

Inhibiting effect of model oxygenated compounds on the HDS of dibenzothiophenes over CoMoP/Al₂O₃ catalyst.

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Introduction

The limited crude oil resources and the limitations in term of CO₂ emissions trigger a strong interest for the development of sustainable and ecological sources for fuels and petrochemicals. In this context, a potentially interesting resource could be biomass, and more particularly lignocellulosic material which is available in large quantities in nature (wood, straw, etc...). Two thermal routes are currently studied to transform lignocellulose into liquid fuels: gasification followed by Fischer-Tropsch synthesis and liquefaction followed by a specific treatment to improve the stability and the heating value of the liquid products (because they contain high amounts of oxygenated compounds (15 – 40 wt %)) [1]. In the case of liquefaction, the simplest and most economic treatment would be to hydrotreat the liquid products blended with gas oil cuts so as to use HDS units that already exist on refinery sites. On the other hand, the restrictive regulations adopted by the European Community need to be satisfied. For instance, the sulfur level in diesel fuel and gasoline will have to be lowered to 10 ppm by 2009 [2]. The modeling of such a process requires to know the detailed conversion mechanisms of oxygenated compounds as well as the complex catalytic interactions which exist between sulfur and oxygenated compounds.

In the present work, the effect of oxygenated model compounds (guaiacol and phenol) on the hydrodesulfurization of 4,6-dimethyldibenzothiophene (46DMDBT) and dibenzothiophene (DBT) was studied under conditions close to those used in deep hydrotreating of diesel fuels. The selected oxygenated molecules are representative of those present in ex-biomass liquid products and the sulfur molecules are the most refractory in HDS [3]. These studies on model molecules allowed to rigorously evaluate the effect of the oxygenated compounds on the hydrogenolysis (DDS) and hydrogenation (HYD) pathways involved in the 46DMDBT and DBT transformations.

Materials and Methods

The transformation of 46DMDBT (or DBT) and of oxygenated compounds were studied, separately and in mixtures, in a fixed bed microflowreactor at 340 °C, under 4.0 MPa of total pressure over a conventional CoMoP/Al₂O₃. 46DMDBT (or DBT) (500 ppm S) and the oxygenated compound (0 to 5 wt % of oxygenated compounds corresponding to 0 to 0.051 MPa of partial pressure) were dissolved in a mixture of toluene and orthoxylene (used as the internal standard for the transformation of the oxygenated products) to which dimethyldisulfide (DMDS) (9500 wt ppm S) was added to generate H₂S.

For a better precision in the activity measurements, the contact time was chosen such as to keep also the overall conversion of sulfur compounds nearly constant around 25 % (24-27 %) whatever the oxygenated compound content.

Results and Discussion

The reaction scheme of the transformation of guaiacol was confirmed according to the literature under conditions of deep HDS of diesel fuel [4]. Phenol was the main product, whatever the conversion of guaiacol. Nevertheless, the yield of hydrodeoxygenation products (HDO), cyclohexane and benzene, remained low and corresponded to a low transformation of phenol under these conditions. Indeed, phenol was less reactive than guaiacol and its transformation involved two main pathways : the direct C-O bond rupture (DDO) leading to the formation of benzene and the hydrogenation of the aromatic ring followed by C-O bond rupture (HYD) to lead to the formation of cyclohexene and cyclohexane by hydrogenation.

The transformation of 46DMDBT and DBT in the presence of various amounts (from 0 to 5 wt%) of oxygenated compounds showed a higher inhibiting effect of guaiacol than of phenol on the conversion of 46DMDBT and DBT. The decrease of the global HDS activity which is similar for both sulfur molecules was observed for small amount of guaiacol added (lower than 2 wt %). This corresponds to a decrease of both the HYD and DDS contributions measured respectively by the transformation of 46DMDBT (for the HYD way) and DBT (for the DDS way). This effect was partially reversible in the presence of guaiacol. Phenol also inhibited the conversion of 46DMDBT and DBT but to a lesser extent. A similar loss of activity of approximately 65% for the transformation of 46DMDBT and DBT was observed in the presence of guaiacol which was only of 35% in the presence of phenol. This negative effect of the oxygenated compounds decreases when the conversion of sulfur compounds increases. Oxygenated compounds competed with the sulfur compound for the adsorption on the catalytic sites and the adsorption of guaiacol was higher than this one of phenol. If we suppose that the phenomenon can be described with a simple Langmuir-Hinshelwood rate equation, this will lead to a negative apparent kinetic order of the hydrodesulfurization reaction with respect to the oxygen compounds (the inhibitor). This means that the latter is more strongly adsorbed than the sulfur compounds.

Significance

We can conclude that it is possible to transform simultaneously oxygenated and sulfur molecules under deep HDS conditions. However, oxygenated compounds competed with sulfur compounds on the catalyst surface and an inhibition effect was observed depending of the oxygenated molecules. We are currently investigating other oxygen functions in order to model the impact of an ex-biomass product in co-treatment with HDS of diesel fuels.

References

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