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Intermediates in the hydrodesulfurization of 4,6-dimethyl-dibenzothiophene over Pd/γ-Al$_2$O$_3$

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Abstract

The hydrodesulfurization (HDS) reaction network of 4,6-dimethyl-dibenzothiophene (4,6-DM-DBT) was investigated over Pd/γ-Al$_2$O$_3$ at 300 °C and 5 MPa. 4,6-DM-DBT reacts almost exclusively through the hydrogenation pathway, with only 1% reacting via the direct desulfurization route. No significant further hydrogenation of the desulfurized compounds occurred. Three (partially) hydrogenated intermediates of the HYD pathway were observed: 4,6-dimethyl-1,2,3,4-tetrahydro-dibenzothiophene (4,6-DM-TH-DBT), 4,6-dimethyl-hexahydro-dibenzothiophene (4,6-DM-HH-DBT), and 4,6-dimethyl-perhydro-dibenzothiophene (4,6-DM-PH-DBT). These three intermediates were synthesized and their HDS studied. Hydrogenation and dehydrogenation reactions occurred readily between the intermediates. 4,6-DM-TH-DBT and 4,6-DM-HH-DBT interconverted rapidly and were in equilibrium in the HDS of 4,6-DM-DBT and close to equilibrium in the experiments starting from the intermediates. The partly saturated 4,6-DM-TH-DBT and 4,6-DM-HH-DBT intermediates could be desulfurized much easier than 4,6-DM-DBT. This shows that the molecule planarity must be removed to weaken the steric hindrance caused by the methyl groups and to provide better access to the sulfur atom. Temperature had a stronger promotional effect on desulfurization than on hydrogenation and enhanced sulfur removal from the reaction intermediates.

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1. Introduction

The maximum allowed amount of sulfur in gasoline and diesel fuel was reduced to 50 ppm in many parts of the world in 2005 and probably will be reduced even further by the end of the decade. Deep hydrodesulfurization (HDS) technology must be implemented to attain this low level of sulfur. Molecules such as 4,6-dialkyl-dibenzothiophene, with alkyl groups adjacent to the sulfur atom, are very difficult to desulfurize and are problematic in deep HDS [1,2]. 4,6-Dimethyl-dibenzothiophene (4,6-DM-DBT) is therefore commonly used as a model molecule in HDS studies.

Extensive research with metal sulfide catalysts has shown that the HDS of dibenzothiophene (DBT) and 4,6-DM-DBT occurs by two reaction pathways [1–3]. In the direct desulfuriza-

tion (DDS) pathway, the C–S bonds of the reactant molecule are broken by hydrogenolysis, leading to the formation of 3,3′-dimethyl-biphenyl. In the hydrogenation (HYD) pathway, the reactant molecule is first hydrogenated to intermediates, the C–S bonds of which are then broken to form 3,3′-dimethyl-cyclohexylbenzene and 3,3′-dimethyl-bicyclohexyl. Whereas the HDS of DBT occurs mainly by the DDS pathway, the HYD pathway dominates the HDS of 4,6-DM-DBT. A generally accepted explanation for this phenomenon is that in the DDS pathway, the reactant must adsorb in a σ mode, perpendicular to the catalyst surface. In this mode, the neighboring methyl groups hinder bonding with the catalytic sites because they extend further into space than the lone pairs of the sulfur atom, which are responsible for the σ bonding.

The HDS of 4,6-DM-DBT is dominated by the HYD pathway and thus depends on the hydrogenating ability of the catalyst. Because metals are much better hydrogenation catalysts than metal sulfides, metal catalysts might be suitable for deep HDS. Unfortunately, metal catalysts are thermodynamically un-

stable in the presence of sulfur-containing molecules, and the metal particles may change in metal sulfide particles. The noble metals on the right side of the periodic table should be less sensitive to sulfur; indeed, several investigations have shown that Pt and Pd in particular are less susceptible to transformation to inactive sulfides than other metals. Furthermore, the support has been shown to play an important role, with such supports as zeolites and silica–alumina stabilizing Pt particles much better than other supports. Thus the influence of the metal and the support on the hydrogenation of aromatics in diesel fuel over PtPd on amorphous silica–alumina (ASA) [4], benzene over Pt/zeolite MOR and Pt/LTL [5–7], toluene [8] and tetralin [9] over PtPd/Al$_2$O$_3$, toluene and naphthalene over PtPd/ASA [10], toluene over PtPd/ASA and PtPd/zeolite Y [11], naphthalene over PtPd/Mg–Al oxide [12], and tetralin over PtPd/ZrO$_2$-MCM [13] have been studied.

Few studies on the HDS properties of noble metals have been published, however, and these dealt only with their general activities and the DDS to HYD ratios [14–19]. Therefore, we started with an investigation of the reaction network of the HDS of 4,6-DM-DBT over Pd, because this metal has been reported to have the best resistance against H$_2$S. Because this network is complex, it is not enough to study only the reaction of 4,6-DM-DBT; the reactions of some or all of the intermediates should be studied as well. Therefore, we synthesized three key intermediates—4,6-dimethyl-1,2,3,4-tetrahydro-dibenzothiophene (4,6-DM-TH-DBT), 4,6-dimethyl-1,2,3,4,4a,9b-hexahydro-dibenzothiophene (4,6-DM-HH-DBT), and 4,6-dimethyl-perhydro-dibenzothiophene (4,6-DM-PH-DBT)—and studied their HDS in addition to that of 4,6-DM-DBT. We addressed the following questions: How does the DDS occur, and how does the last part of the HYD—that is, the final removal of sulfur from the hydrogenated DBT intermediates—occur?

2. Experimental

2.1. HDS experiments

All of the experiments were performed over a 0.50 wt% Pd on γ-Al$_2$O$_3$ catalyst (Condea, 35–60 mesh $\approx$ 400–250 μm, BET surface area 220 m^2/g, total pore volume 0.6 ml/g, metal dispersion 56% as calculated from the strong hydrogen chemisorption), diluted with SiC in a continuous mode in a fixed-bed Inconel reactor [20]. We used 50 mg of catalyst in the HDS experiments with 4,6-DM-DBT and 20 mg of catalyst for the more reactive hydrogenated intermediates. Before the HDS experiments, the catalyst was activated by in situ reduction in a 50 nml/min hydrogen flow at 300 °C and 0.5 MPa for 2 h. Then the total pressure was increased to the reaction pressure of 5 MPa, and the liquid reactants were fed to the reactor. Most of the HDS and hydrogenation experiments were performed at 300 °C; only one HDS experiment with 4,6-DM-DBT was done at 280 °C. The gas phase feed consisted of 130 kPa decane (as solvent), 8 kPa dodecane (as internal standard), 1 kPa sulfur-containing reactant, and ~4.85 MPa hydrogen. The following sulfur-containing reactants were used:

4,6-DM-DBT (Acros; 95%) and its partially and fully hydrogenated derivatives 4,6-DM-TH-DBT, 4,6-DM-HH-DBT, and 4,6-DM-PH-DBT. These sulfur-containing intermediates were prepared in our laboratory by (partial) hydrogenation of 4,6-DM-DBT, as described herein. Possible further hydrogenation of the desulfurized reaction products was investigated through a hydrogenation experiment with 1 kPa 3,3′-dimethyl-biphenyl (3,3′-DM-BP, 99%; Aldrich). To simulate the presence of sulfur components in the system, the reaction was done in the presence of 1 kPa dibenzothiophene (DBT, 98%; Fluka). To diminish a possible influence of catalyst deactivation, all investigations of the conversion and product yields as a function of weight time started at the highest weight time (lowest flow rate), with the weight time decreased thereafter. We expected palladium to be partly sulfided under these experimental conditions [21].

2.2. Preparation of 4,6-DM-TH-DBT

The production of 4,6-DM-TH-DBT was performed in a similar reactor as used in the HDS experiments. The reactor was loaded with 400 mg 8 wt% Mo/γ-Al$_2$O$_3$ prepared by incipient wetness impregnation [22]. Before the reaction, the catalyst was activated by in situ sulfidation with a mixture of 10% H$_2$S in H$_2$ (50 nml/min) at 400 °C and 1 MPa for 4 h. The temperature was decreased to 320 °C, and the total pressure was increased to 5 MPa, and then the liquid reactants were fed to the reactor. The gas phase feed consisted of 130 kPa toluene (as solvent), 2.5 kPa 4,6-DM-DBT (almost the limit of solubility, 45 mg/ml), 20 kPa H$_2$S, and ~4.85 MPa H$_2$. The reaction was carried out at weight time $\tau = 4.9$ g min/mol. Under these conditions, the product mixture consisted of 69% 4,6-DM-DBT, 18% 4,6-DM-TH-DBT, 6.5% 4,6-DM-HH-DBT, 0.5% 4,6-DM-PH-DBT, and 6% desulfurized products.

After partial evaporation of the solvent, unreacted 4,6-DM-DBT was recovered by crystallization in toluene and separation by filtration. The remaining mother liquor was added to commercial silica and evaporated to dryness. The reaction products were separated by column chromatography over silica, using petrol ether as the eluent. The fractions containing 4,6-DM-TH-DBT were further purified by vacuum distillation. MS, ^{1}H, and ^{13}C NMR spectroscopy revealed the final product to be 4,6-dimethyl-1,2,3,4-tetrahydro-dibenzothiophene.

2.3. Preparation of 4,6-DM-HH-DBT and 4,6-DM-PH-DBT

4,6-DM-HH-DBT and 4,6-DM-PH-DBT were prepared by hydrogenation of 4,6-DM-DBT under high hydrogen pressure in a 300-ml stainless steel autoclave. The autoclave was loaded with 10 g of 10 wt% Pd/C catalyst, 10 g of 4,6-DM-DBT, and 180 ml of glacial acetic acid (as solvent, crucial for a high conversion). The reaction was carried out at 200 °C and 15 MPa H$_2$ for 5 h. The hydrogenation product consisted of 47% 4,6-DM-DBT, 4% 4,6-DM-TH-DBT, 42% 4,6-DM-HH-DBT, 4% 4,6-DM-PH-DBT, and 3% desulfurized products.

After the autoclave was cooled to room temperature, the catalyst was filtered off. Because the catalyst adsorbed a large amount of products, it was refluxed in chloroform for 1 h and