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Reactivities in deep catalytic hydrodesulfurization: challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene

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Abstract—The organosulfur compounds present in fossil fuels vary widely in their reactivities in catalytic hydrodesulfurization. In naphtha, thiophene is so much less reactive than the thiols, sulfides, and disulfides that the latter can be considered to be virtually infinitely reactive in practical high-conversion processes. Similarly, in gas oils and petroleum residua, the reactivities of (alkyl-substituted) 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene are much less than those of other sulfur-containing compounds. Consequently, in deep hydrodesulfurization, the conversion of these key substituted dibenzothiophenes largely determines the required conditions. Because of the growing technological importance of deep desulfurization of heavy feedstocks, we infer that 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene are the most appropriate compounds for investigations of candidate catalysts and reaction mechanisms. © 1997 Elsevier Science Ltd

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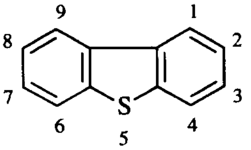
REACTIVITIES IN HDS: WHAT IS KNOWN

The goals of this note are to review briefly what is known about reactivities of organosulfur compounds in fossil fuels and to draw inferences about how these results may guide precess modelling, testing of new catalysts, and fundamental investigations of reaction networks, kinetics, and mechanism.

Years of research on catalytic hydrodesulfurization (HDS) [1,2] have led to technologically valuable generalizations about how the reactivity of a compound undergoing HDS depends on its structure. Under conditions typical of industrial HDS, the reactivities of compounds predominant in naphtha (thiols, sulfides, and disulfides) are much greater than those of thiophenic compounds [3]. The reactivities of the latter depend strongly on the number of rings in the reactant (Fig. 1), with thiophene being the most reactive and dibenzothiophene the least. In the family of (substituted) dibenzothiophenes, which are present in the heavier fractions of oil (e.g., residua), methyl groups in the 4 and in the 4 and 6 positions lead to order-of-magnitude reductions in the reactivity, whereas methyl groups in the other positions have only little effect on the reactivity (Table 1) [5].

The foregoing reactivity pattern has been observed



Dibenzothiophene

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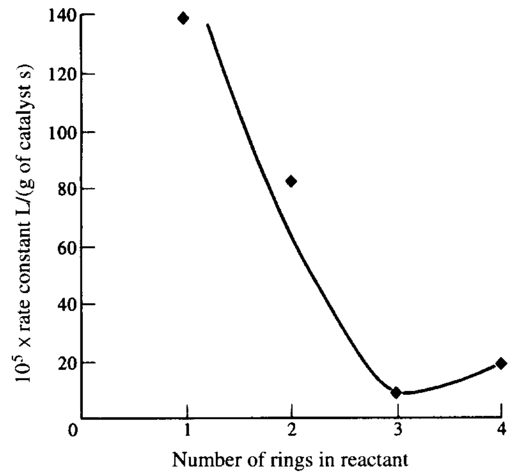

Fig. 1. Dependence of reactivity on the number of rings in thiophenic compounds. The reactants were thiophene, benzothiophene, dibenzothiophene, and benzo[*b*]naphtho[2,3-*d*]thiophene. Reactivities were determined in a batch reactor with each individual reactant in *n*-hexadecane solvent at 300°C and 71 bar; the catalyst was Co-Mo/γ-Al_2O_3 [4].

for pure compounds reacting with H_2 in the presence of Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalysts [1–3]. Similar results have been found for the same compounds reacting in various oil fractions [7–12] and coal liquids [6].

The reactivities summarized in Table 1 for compounds in a mixture of the neutral oils fraction of a coal-derived liquid (containing largely polycyclic aromatic hydrocarbons and nonpolar oxygen-containing compounds such as dibenzofuran) are less than those determined for the individual compounds reacting in *n*-hexadecane. The reactivity of a compound with H_2 in a mixture is typically less than that of the compound in a nearly inert solvent such as *n*-hexadecane, and the difference is often attributed to the competitive adsorption of the mixture components on the catalyst; aromatic compounds containing nitrogen are the strongest inhibitors [2]. The inhibiting effects also depend on the type of molecule being desulfurized. For example, high concentrations of aromatics (e.g., naphthalene) exert a moderate inhibiting effect on dibenzothiophene conversion, but only a weak inhibiting effect on the conversion of 4,6-dimethyldibenzothiophene [13].

A reaction network determined for dibenzothiophene conversion with H_2 in the presence of Co-Mo/Al_2O_3 [14] (Fig. 2) accounts well for the available data [1,2], indicating competitive, hydrogenation (prehydrogenation and saturation of an aromatic ring) and direct hydrogenolysis (cleavage of C-S bonds). The data available for 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene indicate that both the hydrogenolysis and hydrogenation pathways are significant but that the rate of hydrogenolysis relative to the rate of hydrogenation is less for these substituted dibenzothiophenes than for dibenzothiophene itself [5, 16–18]. The data of Table 2 represent

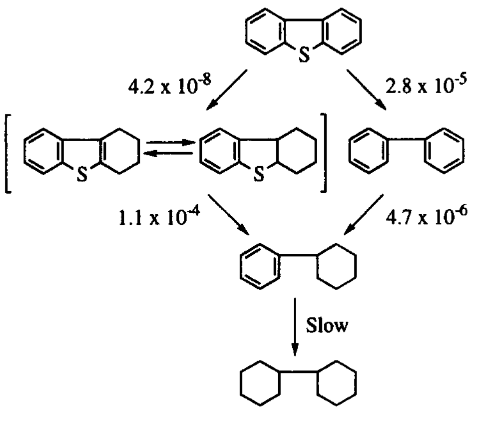

Fig. 2. Reaction network for dibenzothiophene hydrodesulfurization and hydrogenation catalyzed by Co-Mo/γ-Al_2O_3 [14]. The pseudo-first-order rate constants, shown next to the arrows, are given in units of L/(g of catalyst s). The temperature was 300°C and the pressure 102 bar. These results were obtained in the near absence of H_2S; H_2S changes the values of the rate constants. For a recent statement of the kinetics in this network, see [15].

Table 1. Reactivities of methyl-substituted dibenzothiophenes

Reactant/solvent	Temperature (°C)	Pseudo-first-order rate constant (L/(g of catalyst s))	Reference
Dibenzothiophene/*n*-hexadecane	300	7.38×10^{-5}	5 (b)
Dibenzothiophene/neutral oils	355	5.8×10^{-5}	6
2,8-Dimethyldibenzothiophene/*n*-hexadecane	300	6.72×10^{-5}	5 (b)
3,7-Dimethyldibenzothiophene/*n*-hexadecane	300	3.53×10^{-5}	5 (b)
4,6-Dimethyldibenzothiophene/*n*-hexadecane	300	4.92×10^{-6}	5 (b)
4-Methyldibenzothiophene/*n*-hexadecane	300	6.64×10^{-6}	5(b)
4-Methyldibenzothiophene/neutral oils	355	1.8×10^{-5}	6

Reaction conditions: flow reactor, reactants present in liquid phase with H_2 at 102 bar when the solvent was *n*-hexadecane and 120 bar when the solvent was neutral oils; the catalyst was Co-Mo/γ-Al_2O_3 in the former case and Ni-Mo/γ-Al_2O_3 in the latter.

Table 2. Pseudo-first-order rate constants for HDS of dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene catalyzed by $CoMo/Al_2O_3$ at 350°C and 50 bar [18].

Reactant	Hydrogenolysis rate constant (h^{-1})	Hydrogenation rate constant (h^{-1})	Total HDS rate constant (h^{-1})
Dibenzothiophene	123	15	138
4-Methyldibenzothiophene	26	15	41
4,6-Dimethyldibenzothiophene	6	11	17

HDS of dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene in the presence of a $Co\text{-}Mo/Al_2O_3$ catalyst, showing the relative importance of the hydrogenolysis and hydrogenation pathways [18]. Dibenzothiophene is desulfurized predominantly by the hydrogenolysis pathway, whereas 4,6-dimethyldibenzothiophene is desulfurized predominantly by the hydrogenation pathway. Thus, it is not surprising that the catalysts $Ni\text{-}Mo/Al_2O_3$ and $Ni\text{-}Mo\text{-}P/Al_2O_3$, which are generally regarded as superior to $Co\text{-}Mo/Al_2O_3$ as hydrogenation (and HDN) catalysts and inferior to $Co\text{-}Mo/Al_2O_3$ as HDS catalysts (as illustrated by their performance in HDS of dibenzothiophene), are better than $Co\text{-}Mo/Al_2O_3$ for the conversion of 4,6-dimethyldibenzothiophene (Table 3) [7,13].

IMPLICATIONS OF THE REACTIVITIES

The reactivity data characterizing HDS of naphtha show that at the high conversions attained in practice, all the compounds except thiophenes are removed virtually completely; thus, thiophene is the key component, and predictions of the overall sulfur removal can be based to a good approximation on the removal of thiophene [3]. Similarly, in the latter stages of deep desulfurization of gas oils (e.g., to give 0.05 wt% S in the product, as is now typical in practice), the more reactive compounds are virtually all converted. For example, the data of Fig. 3 show removals of organosulfur compounds from oil measured by gas chromatography with a sulfur-specific detector. At the highest conversions, the predominant remaining organosulfur compound is 4,6-dimethyldibenzothiophene.

Table 3. Comparison of catalysts for HDS of dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene at 350°C and 50 bar [18]

Reactant	Rate constant for reaction catalyzed by $Ni\text{-}Mo\text{-}P/Al_2O_3$ relative to that for reaction catalyzed by $Co\text{-}Mo/Al_2O_3$
Dibenzothiophene	0.76
4-Methyldibenzothiophene	1.01
4,6-Dimethyldibenzothiophene	1.61

Thus, predictions of the overall sulfur removal must take into account the removal of the key components, which can be measured by gas chromatographic analysis of the feed and product. The generalization is applicable to the heavier feedstocks (residua) as well. Models accounting for the reactivities of several fractions of organosulfur compounds in residua have been presented [19], with the HDS of each being represented as first-order in the reactant, as expected [2,3].

In deep HDS, which is becoming the rule rather than the exception because of increasingly stringent fuel sulfur specifications needed to meet air-quality standards, the key, relatively unreactive, compounds, (substituted) 4-methyldibenzothiophene and (substituted) 4,6-dimethyldibenzothiophene, must be substantially converted, and the more reactive organosulfur compounds must be almost completely converted. An important challenge is to find more active catalysts for deep HDS, and this challenge can be stated without much oversimplification as that of finding more active catalysts for HDS of (substituted) 4-methyldibenzothiophene and (substituted) 4,6-dimethyldibenzothiophene.

Another practical inference is that in the search for improved catalysts it may be fruitful, particularly in the initial stages of investigations of candidate catalysts, to use the performance in HDS of 4-methyldibenzothiophene and/or 4,6-dimethyldibenzothiophene as a guide. By investigating the reactivities of these pure compounds, it may be possible to determine the reaction networks and relative rates of hydrogenation and hydrogenolysis and thus to gain insights into the workings of the candidate catalysts.

Furthermore, it may be possible to modify the reactivities of compounds such as 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene by converting them in pretreatment processes. Routes that have been pursued recently for conversion of the relatively unreactive organosulfur compounds include isomerization, dealkylation, and hydrocracking prior to desulfurization [20–22].

The marked differences in reactivities of the various organosulfur components in residua have important implications for the recognition of optimal processing conditions and of optimal catalysts or catalyst com-

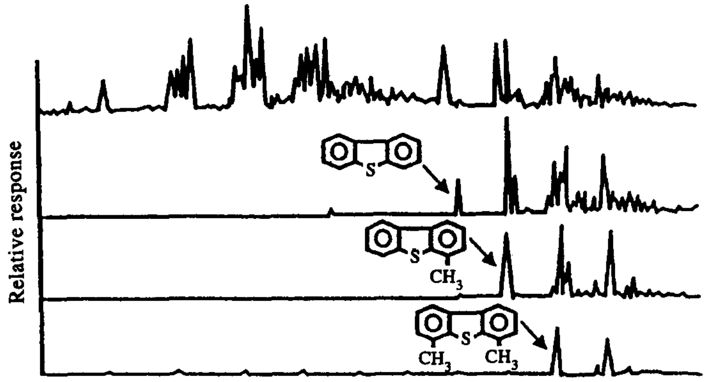

Fig. 3. Gas chromatographic traces showing the removal of organosulfur compounds from oil [10]. The upper trace represents the feed, and the traces in descending order represent products with increasing conversions in HDS. The data illustrate the relatively low reactivity of 4,6-dimethyldibenzothiophene.

binations in deep HDS [23]. A process engineer should be able to estimate the fractional sulfur removal at high HDS conversions rather well by measuring the fractional removal of these key components and accounting for the almost complete removal of the others. Changes in the conversions of these key compounds during operation might be useful measures of the changes undergone by a catalyst as it ages. Furthermore, it seems to be feasible to determine processing correlations, such as those for prediction of catalyst activity loss in HDS, in terms of the catalytic activity for conversion of the key components. Kinetics representing the dependence of reaction rate on temperature and reactant and inhibitor concentrations, determined from data for conversion of the key components, might form the basis for models of process operation.

Furthermore, in fundamental investigations of catalyst structure–property relationships and reaction mechanisms, it would be advantageous to investigate these relatively unreactive compounds, although, under some conditions (e.g., ultrahigh vacuum), this may not be possible. Questions to be answered include the following:

1. How do the rates of hydrogenation and hydrogenolysis of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene depend on reaction conditions (e.g., temperature, concentration of H_2, concentration of H_2S, and concentrations of other inhibitors)?
2. How do the methyl (or other alkyl) substituents affect these reactivities? Do these substituents sterically hinder the adsorption or subsequent steps in the surface reactions? Are the effects of these substituents (Table 1) too small to be described as steric [2]? How should they be described?
3. How do changes in the catalyst morphology (e.g., the dimensions of CoMoS domains [1]) affect the rates of the hydrogenation and hydrogenolysis reactions, and do the effects of the substituents vary depending on this morphology?
4. Can answers to questions such as these lead to ideas about how to make better catalysts and develop better processes?

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