species among which an acidic species capable of destroying the zeolite structure would be found.

Sulfate from different elements can break down giving rise to the corresponding oxides in a temperature range of 500–1000°C (650–950°C for $Al_2(SO_4)_3$ and $Ce_2(SO_4)_3$) [9]. During this process, both SO_2 and SO_3 are released. Moreover, the reduction process can also occur in the FCC reactor in the presence of hydrogen or hydrocarbon, H_2S being thus formed [9]:

$$4H_2 + MSO_4 \rightarrow MO + H_2S + 3H_2O.$$

Therefore, the regenerator contains: (a) SO_2 and SO_3 derived from sulfate decomposition and coke-contained S combustion, (b) water steam coming from coke hydrogen, (c) oxygen used for combustion, and (d) vanadium pentoxide. In this reaction mixture consisting of various sulphur compounds SO_3 formation should be stressed:

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3 \quad \left(K_p = 0.005686\ \mathrm{Pa}^{-1/2} \text{ at } 700°\mathrm{C}\right).$$

This reaction is industrially catalyzed through an oxidation promoter such as vanadium pentoxide, the maximum performance temperature being 600°C. On the other hand, SO_3 results from the sulfuric acid decomposition

$$H_2SO_4 \leftrightharpoons SO_3 + H_2O + Q.$$

This equilibrium is completely shifted to the right above 500°C, but a given type of acidic species is likely to form in the catalyst surface under the following reaction conditions: 700°C with sulfite, with an excess water steam and mainly with V_2O_5, the latter being a catalyst industrially used to promote the sulfuric acid formation reaction. This or these acidic species could have a destructive effect on zeolite while competing with the volatile species H_3VO_4 in the deactivation process. This is likely to occur through SO_3 adsorption on the already steam saturated surface of the catalyst. The mechanism would be like the one suggested for vanadic acid [10] where atoms having a large basic character (SO_x species) would interact with the most acid sites of the zeolite to effect neutralization and subsequently destroy the crystalline structure in the presence of steam and vanadic acid.

At present, we have neither evidence that sulfate alone leads to catalyst destruction nor that the combination of sulfate and vanadium acts synergistically. It is the subject of actual research.

Moreover, bearing in mind the existence of these acid species, an explanation could be given about the reason why there is such a low crystallinity loss (−30%) when a USY zeolite experiences a hydrothermal deactivation at 750°C with 50% water steam in the absence of any type of sulfur compound and with 10000 ppm impregnated vanadium [11]. The crystallinity loss would not justify the activity drop observed in the FCC process. As a result, it would be reasonable to think that vanadic acid is not the only one responsible for deactivation. That loss would also explain the reason why the DEMET process [12], currently being marketed, allows the extraction of up to 60% vanadium from the FCC catalyst after the deactivation thereof in the plant. This fact would be an evidence that a large amount of vanadium is not irreversibly adsorbed on the catalyst.

Acknowledgement

This research was supported by Instituto Venezolano del Petróleo (INTEVEP).

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