

SOX Control In Fluid Catalytic Cracking

Z. C. Mester, E. J. Aitken and P. G. Ritz

Unocal, Division of Science and Technology, Brea, CA 92621

Introduction

Refineries today face a growing challenge to stay in compliance with the increasingly stringent environmental regulations. In fluid catalytic cracking (FCC), which is the largest volume gasoline producing process, the main air pollutants are carbon monoxide, sulfur oxides (SOX), nitrogen oxides (NOX), hydrocarbons and particulates.

At high regenerator temperature operation SOX emissions represent the greatest problem, therefore SOX emission control is of primary importance. As an example, in California the current standard is 60kg SO₂ per 1000bbl feed which is less than half of the previous 130kg SO₂ per 1000bbl feed limit. The EPA also proposed a 90% SOX reduction for FCC operations, but this regulation is still pending (1). The following options are available to the refinery to control SOX emissions: selection of low sulfur feed, flue gas scrubbing, feed hydrotreating and catalytic SOX reduction. The first method is of limited use because low sulfur feeds are not easily available. Flue gas scrubbing is effective but also capital intensive and may pose liquid or solid waste disposal problems. Hydrotreating has the advantage of not only reducing SOX but improving liquid yields too. In the long run this process offers economic advantages, however the high initial investment is a major drawback for many refineries. During the last few years catalytic SOX control emerged as an effective and economically attractive alternative to the above methods (2, 3, 4, 5).

SOX catalysts convert sulfur oxides, formed during coke burn-off in the regenerator, to solid sulfur containing species and release them as hydrogen sulfide in the reactor. This step rejuvenates the catalyst which is then recirculated to the regenerator and the cycle is repeated. In the following we present results of our investigation on the effectiveness of some SOX catalysts using TGA, fluidized bed reactor and in-situ infrared spectroscopy.

Results

The following materials were investigated for SOX performance: alumina, rare earth oxide/alumina, and rare earth oxide/alumina/cobalt oxide. The materials were first evaluated by TGA analysis. The samples were exposed to a gas mixture containing 2000 ppm SO₂, 4% O₂ and nitrogen. The weight gain of the samples were monitored as a function of the temperature with a 10°C/min ramp between 25 - 750°C. The materials were then cooled down to 25°C under nitrogen; hydrogen was introduced and the temperature was ramped as above. This adsorption-reduction cycle was repeated several times to assure good reproducibility. Each sample started to adsorb SOX appreciably around 300°C. Percent weight gains at 750°C were as follows: 2% for alumina, and 5% for the other two samples. The adsorption curves for the rare earth containing samples passed over a maximum around 650-700°C indicating decomposition beyond this temperature range. In the reduction step the cobalt containing sample started to reduce at the lowest temperature (500°C), followed by rare earth oxide/alumina and alumina (540°C).

The next stage in evaluating SOX materials involved the use of a bench scale fluid bed reactor. In a typical experiment the sample (< 5g) was fluidized by a mixture of SO₂ (2000 ppm) / O₂ (3%) / N₂ (balance) at a temperature which corresponded to FCC regenerator temperatures (650-750°C). After a fixed length of reaction time

(2 hrs), the samples were analyzed for sulfur. The unit can be used to simulate the entire catalytic cycle where the gettinger step is followed by hydrogen reduction and steam injection at temperatures corresponding to those of typical FCC operations. The SOX gettinger experiments at 730°C showed that alumina was the weakest adsorber. The rare earth/alumina and the cobalt impregnated samples had about the same gettinger capacity, each adsorbed 2.5 times more sulfur than alumina alone. When the SOX loaded materials were reduced in a flow of hydrogen at 540°C for 0.5 hrs, the cobalt containing sample regained 62% of its original gettinger capacity, followed by alumina (55%) and rare earth/alumina (40%).

In order to assess the relative rates of SOX uptake and H₂ reduction, in-situ infrared experiments were conducted. In these experiments the formation of surface sulfates - by exposure of the material to an SO₂ (1500 ppm) / O₂ (3%) / N₂ (balance) gas mixture - and the elimination of the surface sulfates - by exposure to H₂ - were followed by monitoring the appropriate band as a function of time. The SOX adsorption step took place at 600°C and the H₂ reduction was carried out at 525°C. The surface sulfur oxide species formed on the materials were predominantly sulfates. For the rare earth containing samples rare earth sulfates were detected as indicated by the appearance of two broad bands centered at 1125 cm⁻¹ and 1050 cm⁻¹. However, a sulfite species also formed on alumina, as evidenced by a band at 1040 cm⁻¹, in addition to a sulfate like species (1370 cm⁻¹). The SOX gettinger rate, measured by the increase in intensity of the surface S-O stretching vibrational bands, was dependent upon the composition of the materials. For alumina the adsorption rate decreased drastically after approximately 8 min of SO₂ exposure indicating that maximum gettinger capacity was being reached. The gettinger rates (normalized adsorption intensity per minute) in the first 8 min of exposure were: 0.0035 for the sulfate band and 0.0045 for the sulfite band of alumina; 0.016 for the rare earth oxide/alumina and rare earth oxide/alumina/cobalt oxide samples. During the hydrogen reduction step the time required to reduce the band intensity to 50% of the intensity prior to hydrogen exposure decreased in the order: 12 min (sulfate band for alumina), 9 min (sulfite band for alumina), 9 min (sulfate band for rare earth oxide/alumina) and 2 min (sulfate band for rare earth oxide/alumina/cobalt oxide).

Conclusions

TGA proved to be a useful method to reveal the SOX gettinger potential and regenerability of the materials in a wide temperature range. The fluid bed experiments were useful in evaluating the materials under more realistic conditions related to FCC operations. The infrared study helped to establish the relative rates of SOX gettinger and reductions by hydrogen. The results showed that the rare earth containing materials were superior to alumina in SOX gettinger. It was also shown that cobalt had an accelerating effect in restoring catalyst activity.

References

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