

## Laboratory evaluation of SO<sub>x</sub> reduction additives for FCC

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### Introduction

Due to environmental concerns and the use of heavier feedstock, the control of emissions including SO<sub>x</sub> (SO<sub>2</sub> & SO<sub>3</sub>) from fluid catalytic cracking (FCC) has drawn great interest both in industry and academia [1]. Among various SO<sub>x</sub> reduction technologies, the use of additives in FCC units provides a simple and cost-effective method and has been found essential by most refiners [2, 3]. However, the evaluation of the additives at the research and development stage in the laboratory not equipped with costly FCC circulating pilot plant is challenging.

The objective of this study is to evaluate commercial SO<sub>x</sub> reduction additives for FCC units using various characterization techniques and bench-scale reactors. The activity testing is based SO<sub>x</sub> uptake capacity under FCC regenerator conditions and release under FCC riser conditions. The results obtained in this study will be used to establish a reliable protocol at bench-scale in the future to evaluate new additives. In addition, insights on the SO<sub>x</sub> uptake and release mechanisms will be addressed.

### Materials and Methods

The catalytic additives used in this study were commercially available SO<sub>x</sub> reduction additives as well as new additives prepared by INTERCAT<sub>JM</sub>.

All the physical and chemical analyses were carried out at Intercat QC lab, Johnson Matthey. Microanalysis was performed on a Hitachi S-4800 field emission Scanning Electron Microscope (SEM) equipped with EDAX energy dispersive X-ray spectrometer (EDS). Cross-section samples were obtained by embedding, polishing and coating. Operation voltage: 25 keV; Working distance: 15 mm; EDS results were semi-quantitative.

Both SO<sub>x</sub> pickup and release abilities were tested using quartz reactors in a fixed fluid bed configuration. SO<sub>x</sub> pickup was carried out by flowing 100 mL/min 1000ppm SO<sub>2</sub> and 1%O<sub>2</sub> balance N<sub>2</sub> over a sample of 4 g after it had been heated in N<sub>2</sub> at 700°C for 30min. The effluent gas was monitored by an MKS FTIR multi-gas analyzer. TPR with reducing gas (e.g. 25% H<sub>2</sub>) balance He was used to study the S release of a sulfated sample at 3°C/min. The effluent gas was sampled at desired time intervals and analyzed by FPD.

### Results and Discussion

Figure 1 gives an example of the morphology and EDX mappings of selected elements of a SO<sub>x</sub> reduction additive commercially produced by INTERCAT<sub>JM</sub>. Apparently, most of the particles are in good microsphere morphology and they are in the same particle size range, with an average particle size around 80 µm, same as the cracking catalysts used in the FCC units. In addition, all the elements are distributed evenly, a critical requirement for the high performance as found in the commercial applications.

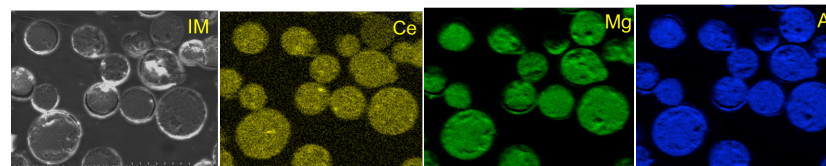


Figure 1. EM image and EDX scans of selected elements for a SO<sub>x</sub> reduction additive.

Figure 2 compares the SO<sub>x</sub> pickup and release abilities of a newly developed SO<sub>x</sub> reduction additive (refer to New SO<sub>x</sub> additive) and a commercial SO<sub>x</sub> reduction additive (refer to SO<sub>x</sub> additive). These samples were all pre-deactivated in the lab. The new additive exhibits similar even higher capacity for SO<sub>x</sub> pickup. With respect to the S release, similar amounts of H<sub>2</sub>S were release for the sulfated samples, but the new additive appears to have lower S release temperature, indicating easier S release. These lab results suggest that the newly developed SO<sub>x</sub> reduction additive is having comparable or even better SO<sub>x</sub> reduction ability than the commercial SO<sub>x</sub> additive, which is consistent with commercial trial results.

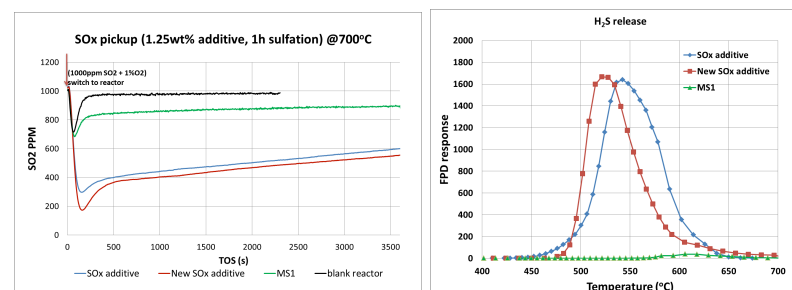


Figure 2. SO<sub>2</sub> breakthrough at 700°C (left) and Temperature Programmed S Release of pre-sulfated SO<sub>x</sub> additives (right). (MS1 is a clay used as a diluent in the testing)

### Significance

This work will establish a reliable and feasible laboratory analysis/testing protocol for the development of FCC SO<sub>x</sub> reduction additives. It will also lead to a more comprehensive understanding on the FCC S chemistry.

### References

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3. Evans, M. Petroleum Technology Quarterly 2008, Q2, 1 – 4.