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Kinetics of Hydrodesulfurization of Dibenzothiophene on Sulfided Commercial Co-Mo/γ-Al_2O_3 Catalyst

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حركية تفاعلات اذالة الكبريت الهيدوجينية لمادة dibenzothiophene على عامل حفزي كبريتي تجاري

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الخلاصة: تركيبة تفاعلات إذالة الكبريت الهيدروجينية لمادة dibenzothiophene دورست معمليا على عامل حفزي كبريتي تجاري عند درجات حرارية ما بين 633 الى 683 درجة مطلقة و عند 10 ضغط جوي. تركيزات ضعيفة لمادة DBT الحاصل عليها من عملية أذالة الكبريت الهيدروجينية استخدمت. اثبت ان نموذج رياضي من الدرجة الاولى الكاذبة يمكن ان يستنبط النتائج المعملية لمادة DBT المستهلكة. الطاقة المنشطة لتحويل مادة DBT وجد انها تساوي 51.7 kcal/mol ,, وجد ان المنتجات الرئيسية المحصول عليها هما (CHB) Biphenyl (BP) and cyclohexylbenzene . وان اثنين من شبكة التفاعلات وهما التفاعلات المتوازي والمتوازية المتتابعة جربت. ووجد ان التفاعلات المتوازية المتتابعة تعطي وصف افضل لتوزيع مادتين BP and CHB . وان نسبة مادة BP الى مادةCHB تعتمد على درجة الحرارة. ان قيم الطاقة المنشطة لتحويل مادة DBT الى مادة BP (E_{BP}) وتحويل نفس المادة الى CHB (E_{CHB1}) وتحويل مادة BP الى CHB (E_{CHB2}) وجدة قيمها في شكل تنازلي $E_{CHB2} < E_{BP} < E_{CHB1}$. وان النتائج تقترح وجود مواقع مختلفة على العامل الحفزى قادت لانتاج مادتين على العمل الحفزى.

المفردات المفتاحية: تركيبةتفاعلات إزالة الكبريت بواسطة الهيدروجين, Cyclohexylbenzen, Biphenyl, CoMo/A1$_2$O$_3$, عامل حفزي كبريتي تجاري.

Abstract: Kinetics of hydrodesulfurization of dibenzothiophene (DBT) has been studied on a commercial CoMo/γ-Al_2O_3 catalyst at 633 - 683 K and 10 atm. A low DBT concentration typically obtained in hydrodesulfurization operations was used. Pseudo-first-order model was found to fit the experimental data for the consumption of DBT. The activation energy for the conversion of DBT was found to be 51.7 kcal/mol. Biphenyl (BP) and cyclohexylbenzene (CHB) were obtained as dominant products. For the reaction network, both parallel and parallel-sequential routes were explored. The latter was found to give a better description of the BP and CHB distributions. The ratio of BP to CHB depended on the reaction temperature. The values of activation energies of DBT hydrogenolysis to BP (E_{BP}), DBT hydrogenation to CHB (E_{CHB1}) and hydrogenation of BP to CHB (E_{CHB2}) were found to be in a decreasing order of $E_{CHB2} > E_{BP} > E_{CHB1}$. The result suggests the presence of different catalytic sites leading to the two products on the catalysts.

Keywords: Hydrodesulfurization, Dibenzothiophene, CoMo/Al_2O_3, Biphenyl, Cyclohexylbenzene, Kinetics

1. Introduction

Research interest in catalytic hydrodesulfurization (HDS) of petroleum feedstock has been increasing recently. This is partly due to the necessity of processing feedstocks that have large amounts of sulfur-containing compounds and also as a result of more stringent environmental regulations with respect to emission of sulfur-containing gases to the atmosphere. Sulfur removal has economic benefits of prolonging catalyst life and decreasing corrosion of the process equipment downstream. Perhaps one of the most important factors that spurred interest in HDS is a recent review of the allowable sulfur content of fuels, flue gases and other petroleum products, in the U.S. The Environmental Protection Agency (USEPA) guidelines, for instance, restrict the amount of sulfur allowed in diesel fuels to 1.3×10^{-2} g/dL^3 by the year 2010 (USA-EPA, 2001). This requires reduction of about 97% from the current level. Achieving this limit will require a major improvement or redesign of the catalysts employed for HDS.

Therefore, it is necessary to gain further understanding of the chemical reactions involved. This could be achieved by studies of kinetics and networks of the reactions. Dibenzothiophene (DBT), as a typical sulfur-containing compound in the petroleum feedstock, has been studied extensively. A recent study has shown that at certain conditions, the DBT kinetic closely resembles that of an overall behavior of DBTs in a light oil fraction (Steiner, *et al*. 2002). Aspects of the HDS of DBT kinetics have

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*Corresponding Author's e-mail: baba@squ.edu.om been reported. The reaction was shown to follow a pseudo-first-order kinetics and both parallel and consecutive reaction networks were identified (Girgis, *et al.* 1991; Farag, *et al.* 1997; Wang, *et al.* 2004; Pille, *et al.* 1994; Broderick, *et al.* 1981). When the reaction of DBT was tested on CoMo/MCM-41, a pseudo-first-order kinetic model was found to represent the experimental data better than a Langmuir-Hinshelwood model. This is a typical observation for low DBT concentrations. It has also been shown that the relative significance of hydrogenolysis and hydrogenation routes depended on Co/Mo ratios (Wang, *et al.* 2004). Furthermore, the two routes could also be substantially affected by the presence of Naphthalene or hydrogen sulfide for the HDS of DBT or 4,6-dimethyldibenzothiophene (Farag, *et al.* 1999).

Sulfided promoted CoMo/Al_2O_3 and other transition metal catalysts have been widely researched and shown to be effective for the reaction (Topsoe, *et al.* 1984; Prins, *et al.* 1989; Yang, *et al.* 2002; Venezia, *et al.* 2002; Damyanova, *et al.* 2003; Papadopoulou, *et al.* 2003; Al-Zeghayer, *et al.* 2005). Further understanding of the nature of interactions between the reactants and catalysts and effects of reaction conditions thereupon is important. Therefore, the objective of this work was to describe the kinetics of DBT hydrodesulfurization on a sulfided commercial CoMo/γ-Al_2O_3 catalyst. Effects of variation of reaction temperature and feed flow on products were explored.

2. Experimental

2.1 Materials

The materials used for the catalyst testing were Dibenzothiophene (DBT), Tetralin, Decalin and Dimethyldisulfide $(CH_3)_2S_2$ (DMDS). All chemicals were of analytical grade quality supplied by Aldrich Chemical Company. A commercial catalyst was obtained from a supplier. Its composition and physical properties as given by the manufacturer are shown in Table 1. The catalyst was sulfided to a catalytically active form using a solution of dimethyldisulfide (2 wt% sulfur equivalent) in decalin solvent at 623 K until H_2S breakthrough was observed.

Table 1. Chemical and physical properties of the commercial catalyst

Components		**wt% dry basis**
Molybdenum oxide (MoO_3)		15.40
Cobalt oxide (CoO		3.20
Sodium oxide (Na_2O)		0.03
Iron (Fe)	0.03	
Sulphate (SO_4)	0.30	
Silicon dioxide (SiO_2)		0.10
Physical properties		
Poured bulk density, lb/ft^3	33.0	
Compacted bulk density, lb/ft^3	36.0	
Crush strength, lb/m m		3.4
Surface area, m^2/gm		310.0
Pore volume, cm^3/gm		0.8

2.2 Catalyst Testing

The catalysts evaluation was carried out by passing solutions containing dibenzothiophene at a concentration of one or two weight percent in the hydrogen donor solvent (tetralin) through a fixed bed containing 1 g of the catalyst particles. The catalyst particle sizes and reaction conditions were chosen to minimize mass transfer limitations, based on separate preliminary experiments. The use of a hydrogen donor solvent ensured an excess supply of hydrogen readily available for the reaction without a need for adding gas phase hydrogen. The reaction was conducted at temperature range of 633 - 683 K, pressure of 10 MPa, and flowrates required to give measurable conversions were between 0.5 and 2 g/min. Details on catalyst testing and GC analysis were reported earlier (Al-Zeghayer, 2005).

3. Results and Discussion

The major products identified were biphenyl (BP) and cyclohexylbenzene (CHB). Negligible amounts of bicyclohexyl were detected at high conversions. The conversion and products distribution over the catalyst are shown in Fig. 1. The figure shows variation in DBT conversion and BP and CHB selectivities with inverse of weight hourly space velocity (WHSV) from 0 - 250 g catalyst h/g feed. The effect of hydrogen concentration on the reaction was neglected as it was considered to be in excess. The DBT degree of conversion increased rapidly from 0 to 92% in the inverse WHSV range. At the initial conversion, BP appeared to be an exclusive product indicating that it is a primary product. At the highest conversion, its selectivity decreased to 80% with a corresponding increase in the selectivity to CHB from 0 to 20%.

At certain conditions, the kinetics of HDS of

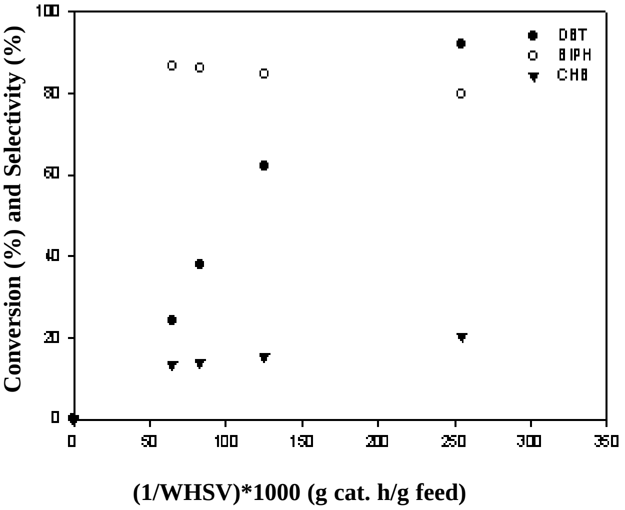

Figure 1. Variation of DBT conversion and products distribution with 1/WHSV

Dibenzothiophene (DBT) was shown to represent that of an aggregate of DBTs in a petroleum feedstock (Steiner, 2002). In an earlier study of kinetics of HDS of DBT in liquid feed, the data were well fitted to a Langmuir-Hinshelwood (L-H) model in a plug-flow reactor (Singhal, *et al*. 1981). However, at a lower DBT concentration, as expected, a first order relation between the rate of consumption of DBT and concentration was obtained. It has been shown that for an analysis of the reaction network, even simple power law could give satisfactory results (Levenspiel, 1972). Therefore, for the catalyst under study, the kinetic data for the reaction were evaluated assuming integral plug-flow reactor. A logarithmic plot of mole of DBT reacted and the inverse of WHSV showed a linear relation (Fig. 2). This indicates a pseudo-first order kinetic similar to earlier reports (Wang, *et al*. 2004; Farag *et al*. 1999; Singhal, *et al*. 1982). However, at a low temperature, DBT adsorption may be important despite the low concentration that was employed. The deviation of the data from the pseudo-first order for a low feed flow or high contact time may be due to adsorption of DBT. At a low temperature, such adsorption and species diffusion may be important. Therefore, the data may deviate from a first-order rate expression.

The distribution of the products and reaction network were explored by changing the reaction temperature and feed flow rate (Fig. 3). Both show a similar trend of change in CHB/BP ratio with DBT conversions. But for all conversion levels, BP was the dominant product; contrary to an earlier work on a similar catalyst (Singhal, *et al*. 1981; Broderick, 1980). Many workers have proposed a reaction network similar to Scheme I in Fig. 4. The products observed were biphenyl and cyclohexylbenzene. In addition, the presence of tetrahydrodibenzothiophene and hexahydrodibenzothiophene were also reported (Broderick, 1980). Other reports suggested their presence as undetected, highly reactive intermediates (Rollmann, 1977). Biphenyl was observed to react to give mainly cyclohexylbenzene (Singhal, *et al*. 1982; Broderick, 1980). It was concluded that the rate of reaction of biphenyl was slow in comparison with the disappearance of dibenzothiophene. Hydrogenation of cyclohexylbenzene to give bicyclohexyl was too slow to be measurable under typical hydrodesulfurization conditions (Broderick, 1980).

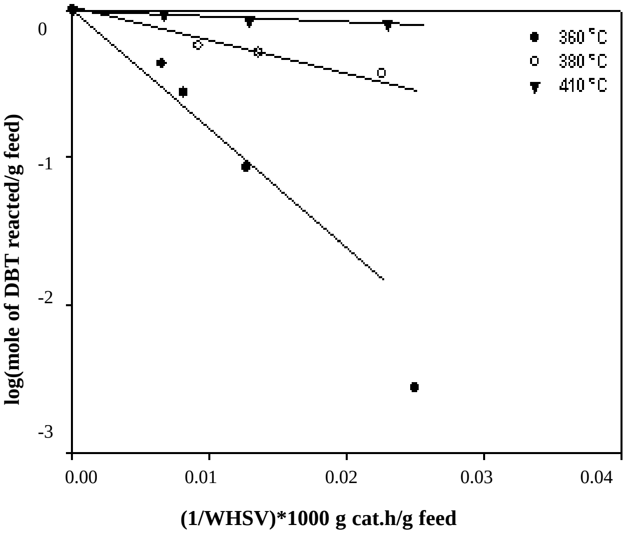

Figure 2. Logarithmic variation of mole of DBT converted versus 1/WHSV

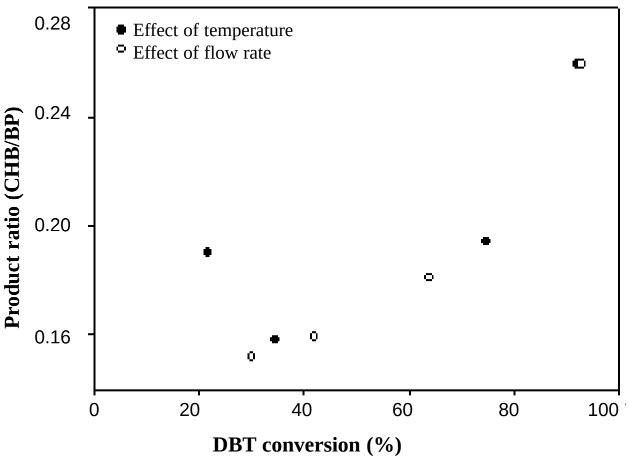

Figure 3. Variation of CHB/BP ratio with DBT conversion

The obvious path for further reaction of biphenyl is a series of hydrogenations, giving first cyclohexylbenzene and then bicyclohexyl. By comparing the relation between product ratios and conversions at constant temperature and also with increasing temperature, we consider that both parallel and sequential paths may be involved in the reaction network as suggested in Scheme I. Perhaps partially hydrogenated dibenzothiophene intermediates were formed. If the rate of hydrodesulfurization of the intermediates (path 3') were very fast, the selectivity profiles would follow both parallel and sequential (complex) path. If the rate were slower, that would have hindered the appearance of cyclohexylbenzene in the early stages of the reaction; but contributed to its appearance by sequential reactions.

The reaction network in Scheme I was used to further

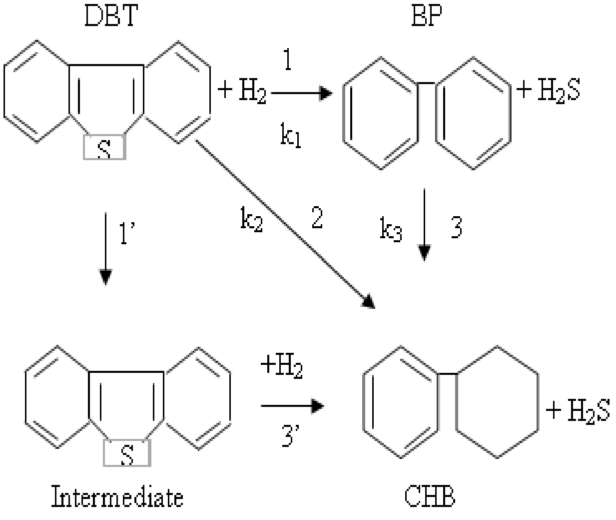

Figure 4. Scheme I

study the kinetics of the reaction. The overall first-order rate constants and the activation energies were determined from the experimental data. To measure these parameters, it was assumed that at low conversion, the reaction of biphenyl could be neglected compared to its rate of appearance and that cyclohexylbenzene formed directly from dibenzothiophene (Sapre, *et al.* 1980). Arrhenius plot for the steady state consumption of DBT is shown in Fig. 5. The activation energy for the disappearance of DBT over the catalyst was calculated to be 51.7 kcal/mole as shown in Table 2. The same table compares the activation energies with those obtained by others with the exception of the (5.3 kcal/mol) value obtained by Bartsch and Tanielian (1974); the energies of activation are in good agreement. The low values obtained by Bartasch and Tanielian indicate a diffusion-controlled reaction.

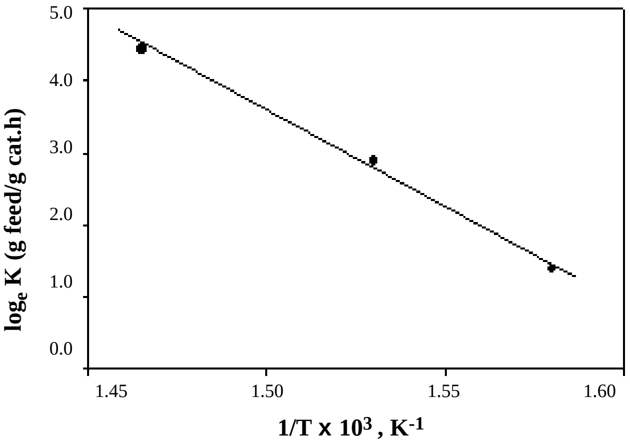

Figure 5. Arrhenius plot for HDS of DBT on the catalyst

Based on the relation between the rate constants for consumption of DBT and that of production of BP and CHB, the activation energies (E_1 and E_2) have been evaluated from the Arrhenius plots. The relation between the product ratio and the conversions obtained assuming the parallel-sequential path was fitted to the experimental data to determine the pseudo first-order rate constant for the reaction of biphenyl to cyclohexylbenzene (k_3). The activation energy (E_3) was also calculated from the Arrhenius relation. The energies have the same order of magnitude as shown in the Table 3. The activation energy for the hydrogenolysis of dibenzothiophene to biphenyl is 50.3 kcal/mole. This is insignificantly greater than the activation energy for hydrogenation of dibenzothiophene to cyclohexylbenzene by about 6.15 kcal/mole. This is contrary to an earlier report that showed the rate of BP transformation to CHB to be two orders of magnitude slower than that of DBT hydrogenolysis, when the reaction was tested on alumina supported molybdenum carbide (Bartsh, *et al.* 1974).

Table 2. Comparison of apparent activation energies for DBT consumption

Temperature range, K	E_a, kcal/mol.K	Solvent
633-683	53.1	Tetralin [this work]
558-623	39.1	Tetralin [16]
573-723	36.0	Aromatics [19]
not stated	5.3	not stated [21]
548-598	28.0-32.8	n-hexane [18]

It was reported that at DBT conversions degrees higher than 40%, the selectivity to CHB decreased with an increasing temperature (Rollmann, 1977). In the low conversion range, the results are in agreement with those of (Broderick, 1980). He used the ratio of rate equations to correlate the differential concentration data for the hydrogenation and hydrogenolysis reaction of dibenzothiophene. However, this observation was limited because the study took account of the parallel reaction scheme without further reaction of biphenyl due to the low conversions (less than 15%). The results obtained by Singhal *et al.* favored the parallel and sequential reaction, which became increasingly important at high conversions (Singhal, *et al.* 1981). Accordingly, the change in selectivity with temperature was said to reflect the differences in the activation energies. In this work, the results covered the full range of conversions. It shows that the activation energy for hydrogenolysis reaction of dibenzothiophene is greater than that for hydrogenation of dibenzothiophene to cyclohexylbenzene. The values of the activation energies for hydrogenolysis (E_1) and hydrogenation (E_2) of dibenzothiophene and the activation energy for hydrogenation reaction of biphenyl to cyclohexylbenzene (E_3) are in a decreasing order of $E_3 > E_1 > E_2$. Thus, the product distribution is partly determined by the temperature employed for the reaction.

4. Conclusions

The pseudo-first-order kinetic model was found to fit the experimental data for the DBT consumption in

Table 3. The Pseudo-first-order rate constants and activation energies for reactions in Scheme I

Temp., K	CHB/BP	g feed / g catalyst h				K, Kcal/mol			
		k	k_1	k_2	k_3	E	E_1	E_2	E_3
633	0.000	4.03	4.03	0.00	0.00				
653	0.145	18.04	15.76	2.28	0.53				
683	0.152	83.73	72.69	11.04	5.00	53.1	50.3	44.1	63.8

k=k1+k2 and C_{CHB}/C_{BP} = k2/k1

hydrodesulfurization on a commercial CoMo/γ-Al_2O_3 catalyst. Biphenyl and cyclohexylbenzene were the major products observed. Their distributions suggest a reaction network that involves both parallel and sequential routes. The differences in activation energies of the respective reaction leading to biphenyl and cyclohexylbenzene indicate the importance of reaction temperature in determining the products distribution. Further, there appeared to be separate sites responsible for production of biphenyl and cyclohexylbenzene.

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