

FCC Gasoline Sulfur Reduction additives: mechanism and active sites.

Fabien Can¹, Arnaud Travert^{1*}, J.P. Gilson¹, Françoise Maugé¹, Ruizhong Hu² and Richard F. Wormsbecher²

¹ Laboratoire Catalyse et Spectrochimie, UMR CNRS – ENSICAEN – Université de Caen, 14050 Caen Cedex, France

² W. R. Grace & Co.- Conn. 7500 Grace Drive Columbia, MD 21044 USA

*arnaud.travert@ensicaen.fr

Introduction

As a result of environmental legislations, refiners are faced to an ongoing demand for sulfur abatements in fuels. Fluid Catalytic Cracking (FCC) units contribute for 30% of total gasoline production but are responsible for 90% of sulfur in gasoline. Recent studies have been conducted by industry and academics in order to improve the understanding of sulfur compound chemistry in the FCC units [1-3]. Among various options (e.g. hydrotreating), the direct removal of sulfur in the FCC unit by use of specific additives is particularly attractive. It has been reported that gasoline sulfur reduction (GSR) additives like Zn/Al₂O₃ could achieve 30%-40% gasoline sulfur reduction [5-6]. To the best of our knowledge, no study at the molecular level of the mechanisms of sulfur removal by these additives has yet been reported. In this work, we have studied by infrared operando spectroscopy and microactivity tests the interaction and reactivity of model sulfur molecules with doped Al₂O₃-based additives.

Materials and Methods

Series of additives consisting in Zn-, Na- and F-doped Al₂O₃ have been studied. Their acid-base properties were characterized by IR spectroscopy of adsorbed probe molecules (CO, pyridine and CO₂). IR *operando* spectroscopy was carried out using an IR reactor-cell at high temperature under flow of reactants. The experimental setup allowed the simultaneous characterization of the surface species by IR and gas phase products by IR, GC and MS. Conventional activity measurements were also carried out in a Short-Contact time microactivity test (SCT-MAT) unit as well as in a conventional plug flow microreactor. Finally, spent additives were characterized by temperature programmed oxidation (TPO) after N₂ flushing at reaction temperature.

Results and Discussion

All the studied additives were found inactive by themselves towards thiophene, but selectively cracked tetrahydrothiophene (THT) into H₂S and butadiene, according to the following activity ranking : Zn/Al₂O₃ > Al₂O₃ > Na/Al₂O₃ > F/Al₂O₃. By contrast, when blended with a FCC catalyst, the Zn/Al₂O₃ additive led to a significant decrease of both THT (by ~100%) and (alkyl)thiophenes (by ~20%) in the gasoline cut. This shows that Al₂O₃-based GSR additives reduce thiophenic compounds by an efficient decomposition of THT produced by hydrogen transfer on the FCC catalyst.

Correlations could be established between THT cracking rates and Lewis acid-base properties of the additives. The specific poisoning of strong tetrahedral Al³⁺ sites in *operando* conditions led to a drastic decrease of THT cracking rates, thus evidencing that such sites are involved in the reaction mechanism. A strong indication that basic sites are also involved is the fact that deactivation linearly correlates with the formation of surface carboxylate species during the

reaction, leading to a blocking of surface oxygen centers. This suggests that THT cracking occurs on Lewis acid-base pairs through successive E2 eliminations (Figure 1).

Na leads to an important decrease of the number of strong Lewis acid sites by inductive effects, thus explaining the lower GSR activity of Na/Al₂O₃ [5]. Fluorine enhances strong Lewis acid sites, but also strongly decrease surface basicity by substitution of μ1-OH groups and electron withdrawing from surface O²⁻ centers. In this case, Lewis basicity becomes the limiting factor for THT cracking. Finally, the promoter effect of Zn on THT cracking has been explained involving the formation of the spinel ZnAl₂O₄ which favors strong tetrahedral Al³⁺ acid sites to the detriment of medium octahedral Al³⁺ acid sites.

Significance

This work evidences a synergy between the FCC catalyst which allows for thiophenic species hydrogenation into THT on the one hand and the GSR additive which efficiently cracks THT. Optimum GSR activity requires additives possessing balanced Lewis acid-base properties.

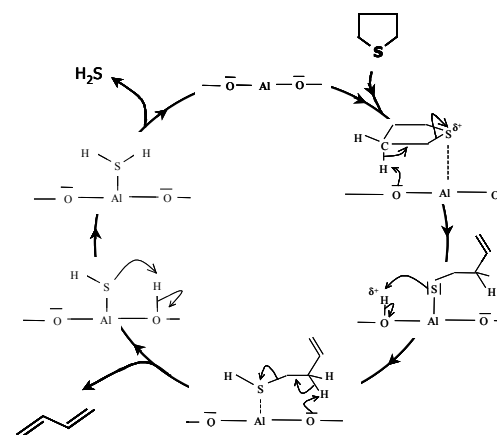


Figure 1. mechanism of THT cracking by Al₂O₃-based GSR additive.

References

1. R.F. Wormsbecher, D.S. Chin, B. Patrose, R.R. Gatte, and R.H. Harding, *Abstracts of the ACS*, 203, 7 (1992).
2. A. Corma, C. Martinez, G. Ketley, and G. Blair, *Appl. Catal. A* 208, 135 (2001).
3. P. Leflaive, J.L. Lemberon, G. Pérot, C. Mirgain, J.Y. Carriat, and J.M. Colin, *Applied Catal. A*, 5895, 1 (2001).
4. R.F. Wormsbecher, and G. Kim, US Patent 5,376,608 (1994), to W.R. Grace & Co.-Conn.
5. R. Hu, X. Zhao, R.F. Wormsbecher, M.S. Ziebarth, US Patent Application 2005/0205464 (2005), to W.R. Grace & Co.-Conn.