EFFECT OF N-CONTAINING MOLECULES ON THE HYDRODESULFURISATION OF DIBENZOTHIOPHENE

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Introduction

The oil industry is under increased pressure from the environmental legislation to limit the sulfur level in gasoline and diesel fuel with a view of reducing exhaust emissions. A sulfur specification of 350 ppm is currently practiced in the EEC and a sulfur content as low as 50 or even 10 ppm is being proposed for the year 2005. Nitrogen-containing molecules inhibit the hydrodesulfurization (HDS) of sulfur-containing molecules, but in normal HDS this is not a big problem because the amount of N-containing molecules in gasoil is much smaller than that of S-containing molecules. N-containing molecules will be harmful in deep HDS, however, because then the amounts of N- and S-containing compounds are comparable.

We have studied the influence of 2-methylpyridine and 2-methylpiperidine on the HDS of dibenzothiophene (DBT) over a sulfided $NiMo/Al_2O_3$ catalyst. DBT was chosen because it allows to study the removal of sulfur by the direct desulfurization pathway (hydrogenolysis) as well as by hydrogenation followed by desulfurization. Pyridine was believed to be the simplest model molecule to study hydrodenitrogenation (HDN). Although the network of reactions taking place in the HDN of pyridine is now well understood, the study of the kinetics of the HDN of pyridine proved to be extremely difficult. The reason for this difficulty is the occurrence of a side reaction of piperidine, the first intermediate in the HDN of pyridine. Two piperidine molecules disproportionate to *N*-pentylpiperidine and ammonia.[1] However, substitution of a hydrogen atom by a methyl group on the α carbon atom of pyridine hinders the disproportionation so much, that it is strongly suppressed and hardly interferes with the other reactions taking place during the HDN of pyridine and piperidine. Therefore we decided to use in our study 2-methylpyridine and 2-methylpiperidine as N-containing molecules.

2-Methylpyridine as well as 2-methylpiperidine suppressed the hydrogenation pathway of the DBT HDS. This indicates that N-containing molecules are harmful in deep HDS because in deep HDS 4,6-dialkyldibenzothiophene molecules must be desulfurized. For these molecules the direct pathway is weak[2] and HDS is mainly determined by the hydrogenation pathway. Although 2-methylpiperidine is a much stronger base than 2-methylpyridine, it hardly influenced the direct HDS of DBT, whereas 2-methylpyridine inhibited this pathway stronger. The difference in inhibition of the two HDS pathways indicates that they occur over different sites on the metal sulfide surface.

Experimental

Catalyst preparation. The $NiMo/\gamma\text{-}Al_2O_3$ catalyst used in this work contained 8 wt% Mo and 3 wt% Ni and was prepared by successive incipient wetness impregnation of $\gamma\text{-}Al_2O_3$ (Condea, pore volume 0.5 cm^3g^{-1}, specific surface area 230 m^2g^{-1}) with an aqueous solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (Aldrich), followed by an aqueous solution of $Ni(NO_3)_2.6H_2O$ (Aldrich). The catalyst was dried in air at ambient temperature for 4 h, then dried in an oven at 120°C for 15 h, and finally calcined at 500°C for 4 h.

Reaction performance. A sample of catalyst (0.05 g) was diluted with 8 g SiC to achieve plug-flow conditions in the continuous-flow fixed-bed reactor. The catalyst was sulfided *in situ* with a mixture of 10% H_2S in H_2 at 400°C and 1.0 MPa for 4 h. After sulfidation, the pressure was increased to 5.0 MPa, and the liquid reactant was fed to the reactor by means of a high-pressure pump (Gilson 307). Experiments were carried out at 573 (HDS) and 613 K (HDN). The composition of the gas-phase feed in most experiments consisted of 1-6 kPa amine reactant, 1 kPa dibenzothiophene, 140 kPa decane (as solvent for the amine in HDN experiments) or 130 kPa toluene (as solvent for dibenzothiophene in HDS experiments), 11-18 kPa heptane and 8 kPa dodecane (as references for GC analysis), 36 kPa H_2S, and 4.8 MPa H_2.

Product analysis. The reaction products were analyzed by on- and off-line gas chromatography with a Varian 3800 GC instrument equipped with a PTA-5 fused silica capillary column (Supelco, 5% diphenylsiloxane/95% dimethylsiloxane, 30 m x 0.25 mm x 0.5 µm). Detection was performed with a flame ionization detector as well as with a pulsed flame photometric detector, which is very useful for detecting small amounts of nitrogen- and sulfur-containing compounds. Weight time was defined as the ratio between the catalyst weight and the molar flow to the reactor. The weight time was changed by varying the flow rates of the liquid and the gaseous reactants, while keeping their ratio constant.

Results and Discussion

HDN network of 2-Methylpyridine. The HDNs of 2-methylpyridine and its intermediate products 2-methylpiperidine, 1-aminohexane, and 2-aminohexane were studied in order to clarify the reaction network of HDN.

2-Methylpiperidine is the only primary product in the 2-methylpyridine HDN, as expected, since the HDN of heterocyclic N-containing aromatic molecules can only occur after ring hydrogenation.[1,3] The HDN of 2-methylpiperidine showed that four compounds such as 1-aminohexane, 2-aminohexane, 2-methylpyridine, and 2-methyl-3,4,5,6-tetrahydropyridine have non-zero selectivity at zero conversion of 2-methylpiperidine and thus might be considered to be primary products (**Figure 1**).

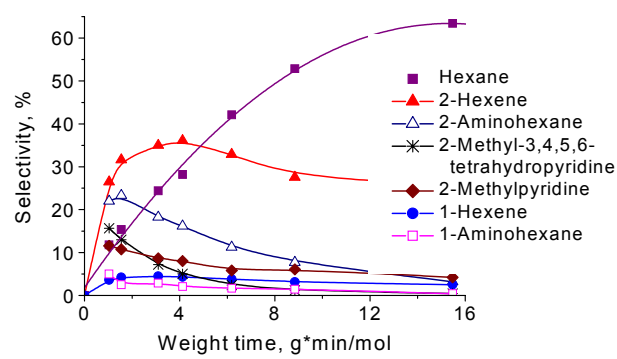

Figure 1. Product selectivities in the HDN of 2-methylpiperidine as a function of weight time.

The presence of most intermediates could be explained by a combination of pyridine ring hydrogenation, piperidine ring opening by elimination, and nitrogen removal by elimination as well as by nucleophilic substitution of the amino group by a sulfhydryl group, followed by elimination of H_2S or hydrogenolysis of the C-S bond. Aminoalkenes, which are expected to be the primary products of the

ring opening of alkylpiperidine, were not observed, probably because of fast hydrogenation to the corresponding amines.

Combining the results of the HDN of 2-methylpyridine, 2-methylpiperidine, 1-aminohexane, and 2-aminohexane, we arrive at the reaction scheme presented in **Figure 2**.

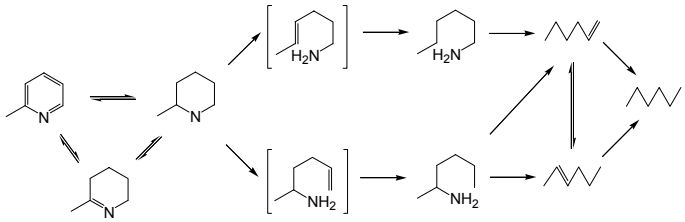

Figure 2. Scheme of the reaction network of the HDN of 2-methyl-pyridine and 2-methylpiperidine.

Comparison of the conversion of 2-aminohexane and 1-aminohexane showed that the reactivity of 2-aminohexane is higher than that of 1-aminohexane. Despite a higher reactivity, much more 2-aminohexane than 1-aminohexane was detected in the HDN of 2-methylpiperidine (**Figure 1**). This proves that the first C-N bond breaking in 2-methylpiperidine occurs predominantly between the nitrogen atom and the carbon atom of the methylene group. The fact that much more 2-aminohexane than 1-aminohexane is formed in the HDN of 2-methylpiperidine further indicates that the methyl group actually has a negative rather than a positive influence on the elimination and hinders the adsorption of 2-methylpiperidine in a conformation in which the nitrogen atom and the β H atom of the methylene group next to the $CH(CH_3)$ group approach the metal sulfide surface.

HDS of Dibenzothiophene and its inhibition by N-containing molecules. The product distribution obtained in the DBT HDS shows that the reaction goes through two parallel pathways (**Figure 3**): (i) direct desulfurization, which yields biphenyl, and (ii) hydrogenation followed by desulfurization, which gives first tetrahydrodibenzothiophene and then cyclohexylbenzene.[2]

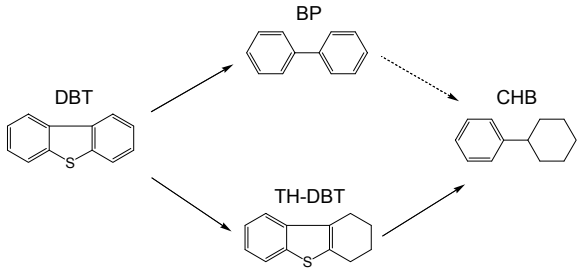

Figure 3. Scheme of the reaction network of the HDS of dibenzothiophene.

The product selectivities in the DBT HDS show that slow hydrogenation of biphenyl (BP) to cyclohexylbenzene (CHB) is also taking place, since the increase of the CHB selectivity with weight time is higher than the decrease of the tetrahydrodibenzothiophene selectivity. The DBT conversion showed first-order behavior when plotting $\ln[(C_{DBT})/(C_{DBT})_0]$ versus weight time.

Basic N-containing compounds have been characterized among the strongest inhibitors for HDS. Our experiments showed that the presence of any amount of N-containing molecule in the feed completely blocks the hydrogenation pathway of the DBT HDS, so that the only product observed is biphenyl. 2-Methylpiperidine is a much stronger base than 2-methylpyridine. Nevertheless, the hydrogenolysis of DBT is inhibited noticeably only at high concentrations of 2-methylpiperidine (**Figure 4**). At 1:1 and 1:2 ratios of DBT to 2-methylpiperidine the conversion of DBT hardly changed. 2-Methylpiperidine did not convert to any products at 573 K and 5 MPa total pressure.

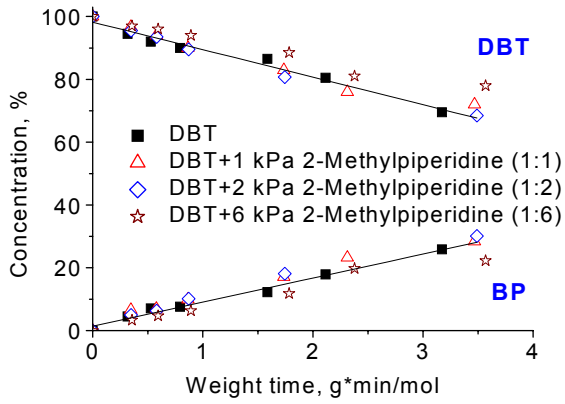

Figure 4. DBT HDS in the presence of different amounts of 2-methylpiperidine.

The experiments performed in the presence of the less basic 2-methylpyridine showed already an inhibition effect at lower concentration of the N-containing molecule (**Figure 5**). In these experiments 2-methylpyridine was partially converted to 2-methylpiperidine.

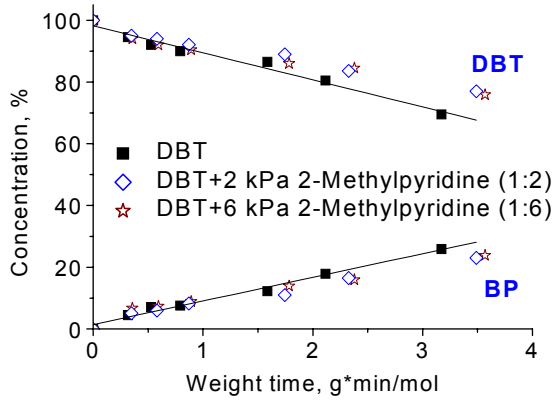

Figure 5. DBT HDS in the presence of different amounts of 2-methylpyridine.

References

(1) Prins, R., *Adv. Catal.* **2002**, 46, 399.
(2) Bataille, F., Lemberton, J. L., Michaud, P., Perot, G., Vrinat, M., Lemaire, M., Schulz, E., Breysse, M., Kasztelan, S., *J. Catal.*, **2000**, *191*, 409.
(3) Nelson, N., and Levy, R. B., *J. Catal.*, **1979**, 58, 485.