Catalysis Letters 65 (2000) 169–174

Activities of unsupported second transition series metal sulfides for hydrodesulfurization of sterically hindered 4,6-dimethyldibenzothiophene and of unsubstituted dibenzothiophene

Nikolaj Hermann, Michael Brorson and Henrik Topsøe

Haldor Topsøe Research Laboratories, Nymøllevej 55, DK-2800 Lyngby, Denmark
E-mail: mib@topsoe.dk

Received 22 November 1999; accepted 18 February 2000

The applicability of transition metal sulfides (TMS) from the second transition series in deep hydrodesulfurization (HDS) was examined and compared to that of a traditional, supported CoMo/Al_2O_3 catalyst. Sulfides of Nb, Mo, Ru, Rh and Pd were studied for HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT). Measurements were carried out with unsupported TMS samples at different temperatures and H_2S partial pressures. The trend in DBT HDS activities agreed quite well with those found by previous authors. It was furthermore found that the activities of the metal sulfides towards the sterically hindered molecule 4,6-Me_2DBT closely followed those for DBT. This is somewhat surprising since the direct sulfur abstraction route was of major importance for DBT while the prehydrogenation route, in which ring-hydrogenation in the DBT skeleton precedes desulfurization, was prevalent for 4,6-Me_2DBT. This suggests that common steps are involved in the two routes. For the unsupported metal sulfides, ring-hydrogenated but not desulfurized DBT and 4,6-Me_2DBT products were found in much larger amounts than for supported and promoted MoS_2-based catalysts. This can be rationalized as being due to a relatively higher hydrogenation/desulfurization selectivity ratio for the different transition metal sulfides. Inhibition by H_2S was found to be most pronounced near the center of the transition series.

Keywords: transition metal sulfides, hydrodesulfurization, 4,6-dimethyldibenzothiophene, dibenzothiophene, hydrogenation

1. Introduction

Although supported MoS_2 and WS_2 phases promoted by Co or Ni form the basis for most present-day industrial hydrodesulfurization catalysis there is a considerable interest in understanding the properties of other transition metal sulfide phases [1,2]. The first systematic studies of unsupported (monometallic) transition metal sulfides were made by Pecorado and Chianelli [3], who found that the activity for HDS of dibenzothiophene (DBT) varied systematically with the nature of the metal across the two heavy transition series: from low activity in the beginning of the series (Zr, Hf) to a maximum near the center (Ru, Os) followed by an activity drop towards the end of the series (Pd, Pt). This relationship between activity and the position of the metal in the Periodic Table is often referred to as a “volcano” type relation. The findings of [3] have later been (qualitatively) reproduced in [4]. HDS of thiophene on unsupported [5] and carbon-supported [6,7] transition metal sulfides also follow the volcano type relation; support interaction effects are expected to be small for the carbon catalysts. The observed periodic trend in HDS activity has been found to correlate with the metal–sulfur bond energy in the metal sulfides [8], which suggests that the number of sulfur vacancies [9–11] on the metal sulfide crystallite surfaces is a key parameter in controlling the activity.

Recently, there has been a world-wide focus on reducing motor vehicle emissions further and this has resulted in the introduction of legislation demanding quite dramatic reductions in the maximum allowable sulfur in future transport fuels. Consequently, the focus for much HDS research has moved to the very most refractory sulfur compounds [12–14]. In the case of diesel fuels these are typically the so-called sterically hindered dibenzothiophenes, i.e., DBTs with alkyl substituents in the 4- or 4,6-positions [15,16]: the compound 4,6-dimethyldibenzothiophene (4,6-Me_2DBT) is typically some ten times less reactive than DBT itself [12, 17,18]. In a mid-distillate refinery stream, for example, no unsubstituted DBT is present when HDS has been performed to a typical present day level of $\sim$300 ppm S [14,16,19]; practically all sulfur is present in the form of sterically hindered DBTs. Finding effective ways to remove such sterically hindered DBTs is therefore essential in order to meet the new environmental requirement of $\sim$50 ppm S in diesel fuel [20].

Catalyst systems particularly suited for HDS of the sterically hindered dibenzothiophenes have been sought and in this connection the study of reaction networks [21] is highly relevant. For traditional alumina-supported CoMo and NiMo catalysts, model feed studies with unsubstituted DBT have shown [22] that the dominating HDS route is that of so-called *direct sulfur abstraction,* i.e., a route leading to

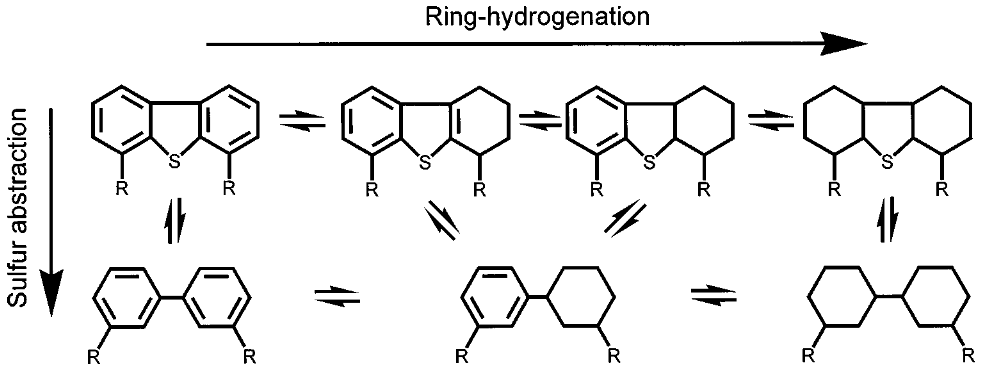

Figure 1. Reaction scheme for hydrodesulfurization (HDS) of dibenzothiophene (DBT, R = H) and 4,6-Me_2DBT (R = CH_3).

biphenyl as the first sulfur-free product. Less important for DBT is the *prehydrogenation route* in which one benzene ring is hydrogenated before sulfur abstraction, i.e., a route in which cyclohexylbenzene is the first sulfur-free product. A general reaction scheme is shown in figure 1. For 4,6-Me_2DBT the situation is reported to be reversed [13,23,24]: here the prehydrogenation route is the dominating one and the direct route only of minor importance. Molecules in which the benzene rings of the DBT skeleton have been hydrogenated but where desulfurization has not taken place are reactive intermediates which are either observed in extremely small (DBT) or quite small (4,6-Me_2DBT) amounts (e.g., [13]).

Since the above studies of differences in reactivities and reaction pathways for DBT and 4,6-Me_2DBT were typically carried out on supported CoMo and NiMo catalysts it was decided to examine a different class of catalysts namely unsupported second transition series sulfides. The aim of the present study was thus to investigate the variation within the transition series of HDS activity of transition metal sulfides towards 4,6-Me_2DBT and compare it with that already reported for DBT. In particular, it has not been known to which extent the volcano curve observed for DBT would be obtained also for 4,6-Me_2DBT. Furthermore, contrary to previous studies [3,4] of DBT, the present experiments have been conducted with substantial and well-defined amounts of H_2S present in the catalyst feed, thereby simulating the typical situation in the bottom of an industrial reactor where HDS of the most refractory sulfur compounds occurs and where H_2S, formed by HDS reactions in the upper part of the reactor, is present.

2. Experimental

Unsupported metal sulfides were prepared either by reaction of metal chloride with Li_2S in tetrahydrofuran (NbS_2 from $NbCl_5$ and MoS_2 from $MoCl_5$) [3] or by reaction of metal salt with gaseous H_2S in water (RuS_2 from $RuCl_3{\cdot}xH_2O$, Rh_2S_3 from $Rh(NO_3)_3$ and PdS from $[Pd(NH_3)_4]^{2+}$). While the NbS_2 precursor material formed from Li_2S and $NbCl_5$, the absence of humidity was essential. The solid materials were isolated by filtration, washed with the solvent and then treated at atmospheric pressure in a tube-furnace with a flow of 10% H_2S in H_2 (Nb, Mo, Rh) or pure H_2S (Ru, Pd) for 2 h at 400 °C. For the materials synthesized in tetrahydrofuran, LiCl was then removed by washing with dilute aqueous acetic acid and the sample was resulfided in the tube-furnace. Exposure of NbS_2 to the atmosphere resulted in irreversible surface-oxide-layer formation (evidenced by Auger spectroscopy) and *severe* lowering of HDS activity. All metal sulfides obtained were characterized by X-ray powder diffraction (XRPD) before catalytic test; the phases NbS_2, MoS_2, RuS_2, Rh_2S_3 and PdS were present in poorly crystalline forms. XRPD after catalytic testing showed that no phase transformations had taken place apart from conversion of PdS to $Pd_{16}S_7$. Surface areas before the catalytic tests were determined by the BET method to be 16 (NbS_2), 24 (MoS_2), 63 (RuS_2), 15 (Rh_2S_3) and 21 m^2/g (PdS). As neither dramatic changes in activity nor XRPD line width decrease were observed, significant sintering did not appear to take place during testing. The supported reference catalyst CoMo/Al_2O_3, had metal loadings of 13.0% Mo and 2.6% Co, and a BET surface area of 231 m^2/g.

Catalytic tests were made by means of a tubular 7.5 mm inner diameter high-pressure reactor with n-heptane solutions of the reactants as feed. The total pressure (reactants + n-heptane + H_2) at reaction temperature was 50 atm corresponding to $p(H_2) = 38$ atm. Liquid feed to gaseous H_2 ratio was 0.3 ml/min : 150 Nml/min. Catalysts were loaded as 600–850 μm mesh granulates diluted with glass microbeads and the amounts (0.39 g NbS_2, 0.47 g MoS_2, 0.10 g RuS_2, 0.20 g Rh_2S_3, 0.25 g PdS and 0.10 g CoMo/Al_2O_3) were chosen so as to give DBT conversions in the range 40–90%. In order to ensure that samples were fully sulfided before the catalytic test, *in situ* sulfidation was made for 4 h at 350 °C by means of a 2.5% solution of dimethyldisulfide (DMDS) in n-heptane and with $p(H_2) = 42$ atm. Under these conditions DMDS decomposes readily to generate H_2S.

Four different feeds were used for testing each catalyst. All feeds contained 1% naphthalene and 0.5% n-nonane, the latter substance was added to serve as internal GC standard. Two of the four feeds both contained 0.5% DBT but differed in their DMDS concentrations (0.5 and 2.5%). The remaining two feeds contained 0.5% 4,6-Me_2DBT and had

DMDS concentrations as the DBT feeds. Decomposition of DMDS yielded $p_0(H_2S)$ of 0.13 or 0.66 atm as a dominating (>90%) permanent background to whatever H_2S was produced by HDS of DBT or 4,6-Me_2DBT. DBT was obtained from Aldrich and 4,6-Me_2DBT was synthesized by a recently published [25], improved procedure in 40% yield with a GC purity of 99%. For the DBT-containing feeds a reactor temperature of 300 °C was employed and for the less reactive 4,6-Me_2DBT a temperature of 320 °C. A catalytic test with a particular catalyst loaded into the reactor comprised five consecutive conditions/feeds each lasting >8 h, sufficient to ensure that steady-state conditions had been reached. The first and last condition/feed was always the same (300 °C, DBT feed with 0.5% DMDS). In this way it could be checked whether the catalyst had maintained its original activity during the course of the test; none of the catalysts displayed dramatic activity differences between start-of-run and end-of-run. The other DBT feed and the two 4,6-Me_2DBT feeds were run in between.

The composition of the liquid product obtained by condensation of the exit gas from the reactor was determined and quantified by GC-FID. The retention times of the various reactant and product species were determined by a GC-MS equipped with the same column (non-polar WCOT, Hewlett–Packard Ultra 2) as the GC-FID. Since many different products were obtained it was decided, when reporting the data in the present paper, to lump them together in three groups: (1) *desulfurized, not ring-hydrogenated* (for DBT: biphenyl (BP), for 4,6-Me_2DBT: 3,3′-Me_2DBP), (2) *desulfurized, ring-hydrogenated* (for DBT: cyclohexylbenzene (CHB) and bicyclohexyl (BCH); for 4,6-Me_2DBT: molecules with $M_r = 188$ (as, e.g., Me_2CHB) and $M_r = 194$ (as, e.g., Me_2BCH)), and (3) *not desulfurized, ring-hydrogenated* (for DBT: tetrahydroDBT; for 4,6-Me_2DBT: molecules with $M_r = 216$ (as, e.g., Me_2tetrahydroDBT), $M_r = 218$ (as, e.g., Me_2hexahydroDBT), and $M_r = 224$ (as, e.g., Me_2dodecahydroDBT)). For the Nb catalyst, product chromatograms revealed that cracking was an important pathway; numerous low-boiling-point substances were present.

Hydrogenation of BP and 3,3′-Me_2BP was studied by means of a feed that contained 0.5% BP (Aldrich), 0.5% 3,3′-Me_2BP (Aldrich), 1% naphthalene, and 0.5% DMDS in n-heptane with 0.5% n-nonane as internal GC standard. The catalyst selected for this study was unsupported PtS that had been prepared in the same way as PdS. XRPD showed that the original PtS had tranformed to elemental Pt during the catalytic testing sequence. The BET area of the PtS sample before catalytic test was 33 m^2/g.

3. Results and discussion

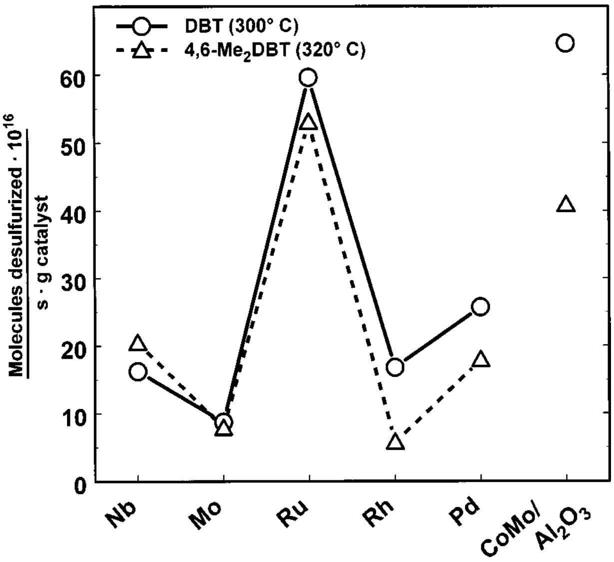

Figure 2. Mass activities of catalysts (unsupported second transition series metal sulfides and CoMo/Al_2O_3) for HDS of DBT (300 °C) and 4,6-Me_2DBT (320 °C) at $p(H_2) = 38$ atm and $p_0(H_2S) = 0.13$ atm. Even though it appears that DBT is primarily desulfurized by the direct sulfur abstraction pathway and 4,6-Me_2DBT by the prehydrogenation pathway, the two trend curves follow each other.

Figure 2 shows the absolute conversion of DBT (300 °C, $p_0(H_2S) = 0.13$ atm) as a function of the metal sulfide catalyst employed. A "volcano" curve dependency can clearly be identified in our measurements. The several orders of magnitude activity differences between the different sulfides observed by Pecorado and Chianelli [3] is, however, not observed by us. In order to get acceptable conversions, HDS of 4,6-Me_2DBT was studied at 320 °C, i.e., 20 °C higher temperature than for DBT. It is most interesting (cf. figure 2) that the activity trends of the metal sulfides for HDS of 4,6-Me_2DBT (at 320 °C) follow those for DBT (at 300 °C). For reference we have also shown the activity data for a traditional CoMo/Al_2O_3 catalyst. Its activity was found (cf. figure 2) to be similar to the most active of the unsupported metal sulfides (RuS_2).

Figure 3 shows the absolute conversions of DBT and 4,6-Me_2DBT normalized to the catalyst surface area present in the reactor. For the CoMo/Al_2O_3 catalyst an active phase surface area of 100 m^2/g has been assumed. Variations across the transition series are seen not to be as pronounced as in figure 2 where activity per mass catalyst is plotted. This difference between the two kinds of plots is also seen in [3].

Figure 4 gives the product distributions for the different catalysts. Data for the Nb catalyst are not included in the figure as cracking resulted in the formation of numerous low molecular weight compounds that together accounted for a substantial part of the converted material. In accordance with previous work (see section 1) it is seen that the main product (82%) from DBT HDS on the CoMo/Al_2O_3 catalyst is biphenyl (BP) with cyclohexylbenzene (CHB) accounting for the remaining 18%. For 4,6-Me_2DBT, on the other hand, and still in accordance with previous work, CHB and BCH (bicyclohexyl) type products accounted for 94% of the converted 4,6-Me_2DBT and only a minor amount (4%) of 3,3′-Me_2BP was obtained. Such product distributions do not necessarily reflect the pathways for HDS: sulfur-

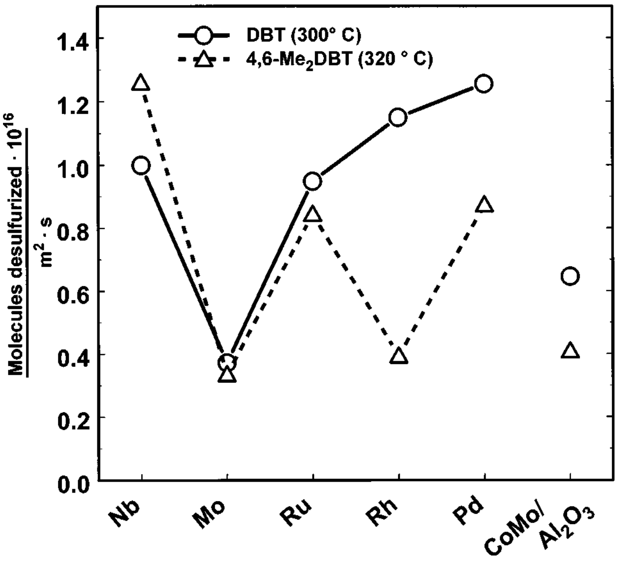

Figure 3. Surface area activities of catalysts (unsupported second transition series metal sulfides and CoMo/Al_2O_3) for HDS of DBT (300 °C) and 4,6-Me_2DBT (320 °C) at $p(H_2) = 38$ atm and $p_0(H_2S) = 0.13$ atm. For the CoMo/Al_2O_3 catalyst an active phase surface area of 100 m^2/g has been assumed.

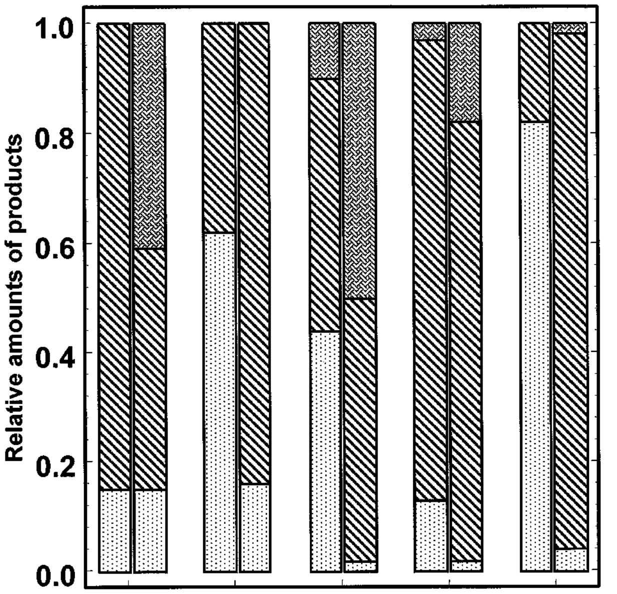

Figure 4. Relative distributions of products obtained at $p_0(H_2S) = 0.13$ atm and 300 °C (DBT)/320 °C (4,6-Me_2DBT). Reaction products have been lumped so as to form three classes that together contain all the converted material: (░) desulfurized, not ring-hydrogenated (e.g., biphenyl), (▧) desulfurized, ring-hydrogenated (e.g., cyclohexylbenzene), and (▦) not desulfurized, ring-hydrogenated (e.g. tetrahydrodibenzothiophene). The exact nature of the (for 4,6-Me_2DBT sometimes numerous) compounds in each of these three different classes is described in section 2.

free products formed in the top of the reactor may become hydrogenated as they pass though the catalyst bed. Thus CHB, for example, may arise *either* from HDS of DBT via the prehydrogenation pathway *or* by hydrogenation of BP formed as a result of HDS by the direct sulfur abstraction pathway (cf. figure 1). For CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts, detailed kinetic studies (e.g., [24]) have shown that CHB and BCH type products for 4,6-Me_2DBT are formed via the prehydrogenation pathway for HDS and *not* by hydrogenation of 3,3′-Me_2BP. So in this case the product distribution does reflect the relative importance of the two HDS pathways.

Thermodynamically the equilibrium for hydrogenation of BP is shifted almost completely toward the fully hydrogenated substance BCH [26].

For the unsupported metal sulfides, BP is a quite abundant product for HDS of DBT whereas 3,3′-Me_2BP is much less important for HDS of 4,6-Me_2DBT (cf. figure 4). This suggests that the prehydrogenation pathway is more important for 4,6-Me_2DBT than for DBT. It should, however, be noted that a feed containing BP and 3,3′-Me_2BP (but no DBT or 4,6-Me_2DBT) over the Pt catalyst showed 4 and 24% conversion (at 320 °C) to cyclohexylbenzene type products at conditions as far as possible identical to those of the HDS experiments. Hydrogenation *after* desulfurization is therefore more important for 4,6-Me_2DBT than for DBT.

Caught-in-the-act evidence for the importance of the prehydrogenation pathway for 4,6-Me_2DBT HDS on the unsupported metal sulfides is found in that HDS intermediates like 4,6-Me_2tetrahydroDBT and 4,6-Me_2hexahydro DBT are observed in sometimes very large proportions (>40%, cf. figure 4).

To the extent that platinum phase(s) present during the catalytic tests can be considered representative for all the unsupported metal sulfides further support for the prehydrogenation pathway being prevalent in 4,6-Me_2DBT HDS comes from combining the following two findings for the Pt catalyst: (1) 3,3′-Me_2BCH was obtained in <2% yield by hydrogenation of 3,3′-Me_2BP in a 4,6-Me_2DBT-free feed, and (2) Me_2BCH accounted for 81% of the ring-hydrogenated desulfurized type products obtained by HDS of 4,6-Me_2DBT. Thus, it seems that Me_2BCH is only formed in large amounts by HDS of already ring-hydrogenated intermediates, i.e., that a prehydrogenation route must be prevalent.

In contrast to supported CoMo and NiMo we find, for the unsupported metal sulfide catalysts, large amounts of hydrogenated but not desulfurized products, in particular for 4,6-Me_2DBT (cf. figure 4). This indicates that compared to the CoMo and NiMo catalysts, the unsupported metal sulfides are relatively better hydrogenation catalysts than they are desulfurization catalysts.

We have found that the apparently different pathways for HDS of DBT and 4,6-Me_2DBT does not lead to any dramatic changes in periodic behavior (cf. the two curves in figure 2). This can be rationalized by assuming that it is similar type of active sites that are involved for both hydrogenation and HDS. There are several experimental results that support this [1]. For example, Lacroix et al. [4]

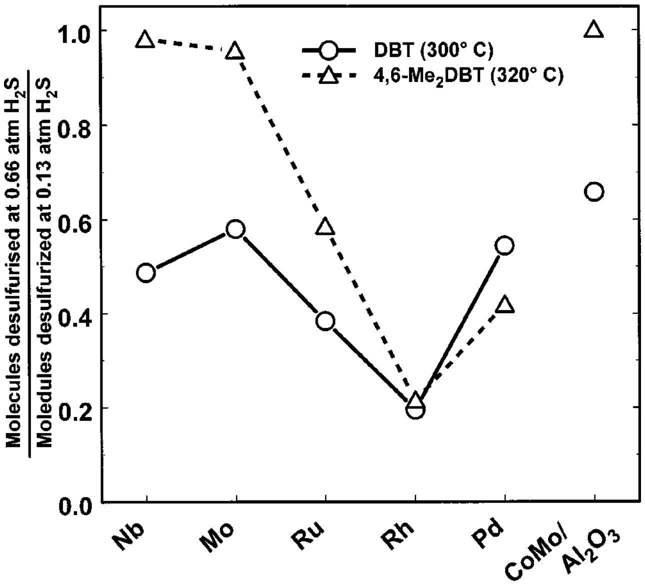

Figure 5. Extent of depression of HDS activity as a consequence of increasing the partial pressure of H_2S from 0.13 atm (defining the 1.0 activity level for the catalyst in question) to 0.66 atm (activity level displayed). H_2S inhibition is clearly more pronounced for the more active transition metal sulfides near the center of the second transition series.

found that hydrogenation of BP over unsupported metal sulfides follows the DBT HDS activities of the same metal sulfides quite closely. Also, Breysse et al. [27] observed that the toluene hydrogenation activities of unsupported Nb, Mo, Ru and Rh sulfides show a steady increase towards the center of the transition series.

H_2S is produced by the HDS reactions and it is a poison for HDS. Figure 5 shows the influence of the H_2S partial pressure on the HDS activity of the different metal sulfide catalysts. For each individual metal sulfide catalyst the activity at $p_0(H_2S) = 0.13$ atm has been defined as 1.00 and the points plotted show to which level the activity is reduced by increasing $p_0(H_2S)$ by a factor of 5. The general trend is that the early and late transition metal sulfide catalysts are little or not inhibited while metal sulfides from the middle of the transition series are strongly inhibited. This trend in H_2S inhibition could be the reason why we found less pronounced differences in DBT HDS activity between the sulfides than, e.g. [3], where the only H_2S present was that formed by the HDS reaction.

As mentioned above, a feed containing 3,3′-Me_2BP was used to study the hydrogenation of this compound without the interfering presence of any 4,6-Me_2DBT. Over the Pt catalyst the expected two isomers of Me_2CHB (*cis* and *trans*) and the expected three isomers of Me_2BCH (*cis*,*cis*; *cis*,*trans*; and *trans*,*trans*; $M_r = 194$) were obtained. Isomerism is here associated with the relative orientations of the substituents (methyl and tolyl, methyl and methylcyclohexyl) on the cyclohexyl ring(s). In metal sulfide catalyzed HDS of 4,6-Me_2DBT we often observed *more* isomers than expected: GC-MS analysis of the HDS products of 4,6-Me_2DBT from the CoMo/Al_2O_3 and Pt catalyst showed 4 and $\geqslant 5$ peaks, respectively, that were associated with molecules with $M_r = 194$. Three of these peaks coincided with the hydrogenation products obtained for pure 3,3′-Me_2BP. Similarly, $\geqslant 5$ peaks of $M_r = 224$ corresponding to the fully ring-hydrogenated but not desulfurized molecule 4,6-Me_2dodecahydroDBT was observed even though only two isomers are expected. These findings suggest that reconstruction of the carbon framework, e.g., methyl group migration, takes place. Since only one peak with $M_r = 182$ (3,3′-Me_2BP) is observed it seems that the reconstruction takes place only after ring hydrogenation of the DBT skeleton. It is our intention to discuss this issue further in a future paper where we will also include data for the third transition series metal sulfides and naphthalene hydrogenation.

4. Conclusion

It has been found that unsupported second transition series metal sulfides display the same volcano curve variation in HDS activity for 4,6-dimethyldibenzothiophene as previously reported for dibenzothiophene. The very pronounced differences in activity between the metal sulfides from the center of the transition series and the metal sulfides from the beginning and end was found to be dampened by the presence of H_2S. Our studies show that, compared to a traditional CoMo/Al_2O_3 catalyst, the bulk sulfides are relatively better hydrogenation catalysts than they are HDS catalysts.

Acknowledgement

We thank Ingeborg Vind Nielsen and Peder Blom for conducting the high-pressure-reactor studies and Lars Kürstein for the GC-MS analyses.

References

[1] H. Topsøe, F.E. Massoth and B.S. Clausen, in: *Catalytic Hydroprocessing; Catalyst Surface and Chemistry*, Catalysis – Science and Technology, Vol. II, eds. R.R. Anderson and M. Boudart (Springer, Berlin, 1996).

[2] R.R. Chianelli, M. Daage and M.J. Ledoux, Adv. Catal. 40 (1994) 177.

[3] T.A. Pecorado and R.R. Chianelli, J. Catal. 67 (1981) 430.

[4] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat and M. Breysse, J. Catal. 120 (1989) 473.

[5] M. Lacroix, H. Marrakchi, C. Calais, M. Breysse and C. Forquy, in: *Heterogeneous Catalysis and Fine Chemicals II*, Stud. Surf. Sci. Catal., Vol. 59, eds. M. Guisnet et al. (Elsevier, Amsterdam, 1991) pp. 277–285.

[6] J.P.R. Vissers, C.K. Groot, E.M. van Oers, V.H.J. de Beer and R. Prins, Bull. Chim. Soc. Belg. 93 (1984) 813.

[7] M.J. Ledoux, O. Michaus, G. Agostini and P. Panissod, J. Catal. 102 (1986) 275.

[8] J.K. Nørskov, B.S. Clausen and H. Topsøe, Catal. Lett. 13 (1992) 1.

[9] H. Topsøe, B.S. Clausen, N.-Y. Topsøe, J.K. Nørskov, C.V. Ovesen and C.J.H. Jacobsen, Bull. Soc. Chim. Belg. 104 (1995) 283.

[10] L.S. Byskov, J.K. Nørskov, B.S. Clausen and H. Topsøe, ACS Div. Petrol. Chem. Prepr. 43 (1998) 12.

[11] C.H.J. Jacobsen, E. Törnqvist and H. Topsøe, Catal. Lett. 63 (1999) 179.

[12] B.C. Gates and H. Topsøe, Polyhedron 16 (1997) 3213.

[13] D.D. Whitehurst, T. Isoda and I. Mochida, Adv. Catal. 42 (1998) 345.

[14] H. Topsøe, K.G. Knudsen, L.S. Byskov, J.K. Nørskov and B.S. Clausen, in: *Science and Technology in Catalysis 1998*, Stud. Surf. Sci. Catal., Vol. 121 (Elsevier, Amsterdam, 1999) ch. 2, pp. 13–22.

[15] D.R. Kilanowski, T. Teeuwen, V.H.J. de Beer, B.C. Gates, G.C.A. Schuit and H. Kwart, J. Catal. 55 (1978) 129.

[16] T. Kabe, A. Ishihara and H. Tajima, Ind. Eng. Chem. Res. 31 (1992) 1577.

[17] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. de Beer, B.C. Gates and H. Kwart, J. Catal. 21 (1980) 523.

[18] X. Ma, K. Sakanishi and I. Mochida, Ind. Eng. Chem. Res. 33 (1994) 218.

[19] K.G. Knudsen, C.V. Ovesen, I.V. Nielsen and K.V. Andersen, in: *Proc. JECAT '97*, Tsukuba, Japan, 25–28 November 1997, PII-26.

[20] K.G. Knudsen, B.H. Cooper and H. Topsøe, Appl. Catal. A 189 (1999) 205.

[21] M.J. Girgis and B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.

[22] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick and B.C. Gates, AIChE J. 24 (1978) 1015.

[23] T. Kabe, A. Ishihara and Q. Zhang, Appl. Catal. A 97 (1993) L1.

[24] T. Isoda, X. Ma and I. Mochida, Prepr. Am. Chem. Soc. Div. Fuel Chem. 39 (1994) 584.

[25] C. Kuehm-Caubère, S. Adach-Becker, Y. Fort and P. Caubère, Tetrahedron 52 (1996) 9087.

[26] C.G. Frye, J. Chem. Eng. Data 7 (1962) 592.

[27] M. Breysse, G. Berhault, M. Lacroix, J. Afonso and G. Pérot, ACS Div. Petrol. Chem. Prepr. 43 (1998) 59.