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Improving kinetic analysis of sequential and parallel reactions of hydrodesulfurization of dibenzothiophenes by establishing reasonable boundaries for reaction rate constants

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Abstract

Hydrodesulfurization (HDS) of dibenzothiophene (DBT), hydrogenation (HYD) of biphenyl (BP) and 3,3′-dimethylbiphenyl (3,3′-DMBP) and their competitive reactions were carried out over a novel Co–Mo/carbon catalyst. Studies were made with a batch stirred micro-autoclave reactor, 100 ml, at temperatures of 300–320°C and 2.9 MPa H_2. The HDS reactions were found to proceed via a network of sequential and parallel reactions and a computer model was developed which could be used to determine all the individual rate constants in the reaction scheme by matching experimental product composition data to theoretical curves as a function of conversion and/or reaction time. Unfortunately, with limited data, many different sets of rate constants can provide good matches with the experimental data. In order to obtain a unique solution for the set of rate constants two boundaries were found necessary. One is the relative hydrogenation activity of DBT to that of biphenyl which can be established with separate competitive experiments. The other is to consider the thermodynamic limitations, on the reactions of refractory sulfur compounds which proceed via ring hydrogenation. The rates of hydrogenation of BP and 3,3′-DMBP were found to be much lower than the rates of HDS of DBT. In addition, it was established that there was almost no inhibition on the HDS of DBT by BP and/or 3,3′-DMBP.

Keywords: Hydrodesulfurization; Dibenzothiophene

1. Introduction

In recent years, much attention has been devoted to the deep desulfurization of petroleum streams. Polyaromatic sulfur compounds, such as dibenzothiophene derivatives, are known to be the most difficult to remove [1–6]. 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 [7,8]. Therefore, consideration of a network of sequential and parallel reactions is necessary in the solution of the kinetic analyses of these species. Unfortunately, even though these sequential and parallel pathways are generally recognized by researchers in the field, there is no common way to report the relative rates. In addition, the determination of the relevant rate constants has often been attempted by curve fitting of limited data with theoretical models and thermodynamic limitations on intermediates are generally ignored. It is well known that the HDS of dibenzothiophenes occur via two different reaction

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pathways, one is direct desulfurization while the other involves hydrogenation prior to desulfurization. For proper evaluation of this complex reaction pathway, it is important to accurately determine the relative values for the rate constants of each step. It is common to describe a catalyst's selectivity as the relative contributions from a direct extraction of the sulfur atom (k_{D_0}) and the contribution from hydrogenation prior to desulfurization (k_{HS_1}). There is almost no general agreement between different authors on the relative contributions of the different pathways, even when using similar catalysts and similar conditions [9–11]. The root of the unexpected differences appears to lie in the fact that the reported rate constants were obtained by using curve fitting techniques with insufficient data and not placing reasonable chemical boundaries on the initially assumed rate constants. Most researchers have found pseudo-first order behavior for the various steps, so it is possible to match theoretical curves with actual data to obtain the best rate constant values. Unfortunately, in most instances, too few data points were obtained to generate unique theoretical fits. It is absolutely imperative that data be obtained for at least four conversion levels which are well spaced in the conversion matrix and extend to over 95% conversion. The partially hydrogenated dibenzothiophene intermediates (H4-DBT) are most often never detected as their desulfurization rates are extremely fast (k_{D_1}). The difficulty lies in the fact that the cyclohexylbenzene product can arise from two different routes. One usefulguideline comes from the fact that the concentration of the cyclohexylbenzene precursors (biphenyl and H4-DBT) must pass through maximum values at specific conversion levels which can easily be calculated from the relative values of the formation and conversion rate constants. However, accurate values for these relative rates can only be predicted if data are available well prior to and well beyond the maximum concentrations for these intermediates, because minor experimental errors can confuse curve fitting optimization.

To set boundaries on the assumed rate constants that are being fit to match the observed data, independent determination of the rate constant for biphenyl hydrogenation should be considered. This has been done by several authors, but the independently measured rate constants were often not used in setting boundaries in the computer fitting of the complete matrix. Perhaps the most definitive method for establishing guidelines on relative reactivities is through carefully selected competitive reactions with model compounds which mimic the chemistry being studied. Unless the data being fit are well spaced throughout the overall conversion and the data have very low limits of error, unique sets of relative rate constants are difficult to achieve. An alternative approach would be to independently establish rate constants for one or more important reaction steps so as to set boundaries on the assumed rate constants that are theoretically being fit. The present study shows that for proper kinetic determination of the relative rate constant values, two boundaries must be considered. The first is to set limits on the relative rates of hydrogenation of the parent dibenzothiophene and its desulfurized product (biphenyl). The second is to include the thermodynamic equilibrium limit on the partially hydrogenated intermediate (tetrahydro-dibenzothiophene).

2. Experimental

2.1. Materials

Biphenyl, 3,3′-dimethylbiphenyl, dibenzothiophene, cobalt acetylacetonate, and molybdenum acetylacetonate were purchased from Wako Pure. Decane and other solvents were commercial products used without further purification. The carbon used as a support was obtained from Mitsubishi which had a surface area of 907 $\mathrm{m^2/g}$ and pore volume of 0.52 ml/g.

2.2. Catalyst preparation

Co–Mo/C catalyst was prepared by impregnation with two-step procedures in which the molybdenum phase was introduced first followed by drying in vacuum at 120°C overnight. The next step is the addition of cobalt phase to this precursor, followed by the same treatment as that used for molybdenum. The sources of molybdenum and cobalt used in the catalyst preparation were Mo-acetylacetonate and Co-acetylacetonate. Methanol was used as the impregnating solvent. The catalyst was prepared with 2 and 10 wt% cobalt and molybdenum, respectively.

2.3. Catalyst sulfidation

The sulfidation of the precursor catalyst after drying in oven at 120°C was carried out in a flow of 5 wt% H_2S in hydrogen at atmospheric pressure. The temperature was increased from room temperature to the final temperature, i.e., 360°C in 35 min. It was kept at this temperature for 2 h after which the sample was cooled down to room temperature with continuous flowing of 5 wt% H_2S/H_2 gas mixture.

2.4. Catalytic activity

The reactor used for catalytic activity measurements was 100 cc magnetically stirred micro-autoclave. Solutions of 1 wt% dibenzothiophene (DBT), a mixture of DBT and biphenyl (BP) (1:1 molar ratio), a mixture of DBT and 3,3′-dimethylbiphenyl (3,3′-DMBP) (1:1 molar ratio) and a mixture of BP and 3,3′-DMBP in decane were used to establish the relative rates of hydrogenation of these compounds. In each run, the autoclave was charged with 10 g of reactant solution then 0.2 g freshly sulfided catalyst was added to this solution. The reactor was purged three times with hydrogen gas before starting the experiments. During all the experiments the stirring speed was kept constant at 1000 r.p.m. The temperature was increased rapidly until the desired reaction temperature. At this moment the time was taken into our consideration. At the end of reaction time, the reactor with its contents was rapidly cooled down to room temperature.

2.5. Analysis

The samples after reaction were collected and filtered, and the catalyst was washed several times with toluene to remove any adsorbed species of the reaction to keep the mass balance at an acceptable level.

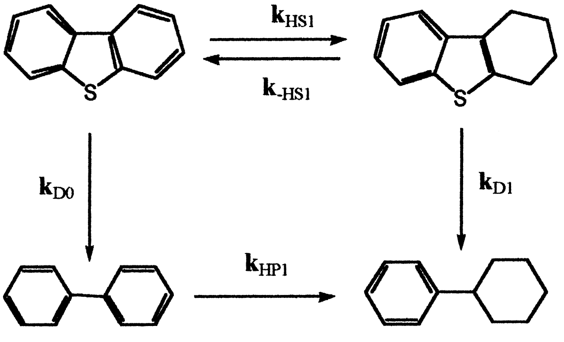
The collected samples were analyzed with the aid of adding a known quantity of a reference material (4,4′-diethylbiphenyl). Analysis of the samples was accomplished with a Yanaco (G-3800) gas chromatograph equipped with a differential flame ionization detector and linear temperature programing. A capillary column (OV-101; 0.25 mm×50 m) was used and permitted good separation.

Quantitative analysis of the chromatograms was obtained by use of an electronic integrator. Response factors were obtained by the aid of the reference materials. Qualitative analysis of the samples was obtained from retention time and mass spectra.

3. Results and discussion

3.1. Reaction scheme

In this investigation the products of HDS of DBT were H_2S, biphenyl, phenylcyclohexane and tetrahydrodibenzothiophene (H4-DBT). *Cis* and *trans* analogs of 3,3′-dimethylphenylcyclohexane and phenylcyclohexane were the products detected in the hydrogenation reaction of 3,3′-DMBP and BP, respectively. HDS and hydrogenation reactions were found to follow pseudo-first order kinetics. The HDS reaction pathway for DBT considered in this kinetic study was as follows:



HDS Reaction Scheme of DBT

where the rate constants k_{D_0}, k_{D_1}, k_{HS_1}, k_{HP_1}, and k_{-HS_1} concern the reactions desulfurization without ring hydrogenation, desulfurization of one-ring hydrogenated sulfur compound, hydrogenation of one ring of the sulfur compound, hydrogenation of one phenyl ring of desulfurized biphenyl, and dehydrogenation of one ring of the hydrogenated sulfur compound, respectively.

3.2. Individual HDS rate constant from the competition reactions

To define the relative rates of hydrogenation of dibenzothiophene and biphenyl, it is useful to add

Table 1
Individual and competitive apparent rate constants in HDS and HYD of DBT, BP and 3,3′-DMBP over Co–Mo/C catalyst

	Individual			Competitive			Calc. ratios
	DBT	BP	3,3′-DMBP	DBT+BP	DBT+3,3′-DMBP	BP+3,3′-DMBP	
k_{DBT}	320.3			320.0	300.0		
k_{BP}		8.3		4.7		8.1	
$k_{3,3'\text{-DMBP}}$			6.7		3.5	6.4	
k_{DBT}/k_{BP}							67.7
$k_{BP}/k_{3,3'\text{-DMBP}}$							1.26

DBT=dibenzothiophene; BP=biphenyl; 3,3′-DMBP=3,3′-dimethylbiphenyl.
Rate constants, 10^5 s^{-1} g cat^{-1}.
300°C and 2.9 MPa H_2.

an analog of biphenyl to the reaction mixture in a competitive experiment. In this way, one can simultaneously determine $(k_{D_0}+k_{HS_1})$ for dibenzothiophene and k_{HP_1} for the biphenyl analog, under the same conditions. In separate experiments, the relative values of k_{HP_1} for biphenyl and the analog may then be determined and this ratio may be applied in the competitive HDS experiment to set guidelines for assigning initial values for k_{HS_1} and k_{HP_1}, prior to curve fitting. Table 1 shows these results over Co–Mo/C catalyst at 300°C under 2.9 MPa hydrogen pressure using 3,3′-DMBP as the biphenyl analog. As can be seen in Table 1, the ratio of the rate constants $((k_{D_0}+k_{HS_1})/k_{HP_1})$ was estimated to be 68. Holding this ratio constant, the other rate constants in the HDS pathway matrix for DBT were estimated using curve fitting techniques. However, in agreement with [12], it can be seen that the individual apparent hydrogenation rate constants of BP and/or 3,3′-DMBP are very low and the presence of such compounds in the reaction stock of HDS of DBT has almost no inhibition on the activity. By contrast, DBT is a serious inhibitor for the hydrogenation of BP and/or 3,3′-DMBP (it reduces the activity about twofold).

3.3. *Hydrogenation thermodynamic limitation of parent sulfur compounds*

Thermodynamic calculations for the overall HDS of dibenzothiophene have been reported by Sabbah and Hebd [13]. These data show that the HDS reaction to produce biphenyl and H_2S is highly thermodynamically favored in the temperature range of industrial practice. More recently, Daage and Chianelli [12] have considered the possible reversibility of partially hydrogenated intermediate sulfur species, i.e. DBT to H4-DBT. Their studies showed that, at typical commercial HDS conditions, the intermediate was limited to a maximum equilibrium concentration of about 20%. So far these studies seem to be the first that considered an equilibrium in the hydrogenation pathway of refractory sulfur compounds. However, they did not report the details of how the values were obtained, the adsorption equilibrium constants or their relationships with temperature.

We have conducted similar studies using the Mopac 93 program (Fujitsu) to theoretically calculate the thermodynamic parameters of the hydrogenation reaction of dibenzothiophene. This allowed the estimation of the thermodynamic equilibrium values at various temperatures. Figs. 1 and 2 show the equilibrium concentration of DBT to H4-DBT and 4,6-DMDBT to 4,6-dimethyltetrahydrodibenzothiophene at 2.9 MPa hydrogen pressure as a function of temperature, respectively. It is clear that the inflection point of these curves lies in a very critical temperature region as it is the region of industrial use. Therefore, thermodynamically the hydrogenation of DBT to form tetrahydrodibenzothiophene (H4-DBT) is only favored at temperatures of <330°C and it becomes almost negligible at high temperature, i.e. >425°C. Moreover, the hydrogenation of 4,6-DMDBT, which is the most refractory sulfur compound to convert, is favored at <260°C and becomes completely unfavored above 380°C. These results clearly indicate that a thermodynamic limitation exists for such compounds during HDS, especially at high temperature. There-

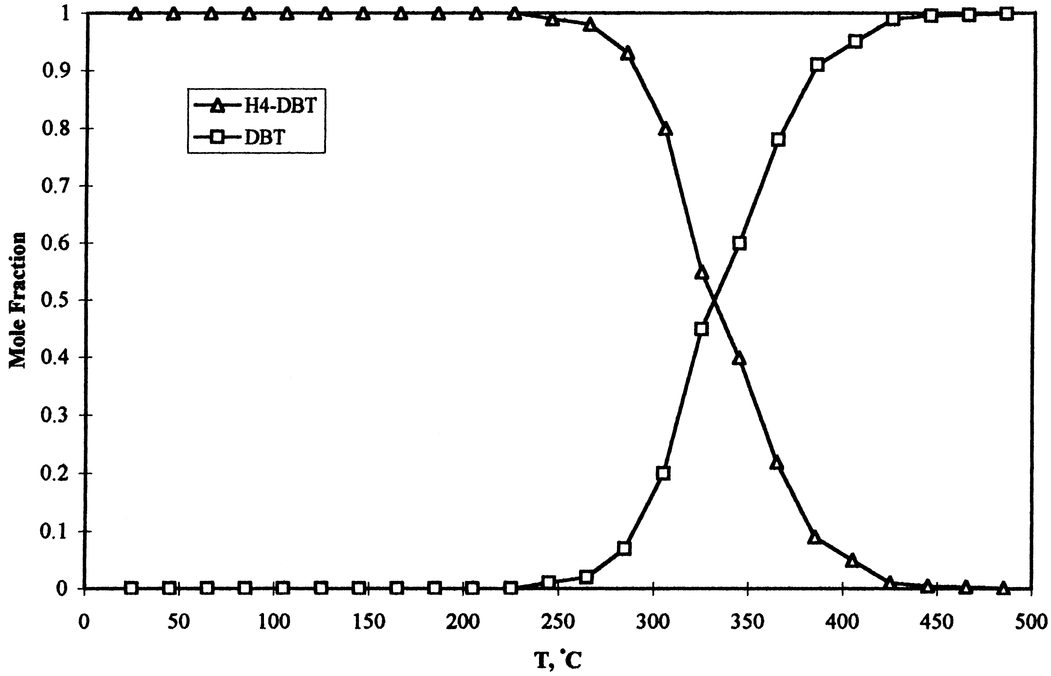


Fig. 1. Thermodynamic mole fractions at equilibrium for the hydrogenation of DBT to H4-DBT versus temperature (at autogenous reaction pressure).

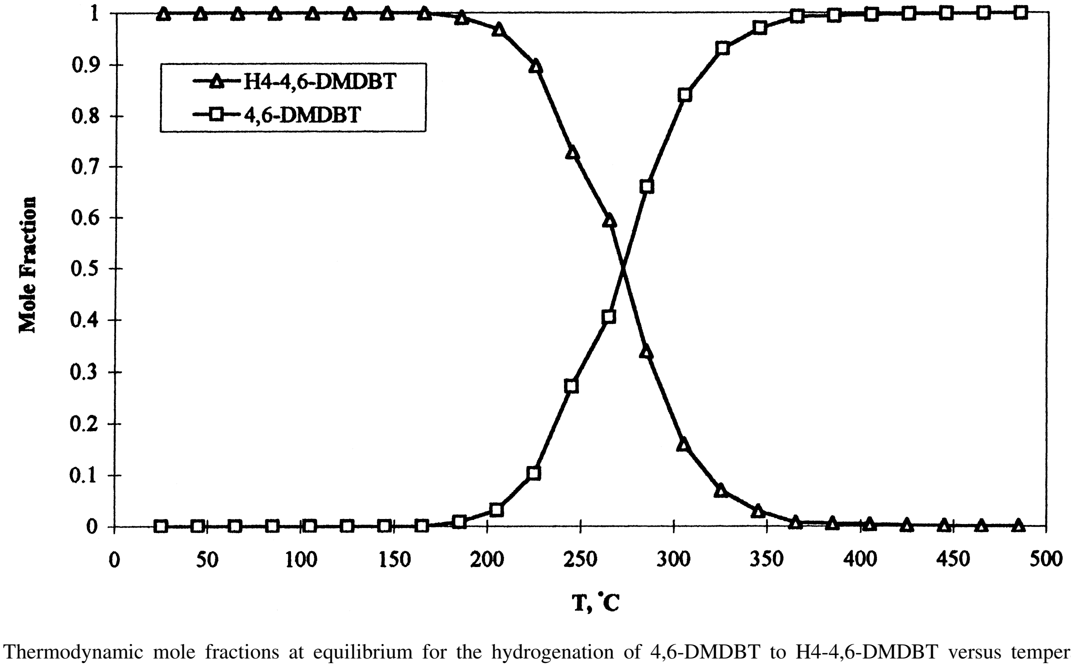


Fig. 2. Thermodynamic mole fractions at equilibrium for the hydrogenation of 4,6-DMDBT to H4-4,6-DMDBT versus temperature (at autogenous reaction pressure).

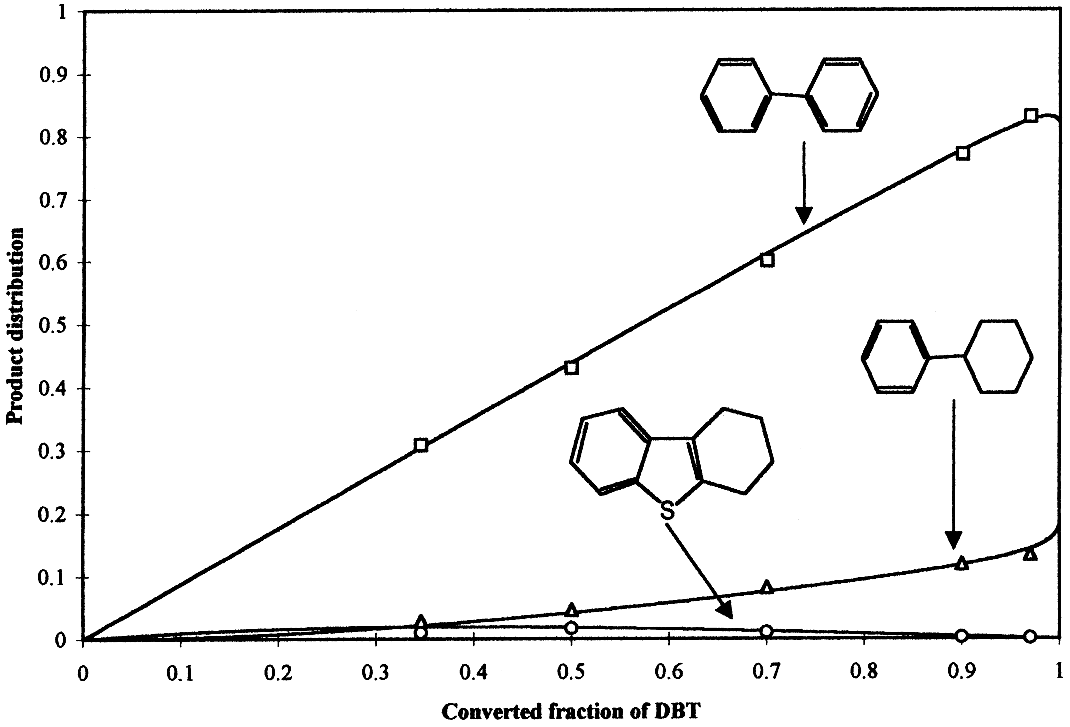


Fig. 3. HDS selectivity of DBT over Co–Mo/C (320°C and 2.9 MPa H_2).

fore, this is an important consideration for the researchers who attempt to design improved catalysts for HDS of refractory sulfur compounds through the enhancement of hydrogenation pathway, as this route is thermodynamically very limited at high temperature.

3.4. Setting reasonable boundaries for rate constants

Having established the thermodynamic equilibrium and measured independently the critical relative rate constants, it has been possible to obtain more accurate estimates for the HDS reaction of DBT than studies reported in the past. The graphs in Figs. 3 and 4 represent product selectivity plots in which the products of HDS are plotted against the percent conversion of DBT. The lines and points represent, respectively, the theoretical and experimental product distributions for first order kinetics with the reaction pathway described above. Fig. 3 illustrates the selectivity for HDS of DBT over Co–Mo/C. Fig. 4 shows the selectivity over Ni–Mo/Al_2O_3 catalyst (the data were taken from [14]). As can be seen in the figures, the theoretical predictions were in quite good agreement with the experimental points. The relative rate constants for all reaction steps are given in Table 2. One can see that the direct desulfurization pathway is much more preferred over Co–Mo/C than Ni–Mo/Al_2O_3. However, the relative activity of desulfurization of partially hydrogenated DBT over Ni–Mo/Al_2O_3 is more than two times that of Co–Mo/C. The results confirm in a quantitative way that Ni–Mo is a more active hydrogenation catalyst than Co–Mo catalyst. This example illustrates how relative rates are affected by different kinds of catalysts. It should be kept in mind that by setting boundaries as described above, only very limited values of the relative rate constants of various steps of HDS are allowed. Therefore, the accurate comparison of activity and selectivity of HDS of a series of catalysts can be achieved by considering these boundaries during manipulating the kinetic scheme of such reactions.

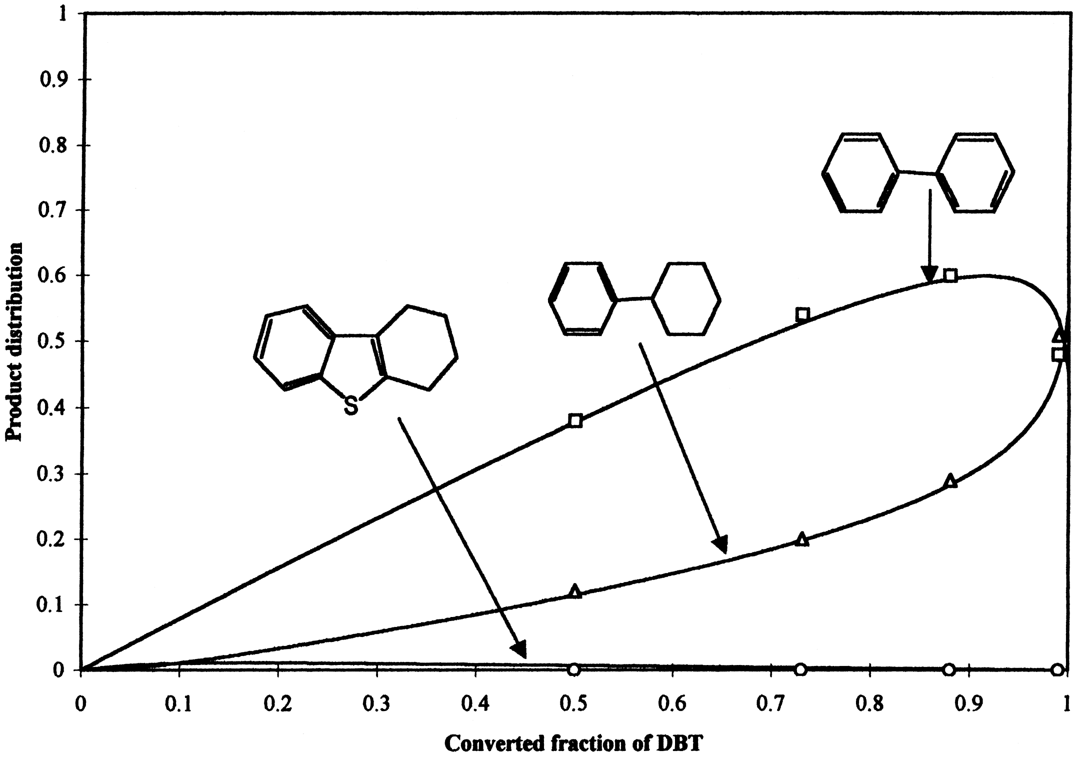


Fig. 4. HDS selectivity of DBT over Ni–Mo/Al_2O_3 (320°C and 2.5 MPa H_2).

Table 2
Rate constants of HDS steps of DBT over Co–Mo/C and Co–Mo/Al_2O_3 catalysts

Catalyst	Rate constant, 10^5 s^{-1} g cat^{-1} at 320°C				
	k_{D_0}	k_{HS_1}	k_{-HS}	k_{D_1}	k_{HP_1}
Co–Mo/C[a]	758.5	101.1	25.3	3160[c]	12.6
Ni–Mo/Al_2O_3[b]	103.0	27.3	6.8	2052.6	14.7

[a] 2.9 MPa H_2.
[b] 2.5 MPa H_2.
[c] Minimum value.

4. Conclusions

The overall hydrodesulfurization reactions of DBT were found to follow pseudo-first order kinetics. These HDS reactions proceeded via a network of sequential and parallel reactions and a computer model was developed which could be used to determine all the important rate constants by matching experimental product composition data to theoretical curves as a function of conversion and/or reaction time. Unfortunately, with limited data, many different sets of rate constants were found to provide good matches between the experimental data and the theoretical calculations. In order to obtain a unique set of rate constants, it was found necessary to set boundaries on the assumed values of several rate constants and to consider thermodynamic limitations on the production of certain key intermediates. One important boundary condition was obtained by separate experimental determination of the relative hydrogenation activity of a mixture of biphenyl and 3,3′-dimethylbiphenyl (1:1 molar ratio). Then competitive experiments were conducted with a mixture of the dibenzothiophene derivative and the non-interfering biphenyl compound. Using the observed biphenyl hydrogenation rate, and the correlations developed in the separate experiments, all the HDS rate constants could thus be obtained. The desulfurization of these sulfur compounds via ring hydrogenation prior to sulfur removal was found to be thermodynamically limited, especially at high temperature. However, there was a clear difference of the relative rate constants of HDS of DBT when the reaction carried out over Ni–Mo/Al_2O_3 and Co–Mo/C catalysts. Ni–Mo/Al_2O_3 catalyst prefers more hydrogenation than Co–Mo/C catalyst.

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