Transformation of refractory model sulphur compounds representative of FCC gasoline: A theoretical and experimental combined approach

Etienne Girard,[a,*] **Alan Silva Dos Santos,**[b] **Philibert Leflaive,**[a] **Sylvette Brunet**[b]
[a] *IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France*
[b] *Université de Poitiers, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), UMR 7285 CNRS, 4 rue Michel Brunet, TSA 71106, 86073 Poitiers France*
**Corresponding author: etienne.girard@ifpen.fr*

Abstract: In the present work, the transformation of various model sulphur compounds –2-methylthiophene (2MT), 3-methylthiophene (3MT) and benzothiophene (BT)– as thiophenic compounds representative of a FCC gasoline was compared under HDS operating conditions over a CoMoS/Al_2O_3 catalyst. By coupling experimental and theoretical approaches, their reaction scheme and the kinetic parameters – activation energy, reaction rate constant and adsorption constant– of these compounds, were determined using the Langmuir-Hinshelwood formalism. The parameters determined for each compound were then used to model adsorption competitions in mixture.

Keywords: Hydrodesulphurization, FCC Gasoline, Kinetic modeling.

1. Introduction

Due to increasing environmental concerns, constraints relative to exhaust gas compositions are reinforced worldwide. Thus, China V and US Tier 3 regulations now impose a 10 ppm maximum of sulphur in gasoline.[1] Gasoline produced by the FCC units in refineries represents 40% of the gasoline composition but accounts for 95% for the total sulphur amount before hydrodesulfurization (HDS).[2] Consequently, there is a strong need for developing HDS catalysts with high activity to achieve ultra-deep HDS of FCC gasoline. Meanwhile, these catalysts should also exhibit high selectivity to minimize olefins hydrogenation (HDO) to preserve high octane values. A straightforward solution considered by refiners is to undercut the FCC gasoline range –typically from 220°C to 160°C– to reduce the amount of sulphur in the selective HDS feed. This results in a completely different balance between alkyl thiophenics and alkyl benzothiophenes and, in turn, in a very different feed reactivity. This challenge consequently urges to provide a better understanding of the competitive adsorption between sulphur compounds on the catalyst surface.

In the present work, the transformation of various model sulphur compounds –2-methylthiophene (2MT), 3-methylthiophene (3MT) and benzothiophene (BT)– as thiophenic compounds representative of a FCC gasoline was compared under HDS operating conditions over a CoMoS/Al_2O_3 catalyst. By coupling experimental and theoretical approaches, their reaction scheme and the kinetic parameters – activation energy, reaction rate constant and adsorption constant– of these compounds, were determined using the Langmuir-Hinshelwood formalism. The parameters determined for each compound were then used to model adsorption competitions in mixture.

2. Experimental

The transformation of sulphur model molecules were studied, separately and in mixtures, in a fixed bed microflow reactor at 250°C, under 2.0 MPa of total pressure over a conventional CoMoS/Al_2O_3. Sulphur compounds (1000 ppmS) alone or in mixture were diluted in n-heptane. For a better precision in activity measurements, the contact time was chosen such as to keep the overall conversion of sulphur compounds nearly constant around 25 % (24-27 %). Kinetic modeling was carried out using the ReactOp Cascade 3.20 (ChemInform St. Petersburg, Ltd.) software.

3. Results and discussion

Benzothiophene was experimentally observed to be more reactive (by a factor of 1.4 and 2.2, respectively) than 3-methylthiophene and 2-methylthiophene (Table 1). Regarding the transformation of BT, ethylbenzene (EB) was the main product of reaction with a selectivity of 88%. Meanwhile, dihydrobenzothiophene (DHBT) originated from the direct hydrogenation product of BT, with a selectivity of 11%. Kinetic modeling could confirm that the formation of ethylbenzene directly from BT wa a minor pathway. Indeed, the rate constant was much lower ($k = 3.8.10^8 h^{-1}$) than that via the formation of DHBT ($k = 12\ 10^{12} h^{-1}$). Regarding the transformation of 2MT and 3MT, pentenes and pentane and methylbutenes and methylbutane were respectively the main products, respectively. However, strong differences of selectivities towards alkanes and alkenes were noticed as shown by the alkane/alkenes ratio for both molecules, which was higher for the transformation of 2MT than for 3MT.

When these sulfur molecules (BT and 2MT) were hydrodesulfurized in mixture, the reactivity order of the two sulfur compounds (2MT and BT) remained the same, BT being more reactive than 2MT. However, significant differences were observed with respect to their transformation alone. In mixture, a decrease in the conversion of both BT and 2MT was observed suggesting a mutual inhibiting effect. Interestingly, this decrease was significantly higher for 2MT (up to 65%) than for BT (11%). These phenomena were also reversible, thus indicating competitive adsorption of the sulfur molecules on the surface of the catalyst. Moreover, dedicated experiments evidenced that inhibition is not due to the formation of H_2S during their transformation but to the non transformed sulfur compounds themselves.

Finally, the stronger inhibiting effect of unconverted BT on the transformation of 2MT could be well described by Langmuir-Hinshelwood kinetics using parameters determined from the single compound experiments. Indeed, the BT adsorption constant was higher than that of 2MT.

Table 1: Transformation of sulphur compounds alone or in mixture. Activity (A.), Adsorption constant determined from kinetic modeling (T=250°C, P=2MPa, $CoMoS/Al_2O_3$)

Sulphur compounds	A. alone ($mmol.h^{-1}.g^{-1}$)	A. in mixture ($mmol.h^{-1}.g^{-1}$)	Adsorption constant (bar^{-1})
2MT	3.8	1.5 (-65%)	7,1
3MT	5.9	-	10.2
BT	8.3	7.4 (-11%)	12.1

4. Conclusions

In conclusion, mutual inhibiting effects between sulphur compounds representative of FCC gasoline were observed under HDS operating conditions. Remarkably, these experimental results in mixture could be described using a Langmuir-Hinshelwood model and kinetic and adsorption parameters determined from single compound experiments.

References

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