

Effects of solvent and inhibition on hydrodesulfurization of 4,6-Dimethyldibenzothiophene over a NiMoP/Al₂O₃ catalyst

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Introduction

It is well known that among all the sulfur containing compounds present in atmospheric gas oil (AGO) [1], alkyldibenzothiophenes with alkyl groups near the sulfur atom (in positions 4 and 6) are the most refractory for the hydrodesulfurization (HDS). This reaction is recognized to proceed through two main pathways: the direct desulfurization route (DDS) and the hydrogenation route (HYD). The reaction takes place in the liquid phase. Since a constantly changing feed is expected depending on the crude source, it is important to assess the effect that different solvents exert on the catalytic activity. There are only few studies related to solvent effects found in the open literature, Ishihara et al. [2] conclude that the solvent effect on the reaction system is associated to competitive adsorption between the reactants and the solvent on the catalytic surface. Nonetheless, such an explanation is not always justified as aromatic hydrocarbons are expected to adsorb more strongly than saturated hydrocarbons and the latter have been occasionally observed to inhibit to a larger extent the HDS reactions, as stated by Vasudevan and Fierro [3].

Besides, nitrogen-containing and aromatics compounds naturally occurring in AGO and light cycle oil (LCO), used as feedstocks for diesel fuel production, have been identified as strong inhibitors of the HDS reactions during the hydrotreatment process (HDT) [1,5]. Regarding the effect of quinoline (Q) on the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) over a NiMoP/γ-Al₂O₃ catalyst, we showed in a previous work [4] that Q inhibited mainly the HYD route. From this work an increase in HDS activity was surprisingly noticed when using 50 ppm of N as compared with an experiment with a lower Q concentration. On the other hand, fluorene (F) was studied by Koltai et al [5] and they proposed that the adsorption occurred the same way as for 4,6 DMDBT leading to an important competitive effect. This strong effect was associated with the similarity of both molecules competing for the same sites. However, the order of magnitude of this effect was unusually high.

Therefore, we decided in this paper to study the retarding effects of quinoline and fluorene on the HDS of 4,6-DMDBT in the presence of two solvents on a NiMoP/Al₂O₃ catalyst. Dodecane and tetradecane were chosen as solvents since they can be representative of diesel and their structures as aliphatic hydrocarbons are very similar.

Materials and Methods

Typical procedure for catalytic tests was as follows: 4,6-DMDBT (0.2g) was dissolved in 100 ml of dodecane or tetradecane and to a concentration of 9.42x10⁻³ mol/l, (equivalent to 400 ppm of sulfur). F and Q were added at concentrations of 0, 1.6, 3.1, 9.1 and 14.1 mmol/l, equivalent to 0, 25, 50, 150 and 250 ppm as nitrogen with tetradecane and Q was added with two solvents at the same concentration. The mixture was poured into the autoclave and the catalyst (0.2g) was transferred to the reactor. Details of the catalytic test are given elsewhere [1]. Samples were periodically removed during the reaction course and analyzed by gas chromatography.

4,6-DMDBT HDS constant rate was calculated using the concentration data at different times. The DDS and HYD rates were obtained by molar balances. The catalyst used was a NiMoP/γ-Al₂O₃ commercial catalysts (IMP/DSD-3+, 2.3 wt% Ni, 9.5 wt% Mo, 1-2wt% P). The extrudates were crushed, sieved to a 150-177 μm size range and sulfided using a mixture of 10 % H₂S and 90 % H₂ at 400°C for 2 h. 4,6-DMDBT was obtained from Fluka (98%+), Q and F from Merck (98 %+), dodecane and tetradecane (99 %) from Aldrich.

Results and Discussion

Table 1 shows the 4,6-DMDBT disappearance rates for the HDS experiments in the presence of inhibiting molecules. When using dodecane as solvent the HDS activity was higher than that for the experiment with tetradecane. A significant drop of the activity was observed when adding Q at 1.6mol/l for both solvents. However, when increasing the content of Q the activity diminished more rapidly for the experiments with dodecane as solvent. Thus, the solvent provoked differences in the inhibition by quinoline. Regarding selectivities, DDS rates observed for both series were significantly different. An attempt to explain these differences will be presented in this paper considering the reaction schemes for both HDS and hydrodenitrogenation reactions and phase equilibrium aspects such as hydrogen solubility for both solvents.

When using F the activity remained almost constant at 1.6 mol/l, but when increasing the concentration the activity diminished almost the same manner that Q with tetradecane as solvent. Then, the inhibiting effect was lower than that reported by Koltai et al. [5]. No significant differences were found when varying the solvent (not shown). Finally a comparison of the inhibiting effect of this compound with respect to the retarding influences by quinoline will be discussed.

Table 1 Reaction rates for the HDS of 4,6DMDBT in the presence of quinoline or fluorene (mol/l) (T=320°C, P=5.5 MPa). The solvent is indicated between parenthesis.

Concentration (mol/l) x 10 ³	Quinoline (dodecane)	Quinoline (tetradecane)	Fluorene (tetradecane)
	k (mol/kg cat s)*10 ⁷	k (mol/kg cat s) *10 ⁷	k (mol/kg cat s)*10 ⁷
0	1429.1	1351.6	1351.6
1.6	537.5	457.4	1321.3
3.1	569.8	369.1	1160.0
9.1	278.9	173.6	837.5
14.1	72.3	107.9	399.5

Significance

The investigation of the effects of solvent and inhibiting of nitrogen and aromatics species on the deep HDS reactions is of the highest importance in order to design more active and selective catalysts for HDT processes of diesel feedstock.

References

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