

Kinetics of the HDS of 4,6-dimethyldibenzothiophene and its hydrogenated intermediates over sulfided Mo/Al₂O₃ and NiMo/Al₂O₃

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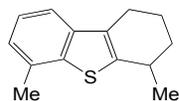
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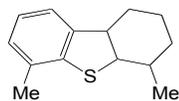
Introduction

Deep hydrodesulfurization (HDS) technology must be implemented to lower the amount of sulfur in gasoline and diesel to the very low level that will be permitted in the future. Molecules such as 4,6-dimethyldibenzothiophene (4,6-DM-DBT), with alkyl groups adjacent to the sulfur atom, are most difficult to desulfurize and are therefore often used as model molecules in deep HDS studies. Extensive research has shown that the HDS of 4,6-DM-DBT over metal sulfide catalysts occurs by two routes [1-3]. One route is through direct desulfurization, in which the C-S bonds of the reactant molecule are broken by hydrogenolysis, leading to 3,3'-dimethylbiphenyl. In the other, hydrogenation route, the reactant molecule is first hydrogenated to intermediates, the C-S bonds of which are broken to form 3,3'-dimethylcyclohexylbenzene (DM-CHB) and 3,3'-dimethyl-bicyclohexyl (DM-BCH).

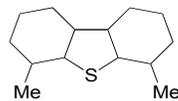
The HDS of 4,6-DM-DBT occurs predominantly through the hydrogenation route, because the methyl groups hinder the σ bonding perpendicular to the catalyst surface in the direct desulfurization route. As a consequence, deep HDS depends on the hydrogenating ability of the catalyst and it does not suffice to study only the reaction of 4,6-DM-DBT; the reactions of the hydrogenated intermediates should be studied as well. Therefore we have synthesized three key intermediates, 4,6-dimethyl-1,2,3,4-tetrahydro-dibenzothiophene (TH-DM-DBT), 4,6-dimethyl-1,2,3,4,4a,9b-hexahydro-dibenzothiophene (HH-DM-DBT), and 4,6-dimethyl-perhydro-dibenzothiophene (PH-DM-DBT), and studied their HDS. The questions that we have addressed are how the final removal of sulfur from the hydrogenated DBT intermediates occurs, and how fast the different reaction steps are.



TH-DM-DBT



HH-DM-DBT



PH-DM-DBT

Materials and Methods

Mo/ γ -Al₂O₃ and NiMo/ γ -Al₂O₃ catalysts with 8 wt% Mo and 3 wt% Ni were prepared by successive incipient wetness impregnation of γ -Al₂O₃ with aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₂·6H₂O. After each impregnation step the catalysts were dried in air at ambient temperature, then dried in an oven at 120°C, and finally calcined at 500°C. Before reaction, the catalysts were activated by in situ sulfidation with 10% H₂S in H₂

at 400°C and 1 MPa for 4 h. HDS reactions were carried out in a fixed-bed inonel flow reactor at 300°C and 5 MPa [4]. The gas-phase feed consisted of 1-kPa reactant (4,6-DM-DBT, TH-DM-DBT, HH-DM-DBT, or PH-DM-DBT), 35-kPa H₂S, 4.8-MPa H₂, 130-kPa toluene (solvent), and 8-kPa dodecane (GC reference).

TH-DM-DBT was synthesized by hydrogenation of 4,6-DM-DBT over sulfided Mo/ γ -Al₂O₃ at 320°C and 5 MPa, while HH-DM-DBT and PH-DM-DBT were prepared by hydrogenation of 4,6-DM-DBT in a 300-ml stainless steel autoclave at 200°C and 15 MPa H₂ over a 10 wt% Pd/C catalyst. Reaction products were separated by column chromatography and purified by vacuum distillation [5].

Results and Discussion

TH-DM-DBT reacted by hydrogenation to HH-DM-DBT and HH-DM-DBT reacted fast back to TH-DM-DBT by dehydrogenation, showing that the tetrahydro and hexahydro intermediates quickly reach equilibrium. All four diastereomers of HH-DM-DBT were observed, two of which could be synthesized in pure form. ¹H and ¹³C NMR, MS/MS, and an X-ray crystal structure determination revealed that one isomer had the (4,4a)-trans-(4a,9b)-cis configuration and the other the (4,4a)-cis-(4a,9b)-cis configuration [5]. These molecules isomerized fast into each other and into the two other isomers during HDS.

HH-DM-DBT reacted slowly to PH-DM-DBT by hydrogenation and to DM-CHB by desulfurization. Also DM-BCH was formed, apparently by desulfurization of PH-DM-DBT. PH-DM-DBT reacted very fast by desulfurization to DM-BCH and 3,3'-dimethyl-cyclohexyl-cyclohexene and 4,6-dimethyl-octahydrodibenzothiophene (with the two remaining double bonds in the thiophene ring) were observed as intermediates in low concentrations. This fast reaction explains why the concentration of DM-BCH was substantially higher than that of PH-DM-DBT in the HDS of HH-DM-DBT. The desulfurization of PH-DM-DBT to DM-BCH was inhibited by H₂S. Over the Mo/ γ -Al₂O₃ catalyst in the presence of H₂S, the concentration of the desulfurized product DM-BCH was always higher than that of DM-CHB, indicating that the desulfurization of HH-DM-DBT is slower than its hydrogenation to PH-DM-DBT. The reverse was true for the NiMo/ γ -Al₂O₃ catalyst. The rate constants of all reaction steps could be determined and compared with those determined over a Pd/ γ -Al₂O₃ catalyst [6].

Significance

This is the first time that the kinetics of the total network of the HDS of 4,6-DM-DBT has been studied. It provides information about the rates of the various steps, which is important for developing better catalysts for deep HDS.

References

1. Girgis, M.J., and Gates, B.C. *Ind. Eng. Chem. Res.* 30, 2021 (1991).
2. Whitehurst, D.D., Isoda, T., and Mochida, I. *Adv. Catal.* 42, 345 (1998).
3. Kabe, T., Ishihara, A., and Qian, W. 'Hydrodesulfurization and Hydrodenitrogenation', Kodansha Ltd., Tokyo, 1999.
4. Egorova, M., and Prins, R. *J. Catal.* 221, 11 (2004).
5. Kukula, P., Gramlich, V., and Prins, R. *Helv. Chim. Acta* 89, 1623 (2006).
6. Röthlisberger, A., and Prins, R. *J. Catal.* 235, 229 (2005).