Lowering gasoline sulfur in fluid catalytic cracking with additives: Bench-scale to commercialization

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Introduction

Sulfur in gasoline reduces the life of vehicle catalytic converters by poisoning the active sites, thus potentially increasing emissions that adversely affect human health and the environment. A significant amount of Sulfur in gasoline originates from gasoline produced in the fluid catalytic cracking (FCC) unit. Catalytic additives may be used in the FCC to reduce Sulfur in gasoline. Such additives are mainly supported metal oxides having Lewis acidity, such as Zn, Zr, Co, Ni, or Mn impregnated on alumina, hydrotalcite, titania, or other Mg(Al)O supports.

Johnson Matthey has developed and commercialized several Lewis acid-based FCC additives for lowering Sulfur in FCC gasoline. Fundamental studies on catalytic reaction pathways and active sites are required to understanding the performance of LGS additives. In this paper we present the major performance and catalytic reaction pathways of Sulfur reduction additives containing Zn on various supports: alumina, mixed metal oxides, and metal impregnated oxides.

Materials and Methods

Three LGS additives, LGS-A, LGS-B, and LGS-C were synthesized to produce fluidizable microsphere catalysts which were characterized according to standard FCC protocols. Additive performance evaluation was carried out in a bench-scale pseudo-FCC unit, an ACE-Model R+. Boiling point distribution of the products was analyzed using GC-SIMDIS and gasoline Sulfur speciation was determined using GC-AED/SCD. Prior to ACE evaluation, the additive was equilibrated via steaming and physically mixed with equilibrated catalyst (e-cat) at the required concentration.

Results and Discussion

The Zn-based additives prepared using various supports showed excellent physical properties. Since LGS is a separate particle FCC additive, it requires that it has similar fluidization properties and attrition of FCC catalysts.

The laboratory evaluation results in Figure 1 show that the use of LGS additives significantly lowers the gasoline Sulfur, especially LGS-A and LGS-C. Under laboratory conditions, it was possible to achieve 20-40% Sulfur reduction with 15% of LGS additives without compromising conversion or yield selectivities. Based on these results, recommendations were made for commercial application of LGS additive in the FCC unit.

Further work was also carried out to study impact of nature of the Lewis acid sites on Sulfur reduction. Based on this experimental work, it was determined that metal support interaction and further optimization of the Lewis acids in the LGS additives are critical for decomposition of Sulfur species.

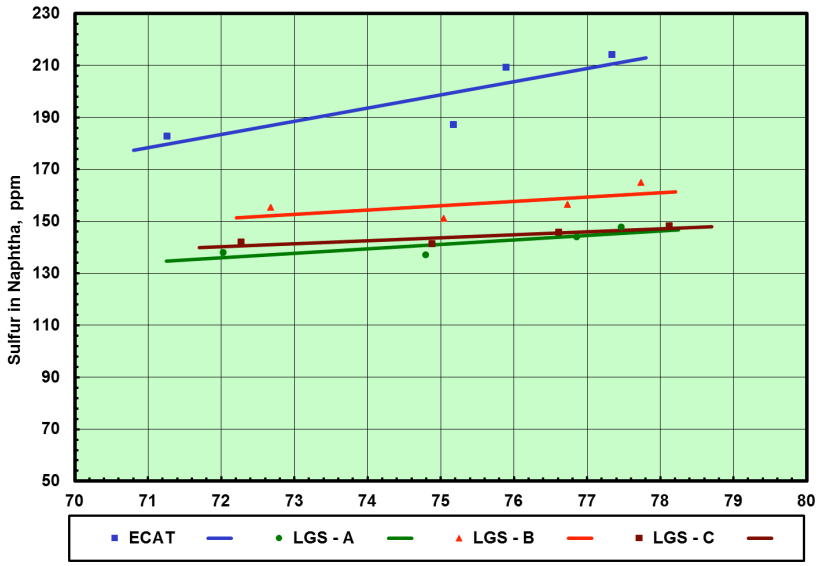

Figure 1: Performance of LGS additives under laboratory FCC conditions.

Significance

LGS additives can play a substantial role in reducing FCC gasoline Sulfur. The active sites in FCC de-sulfurization chemistry are Lewis acid sites. The nature of the support and minor doping of Lewis acids determine the performance of the de-sulfurization catalyst.

Sulfur in gasoline is converted to SO_2 in the exhaust gas upon combustion. SO_2 is a known inhibitor of three-way catalyst performance. The gasoline fuel Sulfur specification has not changed since 1970. Therefore, lowering the amount of Sulfur in gasoline is critical to achieve low emission levels required by regulations and also is beneficial in improving performance of three-ways catalysts installed on 125 million on-road US vehicles.

References

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