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Assessment of limitations and potentials for improvement in deep desulfurization through detailed kinetic analysis of mechanistic pathways

D.D. Whitehurst*, H. Farag, T. Nagamatsu, K. Sakanishi, I. Mochida

Institute of Advanced Materials Study, Kyushu University, Fukuoka, Japan

Abstract

Utilizing an improved method for the assignment of the rate constants to the complicated network of reaction pathways in the hydrodesulfurization (HDS) of polyaromatic sulfur compounds (PASCs), new understanding has been obtained concerning the intrinsic limitations to achieving the new distillate fuels standards. Establishing the relative rates for hydrogenation of the parent sulfur compound and its desulfurized products, and considering thermodynamic limitations on hydrogenated intermediates are critical to these improved kinetics. With this new approach, it has been possible to more accurately assess the differences in performance of different catalysts such as Co–MoS_x/Al_2O_3, Ni–MoS_x/Al_2O_3 and analogous catalysts supported on carbons, the basic causes of selectivity change with temperature, and the mechanistic consequences of inhibitors on the HDS product distributions. Ni promoted catalysts were found to possess much higher hydrogenation activities than comparable Co promoted catalysts. Carbon supported catalysts appear to have potential for HDS at high temperatures. Inhibition by H_2S affects both hydrogenation and direct sulfur extraction HDS routes, but, secondary hydrogenation of desulfurized aromatic products was found to be the most sensitive to inhibition. Naphthalene inhibits all hydrogenation reactions but has little effect on direct HDS.

Keywords: Hydrodesulfurization; Polyaromatic; Kinetics; Intermediates; Thermodynamic

1. Introduction

The recent tightening of fuel specifications to lower the sulfur contents of gas oils to 0.05% S and the potential of even stricter standards in the future have prompted a great deal of interest in understanding the inherent limitations in the deep desulfurization of petroleum streams. Polyaromatic sulfur compounds (PASCs) such as dibenzothiophene derivatives, are known to be the most difficult to remove. Unlike the one and two ring sulfur species where direct sulfur extrusion is rather facile, in the hydrodesulfurization (HDS) of multi-ring aromatic sulfur compounds, often the observed products are produced via more than one reaction pathway. Therefore, consideration of a network of sequential and parallel reactions is necessary. This complex network is difficult to kinetically analyze, yet such analyses are necessary for the understanding of subtle changes in product compositions which result from changes in catalyst formulations and/or reaction conditions and the influence of other feed components (inhibitors) on the progress of the

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*Corresponding author.

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HDS conversion. This report presents a new approach to deconvoluting these complex networks and illustrates how improved kinetic analysis can aid in the evaluation of the present limitations in achieving deep desulfurization of gas oils with today's technology.

In seeking new and improved ways for achieving the ultra low levels of sulfur in the fuels of the future, it is important to understand the nature of the sulfur compounds that are to be converted and to understand how these materials are transformed through interactions with catalytic surface species, the pathways involved during these transformations and the associated kinetic, and thermodynamic limitations. Such considerations dictate the process conditions and reactor process configurations that must be used to promote the desired transformations. These considerations were the subject of a recent review by the present authors and for an in depth overview of the problems the readers are referred to that review [2]. This paper concentrates on the details of kinetic interpretations of experimental details in HDS studies on polyaromatic sulfur compounds.

It has been known for many years that PASCs such as dibenzothiophene derivatives are the most difficult components to desulfurize in gas oils [2–4]. However, within this class of compounds, the reactivities vary by over a factor of 50. It was previously observed that the overall kinetics for the desulfurization of gas oils could be described by lumping the rate constants for the individual sulfur species into four reactivity groups [5]. In order of decreasing HDS, reactivity, these groups correspond generally to alkylbenzothiophenes (group 1), alkyldibenzothiophenes with no substitution in the 4 or 6 positions (group 2), alkyldibenzothiophenes with one substituent on the 4 position (group 3) and alkyldibenzothiophenes substituted in both the 4 and 6 positions (group 4). The relative abundance of the four groups in Iranian gas oil was found to be 39%, 20%, 26% and 15%, respectively [5]. If the new sulfur standards are to be met with this feed, all of groups 1,2 and 3 must be removed completely and over one half of the least reactive materials (group 4) must also be converted without harming any of the other non-sulfur containing fuel components, which represent about 98% of the total fuel.

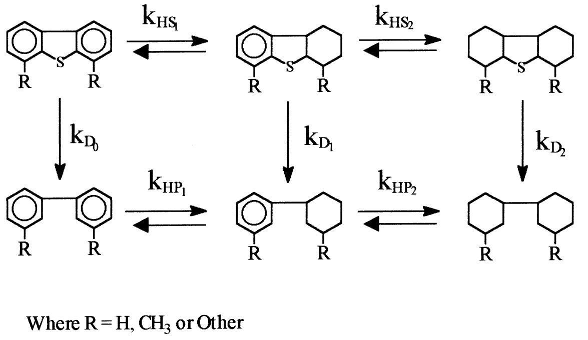
To put these problems into perspective, as discussed above, the PASCs remaining at the 0.20% S level are lower in reactivity, by a factor of 10–50, than the sulfur compounds that are now removed in lowering the sulfur level from 1.2% to 0.20%. Even with catalysts 10 times as active, the reactor volume may have to be doubled to convert the required 75% of the least reactive PASCs to achieve the 0.05% S target. Based on the composition of a typical gas oil and using the first order rate constants for the different classes of sulfur compounds [5] it is possible to theoretically calculate the contact times required to reach different levels of sulfur in this gas oil using conventional technology. Such calculations predict that the reactor volumes will have to be increased by about a factor of 4 to meet the new specifications unless much more active catalysts can be developed than are presently available. Thus, it is important to identify the intrinsic limitations in HDS of dialkyldibenzothiophenes.

2. Experimental

All reagents, except for 4,6-dimethyldibenzothiophene (46DMDBT), were purchased from Waco Chemical 46DMDBT was synthesized according to procedures reported in [1]. Co(Ni)–Mo/C catalysts (Co(Ni) 2 wt%; Mo 10 wt%) were prepared by impregnation of the supports with Mo acetylacetonate and Co or Ni acetates in alcohol solvent. Carbons used as supports (A and B) had surface areas of 2150 and 1350 m^2/g. The commercial CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts, used for activity comparisons, contained similar levels of Co, Ni and Mo. Catalysts were presulfided prior to reaction by flowing 5 wt% H_2S/H_2 gas mixture at atmospheric pressure at 360°C for 3 h. Solutions of 0.1–1 wt% dibenzothiophene (DBT) or 46DMDBT in decane solvent were used for the kinetic measurements. To establish biphenyl ring hydrogenation rates, either biphenyl (BP) or 3,3′-dimethylbiphenyl (33DMBP) were added in equimolar quantities to the 46DMDBT or DBT reagent solutions, respectively. Reactions were conducted in a 100 ml magnetically stirred autoclave. Quantitative analyses of the collected samples were obtained by GC.

3. Results and discussion

The reaction network involved in the HDS of 46DMDBT has been studied for many years, but there



Scheme 1.

is no generally accepted description of this network in the literature. As will be discussed later, thermodynamic equilibria must be included in this network. Thus, we have found it convenient to describe the overall reaction network for the HDS of 46DMDBT as shown in Scheme 1 [2].

In this scheme, the rate constants are expressed with subscripts which define the particular reaction step. For example, all "D" subscripts represent desulfurization steps, all "HS" subscripts describe hydrogenation steps for compounds containing sulfur and all "HP" subscripts describe hydrogenation steps for non-sulfur containing aromatics. Unfortunately, the complexity of such a network containing numerous rate constants does not allow one to define a unique set of rate constants using conventional curve fitting techniques, unless one conducts an inordinate number of kinetic experiments.

To overcome this dilemma, we have found that it is possible to set boundaries on the ratios of several key rate constants and thus reduce the errors in fitting theoretical curves to experimentally derived data [6]. The most important boundary was found to be the relative rates of hydrogenation of the parent DBT and its biphenyl derivative. The reason for this criticality is that the cyclohexylbenzene derivative can be produced by two different reaction pathways, as shown in Scheme 1. Conclusions drawn about the relative contributions of the direct sulfur extraction route (k_{D0}) and the hydrogenative desulfurization route (k_{HS1}) can often be confused unless one clearly knows value of k_{HP1} (biphenyl hydrogenation).

To set this boundary, competitive experiments are conducted to determine the relative rates of hydrogenation of the biphenyl compound in question and some non-interfering standard biphenyl analog. Having established that ratio, then competitive kinetic experiments between the alkyldibenzothiophene compound and the standard are conducted. Utilizing the established ratio of hydrogenation of the standard and the biphenyl derivative in question it is then possible to curve fit the experimental data with theoretically derived curves and achieve accurate estimates of the contributions of all reaction steps [6]. We have written simple spreadsheet programs to allow this curve fitting to be done easily with interactive graphics and have applied it to all of the kinetic data reported herein. To show the utility of this procedure, we will describe below several examples of how this procedure has proven useful in interpreting experimental observations in the HDS of DBT and 46DMDBT. These examples include comparisons of the selectivity of CoMoS and NiMoS based catalysts supported on alumina and various carbons, the effects of temperature on selectivity and the effects of inhibitors on catalyst selectivities.

4. Comparisons of catalyst activities and selectivities

Previously it was reported that supported $NiMoS_x$ catalysts are more active than supported $CoMoS_x$ catalysts for the HDS of 46DMDBT [12]. It was proposed that this higher overall HDS activity was due to a higher hydrogenation activity for the Ni based catalyst. However, in that preliminary report a full kinetic analysis was not completed and only product distributions were used to estimate the relative contributions of the direct and hydrogenative routes for HDS. We report here that a full kinetic analysis confirms the earlier conclusions but the magnitude of the relative contribution of the direct HDS route was about two times larger than previously suspected as the hydrogenation of biphenyls was not fully accounted for. Figs. 1 and 2 illustrate the results of the present study in which the HDS activities for 46DMDBT of several Ni and Co based catalysts are compared. This series of catalysts represents two carbon supports (A-catalysts 1–3 and B-catalysts 4–6, respectively.), in which three methods of catalyst preparation were employed for each carbon. The

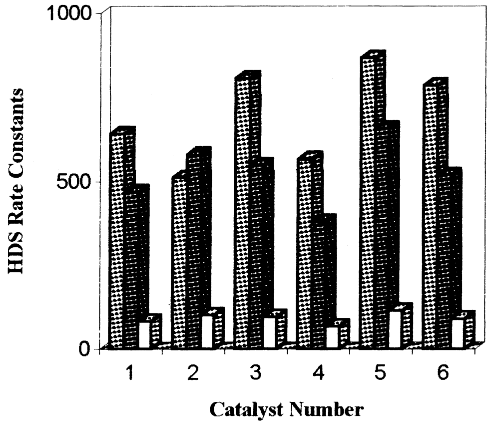


Fig. 1. NiMoS$_x$ catalysts.

catalyst numbers in the two figures indicate that the carbon bases and the preparation methods were the same but either Ni or Co was used in the preparation. These figures show the rate constants on the same scale for ease of comparison. Also shown are the rate constants for the hydrogenation of 1-methylnaphthalene (K_{NAPH}) which were obtained in a separate series of experiments.

First comparing the activities of these catalysts for the hydrogenation of 1-methylnaphthalene (1 MN), one can see that the trends of activities for different carbons and preparations are very similar for both Ni and Co based catalysts. However, Co based catalysts exhibited considerably lower hydrogenation activities. This same trend is noted for the hydrogenation of 46DMDBT (k_{HS1}) and, in general, the ratio of 1 MN hydrogenation to 46DMDBT hydrogenation is about the same (with the exception of Ni-2). Comparing the relative rate constants for direct desulfurization (k_{D0}) and 46DMDBT hydrogenation (k_{HS1}), one can see that indeed, for Ni based catalysts, the fractions of products arising from hydrogenation are much greater than for Co based catalysts. However, it should be noted that the Co based catalysts also have lower direct desulfurization activities than Ni based catalysts. It was also noted that the hydrogenation activities for biphenyls (k_{HP1}) were also higher for Ni based catalysts and without a complete kinetic description of all steps, the magnitude of the different activities would have been in error.

Even though the activities of the Co catalysts appear low in Fig. 2, Co(Ni)MoS$_x$ catalysts supported on carbon have been found to be about 2–3 times more active for HDS of DBT and 46DMDBT than comparable alumina supported commercial catalysts [6]. Thus, there appears to be promise for carbon supported Co(Ni)MoS$_x$ for the deep desulfurization of gas oils and diesel fuels.

5. The effects of temperature on catalyst selectivity

The promising results presented above may still not be adequate to provide catalysts with sufficient activities to replace conventional HDS catalysts in existing equipment and attain the very low levels of sulfur mandated by the new standards. One means to

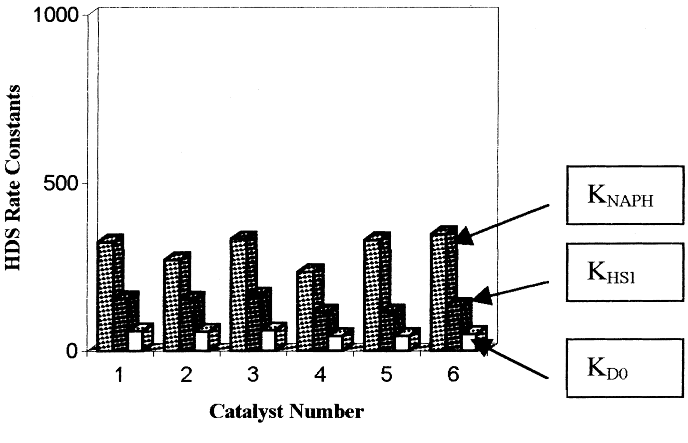


Fig. 2. CoMoS$_x$ catalysts.

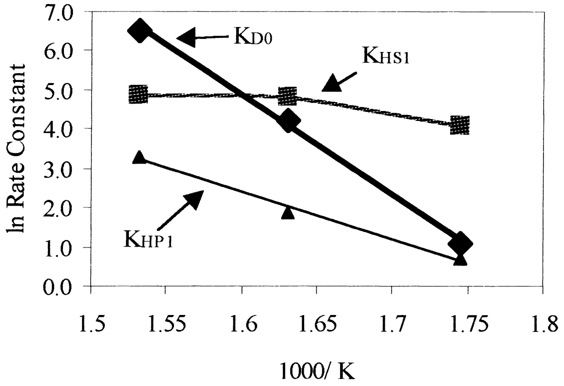


Fig. 3. Response of 46DMDBT rate constants to temperature.

increase activity is to raise the temperature of the reaction. Carbon is a non-acidic support and induces fewer side reactions than alumina at elevated temperature. We therefore investigated the use of carbon supported catalysts at temperatures somewhat higher than conventional HDS. Surprisingly, we observed a dramatic change in selectivity as the temperature was raised above 340°C [6]. The change in the selectivity in the HDS of 46DMDBT over $CoMoS_x/C$ is illustrated in Fig. 3.

As can be seen in these figures, the preferred mode of sulfur removal from 46DMDBT was about 90% by the hydrogenative HDS route at 300°C while at 380°C the preferred route was about 90% by the direct route. We believe that this dramatic shift in preferred reaction pathway in this temperature range is due to a marked shift in the thermodynamic equilibrium limit imposed on the tetrahydro-46DMDBT (THDMDBT) intermediate at the higher temperature [6].

The thermodynamic equilibria were estimated for the 46DMDBT$\Leftrightarrow$THDMDBT pair as a function of temperature using the MoPAC. Computational program manufactured by Fujitsu, Fukuoka Japan. Using these estimated equilibria, we then conducted kinetic analyses for a series of temperatures and determined the rate constants of all of the relevant reaction pathways according to the Scheme 1. Fig. 3 presents these calculations for catalysts supported on carbon. Trends for alumina are similar.

The first point to be noted in this graph is that the rate constants for 46DMDBT hydrogenation increase very little with temperature and appear to pass through a maximum, while the direct desulfurization rate constant increases substantially. The equilibrium concentration of THDMDBT was limited to about 10% at 340°C, while at 380°C this limit was lowered to about 2%. Thus, any gain in hydrogenation activity with temperature was countered by a lowering of the concentration of the intermediate through which the reaction must proceed. By contrast, the direct HDS route does not suffer such a limitation and increases exponentially with increasing temperature.

This increase in activity with temperature is not consistent with a limitation in adsorption of the 46DMDBT on the desulfurization site as previously proposed [7]. Steric restrictions imposed by the adjoining methyl groups on oxidative addition of the thiophenic ring to the active site appears more likely reason for the low reactivity of alkylsubstituted dibenzothiophenes [2]. Though the present data are insufficient to accurately determine the activation energy of this step, comparable studies with DBT indicate that the activation energy for k_{D0} for DBT is about 8 kcal/mol lower than that of 46DMDBT. This is consistent with a higher energy transition state for 46DMDBT than for DBT.

6. Reduction in HDS reaction rates by feed components and by-products

It is generally accepted that both hydrogenation and sulfur extraction rates in HDS processes are lowered by the presence of certain other components in the feed or products (inhibitors) and numerous studies have addressed this problem [2–4,8–14]. The kinetic description of inhibition effects of even the parent molecule, thiophene, is quite complicated and the complications become even worse as the thiophene core is fused to other aromatic rings and/or substituted with alkyl groups. We have used the new computational approaches to aid in understanding which sites are affected by inhibitors and to what degree they are affected. Table 1 presents the results of recalculation of reported inhibition studies [11–14] of H_2S and naphthalene on the HDS of alkyl-substituted dibenzothiophenes.

It has been reported that H_2S is a strong inhibitor for the direct sulfur extraction site but does not inhibit the hydrogenation site [3,4,10,11]. It will be shown later that the major inhibiting effect of H_2S is on the

Table 1
Inhibitor effects on first order rate constants for HDS of DBT, 4MDBT and 46DMDBT

	(NiMo/Al_2O_3, 5 MPa H_2, 290°C) (11)						(NiMo/Al_2O_3, 2.9 MPa H_2, 320°C) (12)		
Starting compound	DBT	DBT	Fractional	4-MDBT	4-MDBT	Fractional	46DMDBT	46DMDBT	Fractional
Additive	None	6/1H_2S	activity	None	6/1 H_2S	activity	None	10% NAPH	activity
Overall rate constant$\times 10^5$ s	15.9	1.2	0.075	4.5	0.70	0.156	29.6	9.6	0.324
Reactant Product									
$\phi\phi\text{-}k_{\mathrm{D0}}\rightarrow\phi\text{-}\phi$	13.3	0.56	0.042	0.91	0.13	0.145	7.0	2.6	0.366
$\phi cy_6\text{-}k_{\mathrm{D1}}\rightarrow\phi\text{-}cy_6$	398	14.00	0.035	25.37	5.54	0.218	308	160	0.519
$cy_6cy_6\text{-}k_{\mathrm{D2}}\rightarrow cy_6\text{-}cy_6$							514	321	0.625
$\phi\phi\text{-}k_{\mathrm{HS1}}\rightarrow\phi cy_6$	2.66	0.66	0.248	3.62	0.53	0.146	22.6	7.1	0.314
$\phi cy_6\text{-}k_{\mathrm{HS2}}\rightarrow cy_6cy_6$							18.5	5.8	0.314
$\phi\text{-}\phi\text{-}k_{\mathrm{HP1}}\rightarrow\phi\text{-}cy_6$	2.66	0.09	0.035	1.81	0.03	0.014	6.2	1.6	0.258
$\phi\text{-}cy_6\text{-}k_{\mathrm{HP2}}\rightarrow cy_6\text{-}cy_6$							3.6	0.975	0.271

hydrogenation of biphenyl to cyclohexylbenzene. Thus, the product distribution changes but relative contributions of the direct sulfur extraction route (k_{D0}) to the hydrogenative route (k_{HS1}) do not change as much as is inferred from the change in yields of biphenyl and cyclohexylbenzene. This can be seen by recalculating the data reported by Vrinat on the effects of H_2S inhibition on benzothiophene and 4-methyldibenzothiophene [11]. The reported data were sufficient to develop rate constants for all of the relevant steps described in Scheme 1.

Examining the table one can see it is true that, for dibenzothiophene, the direct desulfurization route (k_{D0}) suffers the greatest inhibition by H_2S; only 4% of the original activity remained in the inhibited case. However, the hydrogenative route (k_{HS1}) was also severely inhibited by H_2S, only 25% of the original activity remained. The largest inhibition was, in fact, in the hydrogenation of biphenyl (k_{HP1}). These effects were even more dramatic in the case of 4-methyldibenzothiophene. For that compound, k_{D0} and k_{HS1} were both equally inhibited, so the selectivity was not changed by H_2S inhibition. The biphenyl hydrogenation (k_{HP1}) on the other hand suffered severely. These results clearly show that the hydrogenation site is in fact subject to inhibition by H_2S. Thus, unless the reaction matrix is completely deconvoluted, the conclusions one draws may be questioned.

Similar effects are noted for the inhibition of 4,6-dimethyldibenzothiophene (46DMDBT) by naphthalene [12–14]. Table 1 shows the recalculated rate constants for the HDS of 46DMDBT in presence and absence of 10% naphthalene in decalin solvent over a NiMo/Al_2O_3 catalyst at 320°C. These recalculations indicate that the selectivities for 46DMDBT reactions were not severely changed by naphthalene inhibition as all rates were lowered by about the same amount. The activity for hydrogenation of aromatic hydrocarbons was, however, inhibited more than for the hydrogenation of sulfur containing compounds.

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