New insights in the control of the selectivity HDS/HYD in hydrotreatment

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Introduction

Air pollution is caused to large extent by gas emissions (NOx and SOx) from motor vehicles. Catalytic converters are poisoned by SOx and then can't eliminate NOx anymore. To address this environmental problem, drastic specifications for sulphur-containing gasoline have been imposed: the quantity of sulphur in gasoline has to be lower than 10 wt ppm by the year 2009 in Europe. To satisfy these requests for high-purity products, refiners must remove sulphur compounds from gasoline, and that is essentially done by hydrodesulphurization (HDS)[1]. The largest part of sulphur in the gasoline pool coming from FCC gasoline, this fraction has to be treated selectively to remove sulphur without hydrogenation of olefins (HYD) in order to maintain a high octane number. We saw previously[2] on model compounds that the amount of hydrogen sulphide is a key point in the variation of the selectivity HDS/HYD as it is often seen[3]. This work examined the possibility to generalize the impact of hydrogen sulphide on the selectivity.

Materials and Methods

Reaction conditions. The HDS of 3-methylthiophene (3MT) and the HYD of 1-hexene were carried out in a high-pressure fixed-bed reactor (length: 500 mm, inner diameter 16 mm), under 20 bar of total pressure, at a temperature of 185 °C and a residence time of 0.25 h, after in situ sulfidation of the catalyst. The model compounds feed is composed by 1-hexene (4 mol%) and 3MT (0.031 mol%) in n-heptane. Several parameters have been studied independently: variation of partial pressures (hydrogen or hydrogen sulphide), addition in the feed of various inhibitors: xylenes (0-20% weight in feed), pyridine, piperidine (0-10 ppm weight of nitrogen in the feed), and variation of the model compounds concentrations (hexene: 0-8 mol%, 3MT: 0-0.3 mol% in the feed). Mild operating conditions are used in order to avoid HDN and HDA reactions.

Analysis. Reactor effluents were cooled, condensed and separated into a gas phase and a liquid phase. Reaction products in gas phase were analysed on-line by means of a gas chromatograph equipped with a flame-ionization detector and cryogenic system. The catalyst used (a $CoMo/Al_2O_3$) was stabilized during 2 or 3 days in order to get a steady state and liquid samples have been analysed by gas chromatography (ASTM D6733), X-fluorescence to quantify the total amount of sulphur (ISO20884) and a chromatography using a Pulse Flame Photometric Detector to identify sulphur-compounds.

Definitions. In this paper, apparent kinetic constants are used and assuming a first order rate. The selectivity S is defined by the ratio k_{HDS}/k_{HYD} where k_{HDS} and k_{HYD} are apparent kinetic constants of HDS of 3MT and HYD of hexene-1 reaction respectively.

Results and Discussion

Under mild conditions of temperature and pressure, as used in this work, experiments done show that the formation of thiols by addition of H_2S to olefins is a fast catalytic reaction leading to thermodynamic equilibrium between olefins, thiols and hydrogen sulfide. The experimental studies of 3MT hydrodesulfurization and of olefins hydrogenation, alone or in competition, and impact of hydrogen sulfide on these two reactions bring new insights on the transformation of these molecules on the catalyst: there is clearly a competitive adsorption between the organic compounds, an inhibitor effect of H_2S on both reactions, and the olefins reactivity depends of their squeletal configuration.

Attention was therefore later given to the effect of other compounds naturally present during the hydrotreating process, as hydrogen, aromatics and nitrogen containing organic compounds. Inhibiting effect of nitrogen compounds and hydrogen on the selectivity HDS/HYD has been evidenced while no impact has been shown for aromatics.

For all experiments done and whatever was the parameter changed, the selectivity S has been plotted versus the pressure of hydrogen sulphide present in the reactor, and the selectivity appears to be governed only by the amount of hydrogen sulfide (Figure 1).

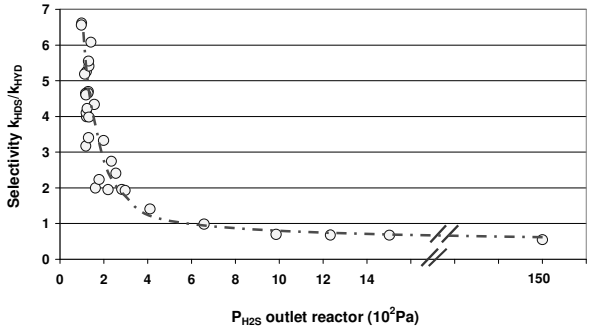

Figure 1. Impact of hydrogen sulfide partial pressure on the selectivity HDS/HYD, for various feeds (T = 185°C, t = 0.25 h).

Significance

Our results indicate that the hydrogen sulfide partial pressure governs the selectivity HDS/HYD, whatever the way to change these parameters (addition of H_2S, dilution by H_2, inhibition of HDS by nitrogen compounds…). Moreover, a kinetic model based on the existence of a single type of active sites was developed and allows to understand such a phenomenon which could be explained by a change of the kinetic limiting step of the HDS reaction with the H_2S partial pressure (for low P_{H2S}: C-S bond breaking, and for high P_{H2S}: hydrogenation of C=C bond).

References

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