Competitive Hydrodesulfurization and Hydrogenation in a Monolithic Reactor

Competitive liquid-phase hydrodesulfurization of thiophene and hydrogenation of cyclohexene on a monolithic CoMo/γ-Al_2O_3 catalyst were studied. The flow pattern in the monolithic catalyst reactor was segmented gas-liquid flow (slug flow). The hydrogen pressure and the temperature were varied between 30–40 bar and 509–523 K, respectively. The experimental data are consistent with rate expressions of the Langmuir-Hinshelwood type where the reactions proceed on two different types of active sites. This kinetic model is based on hydrogenation of the thiophene ring prior to sulfur elimination.

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Introduction

Hydrodesulfurization (HDS) of sulfur-containing petroleum fractions has long been one of the major catalytic operations in the petroleum industry. This has been not only to reduce environmental pollution caused by sulfur but also for economic and technical reasons, in order to process heavier crude and residual feedstocks while preventing the poisoning of the platinum reforming catalysts.

The increasing importance of HDS in recent decades has made this technology the subject of much research. Particular attention has been focused on sulfur-containing heterocyclic compounds, in order to treat heavier oils. Among publications dealing with HDS in general may be mentioned those by Gates et al. (1979), Grange (1980), Ternan (1983), Katti et al. (1984), O'Brien et al. (1986), Harris and Chianelli (1986), and Gellman et al. (1987).

Much attention has also been focused on the catalyst functions for HDS. This topic has been studied extensively by Ratnasamy and Sivasanker (1980), Furimsky (1980), Chianelli (1984), Topsoe and Clausen (1984), Shimada et al. (1985), Thakur and Delmon (1985), Zdrazil and Kraus (1986), and Hisamitsu et al. (1987).

A proper selection of reactor technology is necessary in order to optimize the efficiency of catalytic HDS. Reactor development for hydrotreatment reactions has been reviewed by Dautzenberg and De Deken (1984). Trickle-bed reactors are widely used for hydrotreatment reactions. However, there are several difficulties associated with these reactors. Optimum distribution of gas and liquid is a major problem in trickle-bed reactors. This fact is of crucial importance not only in catalyst efficiency but also in the design of larger reactors. Fine solid particles present in heavy residual feedstocks cause bed plugging, which leads to enhanced pressure drop and consequently to lower effectiveness of the reactor. Replenishing of the catalyst is also a difficulty inherent in trickle-bed reactors. In order to overcome these problems, Dautzenberg and De Deken (1984) also considered back-mixed ebullating-bed reactors and slurry-phase technology as other reactor alternatives. However, there are still problems of scale-up and inefficient separation of catalyst particles, which limit wide use of these reactors.

Recently, a novel type of gas-liquid-solid reactor, the monolithic reactor, was reviewed by Irandoust and Andersson (1988). The catalyst consists of a great number of straight channels with porous walls in which the gas and liquid reactants flow cocurrently, Figure 1.

Among several possible flow patterns in these channels, segmented two-phase flow has the best mass transfer properties (Irandoust and Andersson, 1988). In this flow pattern, the flow through the monolithic channels consists of liquid slugs well separated from each other by distinct gas slugs. This flow provides a recirculation within the liquid slugs that increases the mass transfer both from the gas to the liquid and from the liquid to the wall. There is also a very thin liquid film that separates the gas slug from the solid catalyst. The thinness of this film facilitates mass transfer. Irandoust and Andersson (1989) have recently studied flow and mass transfer characteristics for the segmented two-phase flow in capillaries. Besides low axial dispersion and enhanced radial mass transfer due to the recirculation, the short diffusion length in the solid catalyst provides a high effectiveness factor for the monolithic catalyst.

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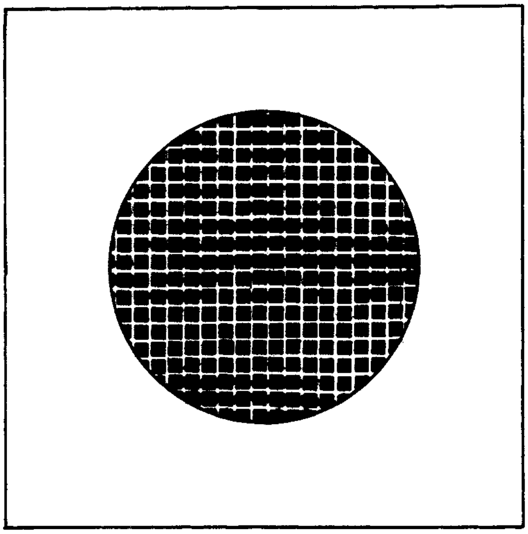

Figure 1. Cross section of monolithic catalyst.

The reactivity of sulfur compounds toward HDS depends on the type of the sulfur they contain, that is, the size and structure of the molecules. Generally, catalytic HDS is a slow reaction and is not suitable for standard wash-coated cordierite monoliths. However, the monolithic support can be manufactured today using high-surface-area materials. Soni and Crynes (1981) performed catalytic HDS on pure γ-alumina monoliths. The activity of the catalyst was about the same as a commercial catalyst. The authors concluded that the mass transfer, liquid distribution, and catalyst wetting were better in the monolith than in a trickle bed. The monolith also minimized bed plugging when fine solid particles were present.

Industrial HDS is generally carried out at between 300° and 425°C and under pressures ranging from 10 to 200 bar. Under these conditions hydrogen also reacts with other unsaturated compounds, in addition to HDS reactions. These facts make the selectivity aspects of hydroprocessing of interest. Nevertheless, although industrial HDS is a medium- or high-pressure process, most laboratory kinetic studies have been made at atmospheric pressure.

The aim of this work is to study the kinetics and selectivity aspects of both the HDS of thiophene and the hydrogenation (HYD) of cyclohexene, in a monolithic reactor operating under conditions similar to those of industrial interest.

The kinetic aspects of HDS have been investigated by Devanneaux and Maurin (1981), Vrinat (1983), Papayannakos and Marangozis (1984), van Parijs and Froment (1986), Papayannakos (1986) and Yitzhaki and Aharoni (1987).

Experimental Method

Support characteristics

The monolithic support used in this study consisted of pure γ-Al_2O_3, manufactured by Corning Glass Works. The support structure consisted of 118 vertical parallel channels with a cell density of 200 cells/in^2. The cell configuration was square, with a cross-sectional area of 1.7mm^2. The average thickness of channel walls was 0.3 mm. The density of the carrier was 1,490 kg/m^3, with a bed porosity of 53%. The pore volume of the carrier was 0.47 mL/g.

Preparation of monolithic Co-Mo catalyst

The monolithic catalyst examined was prepared by two-step impregnation using solutions of ammonium heptamolybdate (AHM) and cobalt nitrate hexahydrate (CNH). The molybdenum was impregnated first, and a calcination step was carried out before the cobalt impregnation. The concentrations of these solutions were selected so as to achieve a composition similar to that of commercial catalysts: 12 wt. % MoO_3, and 4 wt. % CoO.

The surface area of the catalyst in the oxidic form was measured to be 160 m^2/g. The volumetric mass transfer area of the catalyst was 1,900 m^{-1}.

Impregnation with Molybdenum. The incorpoation of Mo into the monolithic catalyst was carried out in the following steps. First the monolithic support was pretreated with air at 500°C for 2 h. After cooling to room temperature, the support was impregnated with a 0.02 M AHM solution for 72 h at pH 3. The weakened solution was then decanted and the catalyst was kept at ambient temperature for 12 h, followed by drying at 70°C for 2 h and at 120°C for 4 h in air. The calcination was carried out first at 350°C for 2 h and then at 500°C for 4 h.

Impregnation with Cobalt. The impregnation with cobalt was performed with the exact volume of solution of CNH that would fill the pores. The concentration of CNH was 1.14 M. Drying and calcination were then carried out as described above.

After final calcination the content of molybdenum and cobalt was analyzed by means of AAS (atomic absorption spectrophotometry), giving 8.2 wt. % Mo and 3.6 wt. % Co (12.3 wt. % MoO_3 and 4.6 wt. % CoO).

Activation. Prior to use, the calcined monoliths were activated by sulfidation in a specially designed tubular furnace, with a mixed flow of H_2 and H_2S (10 vol. % H_2S, 3.6 dm^3/h). The furnace was initially purged with a H_2:H_2S mixture at 150°C for 30 min before the temperature was increased to 400°C. This temperature was kept constant for another 2 h, after which it was reduced to room temperature in H_2:H_2S mixture. The catalyst was then kept in an argon environment for about 24 h before it was transferred into the reactor.

Reactor

The monolithic catalyst was placed in a reactor, Figure 2. The reactor was operated in a semibatch mode with continuous gas flow. The reactor consists primarily of a stainless steel tube (100 cm long, ϕ 2.54 cm ID), in the upper part of which the monolithic catalyst was placed. The lower half of the column served as a recirculation vessel for the liquid. Both gas and liquid entered the reactor from the top through a mass flow regulator and a liquid distributor, respectively, Figure 3.

The desired segmented flow was obtained by using a displacement pump (Lewa), which provided a pulsation of the liquid. The temperature was held constant by using two different heating systems, one on the recirculation pipes to control the inlet temperature and another on the reactor wall to control the reactor temperature. The pressure was held constant by using a back-pressure valve.

Physical properties of the liquid phase

The physical properties of the reaction mixture were estimated on the basis of the properties of cyclohexane.

The density of the solution was 516 kg/m^3 at 236°C and 485 kg/m^3 at 250°C. The vapor pressure of the mixture was

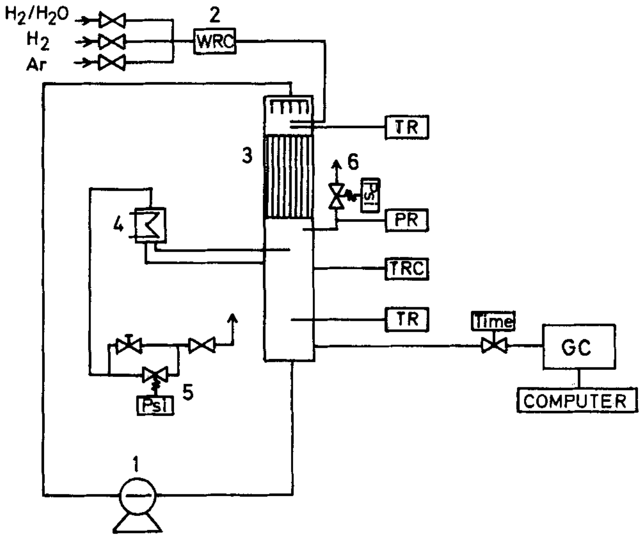

Figure 2. Experimental setup.

1. Displacement pump
2. Mass flow controller
3. Reactor
4. Water Cooler
5. Back-pressure valve
6. Pressure safety valve

determined by the Antoine equation to be 27.2 bar at 250°C and 22.3 bar at 236°C. The solubility of hydrogen in the solution was 8.22×10^{-5} mol/m^3 Pa at 236°C and 8.57×10^{-5} mol/m^3 Pa at 250°C (Young, 1981). The dynamic viscosity of the solution was estimated to be 0.114×10^{-3} kg/m · s at 236°C and 0.106×10^{-3} kg/m · s at 250°C (Reid et al., 1977). The surface tension of the solution versus its own vapor was calculated to be 2.83×10^{-3} N/m and 1.77×10^{-3} N/m at 236° and 250°C, respectively (Reid et al., 1977). Moreover, the hydrogen diffusivity in the reaction mixture was estimated to be 6.51×10^{-8} m^2/s at 236°C and 6.93×10^{-8} m^2/s at 250°C (Reid et al., 1977).

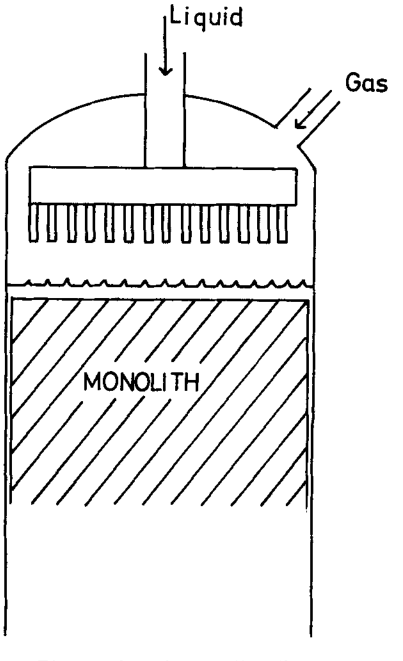

Figure 3. Liquid distributor.

The change of the physical properties due to the reaction has been disregarded.

Chemical analyses

The determination of the compounds was performed by means of gas chromatography (SHIMADZU, GC-MINI3) using a packed column of *n*-octane/porasil. The analyses were taken on line using an autosampler.

In order to confirm the proper identification of the compounds, a few samples were also analyzed by GC-MS. These analyses also made it possible to identify some minor products from side reactions occurring on the catalyst surface, such as isomerization of the solvent and polymerization of intermediate olefins. These products were all present in very small quantities and were assumed to have no influence on the overall reaction rate.

Run procedures

Eight runs were carried out with mixtures of thiophene (2 wt. %) and cyclohexene (1 and 2 wt. %) dissolved in cyclohexane. The liquid batch volume was 0.42 L. The runs were performed as a complete 2^3 factorial design with hydrogen pressure at 30 and 40 bar and temperature at 236° and 250° C and with the initial concentrations of cyclohexene of 1 and 2 wt. %. The catalyst load was 30.3 kg/m^3.

The liquid slug length was 3.4 mm and the gas slug lengths ranged from 5.8 to 8.1 mm, depending on the pressure.

The total average linear velocity of both gas and liquid was varied between 1.72×10^{-2} and 2.13×10^{-2} m/s.

The influence of the flow rate on the reaction rate was also investigated in three more experiments for which only gas and liquid flow rates were changed. These additional runs were performed at 250°C, with a hydrogen pressure of 40 bar and a starting solution containing 2 wt. % of cyclohexene and 2 wt. % of thiophene dissolved in cyclohexane. The gas flow was varied between 3×10^{-3} and 5×10^{-3} m^3/min (STP) and the liquid flow between 75×10^{-6} and 200×10^{-6} m^3/min, corresponding to liquid slug lengths ranging from 3.4 to 9.0 mm and gas slug lengths ranging from 6.0 to 10.0 mm. The average linear velocity of both gas and liquid then ranged from 1.75×10^{-2} to 3.5×10^{-2} m/s.

Theory

Catalyst structure

Hydrodesulfurization catalysts available from commercial manufacturers often contain γ-alumina as a support and have compositions such as 4 wt. % CoO and 12 wt. % MoO_3. In order to explain the action of the catalysts, several different models are proposed. Due to the complex structure of the catalyst, especially in its sulfided form, there is no agreement among workers in this field as to the precise structural features of the active centers where the hydrodesulfurization reaction occurs. At present four different models are in vogue, which accounts for the effects of the promoters and the necessity of γ-alumina as the support. Generally speaking, the catalytic function of the catalyst is attributed to the sulfided Co and Mo, whereas the main function of Al_2O_3 is to stabilize the active sulfided Co-Mo phases (Arnoldy and Moulijn, 1985). The Al^{3+} ions polarize covalent Co-S and Mo-S bonds, which leads to stronger bonds. This strengthening decreases the dispersion loss of the sulfide phase during the HDS reactions. Many excellent publications on this subject have already been presented (Gates et al., 1979; Grange 1980; Ratnasamy and Sivasanker, 1980; Furimsky, 1980; Chianelli, 1984; Topsoe and Clausen, 1984; Zdrazil and Kraus, 1986).

Modeling of the reaction kinetics

Accurate kinetic modeling of a catalytic reaction is important in order to optimize the catalyst function and also to design the catalytic reactor. The kinetics of the HDS reactions have been treated extensively in several articles (Satterfield and Roberts, 1968; Lee and Butt, 1977; Vrinat, 1983; Papayannakos and Marangozis, 1984; Van Parijs and Froment, 1986; Yitzhaki and Aharoni, 1987). However, in spite of all the interest in HDS, the reaction mechanism and kinetics are not completely understood and the results of different studies are not always in agreement.

Generally, the HDS of thiophene is assumed to proceed by two independent routes:

1. Adsorption of thiophene through S and the cleavage of the C-S bonds, resulting in loss of sulfur
2. Flat adsorption of thiophene as a π-complex to the catalyst surface, followed by hydrogenation of thiophene to tetrahydrothiophene (THT) and a subsequent C-S bond cleavage

The general reaction network is given in Figure 4.

The intermediates and reaction products of the hydrogenolysis of thiophene determine the necessary assumptions for the development of reaction kinetics. Product distribution and reaction intermediates during thiophene HDS have been reviewed by Vrinat (1983). In the HDS of thiophene, the possibility of formation of THT has received much attention. The hydrogenation of thiophene to THT is favored only at low temperatures (below 623 K) and at high pressures, while the hydrogenolysis reaction leading to C-S bond scission is not limited thermodynamically (Vrinat, 1983). Devanneaux and Maurin (1981) have discussed the formation of THT as an intermediate in thiophene HDS. These authors reported the formation of THT in all their thiophene runs at low temperature (220°C) and under high pressure conditions (P_{H_2} ranging from 2.2 to 17.5 bar). Furthermore, their kinetic analysis of thiophene HDS showed clearly two reaction pathways, as shown in Figure 4.

These facts imply the occurrence of two different types of catalytic sites, one for the ring hydrogenation to THT and the other for the C-S bond cleavage. This hypothesis has also been favored by a study of the hydrogen-deuterium exchange on CoMo/γ-Al_2O_3 (Smith et al., 1973).

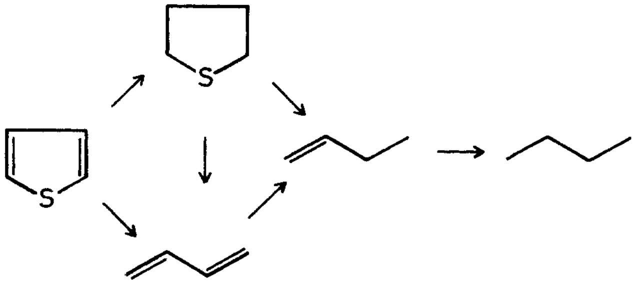

Figure 4. Possible pathways for thiophene HDS.

However, in spite of these results the formation of THT has not always been reported. In the recent study by van Parijs and Froment (1986) THT was not detected, although their experiments were performed at 2–30 bar total pressure and at temperatures of 260° to 350°C. This may indicate the sensitivity of the catalyst to the manufacturing procedure.

In the present work THT was detected in all experiments. Other reaction products of the thiophene HDS were N-butane, 1-butene, cis-2-butene, and trans-2-butene. No 1,3-butadiene was detected.

These facts lead us to the development of the following rate equations, based on a reaction network similar to that frequently referred to in literature (Van Parijs and Froment, 1986). The rate expressions are of the Langmuir-Hinshelwood type with thiophene adsorbing on two different sites. The hydrogenolysis of thiophene and tetrahydrothiophene (THT) into butenes (B) is assumed to take place on one kind of site (site σ). The hydrogenations of thiophene into THT, butenes into butane, and cyclohexene (CH) into cyclohexane are assumed to take place on another kind of site (site τ). Hydrogen competes mutually on both sites. The rate-determining step was assumed to be the surface reaction between adsorbed species. Adsorption and desorption rates are several orders of magnitude higher than the rate of the surface reactions. Furthermore, hydrogen was assumed to adsorb dissociatively at the surface (Vrinat, 1983). The influence of dissolved H_2S was omitted. It was also assumed that only reactive species adsorb on the active sites of the catalyst. The corresponding rate equations are given below. All symbols used can be found in the Notation.

The reaction of thiophene on both types of sites can be written as

$$\begin{aligned} r_T &= k_{T,\tau}\,\theta_{T,\tau}\,\theta^2_{H,\tau} + k_{T,\sigma}\,\theta_{T,\sigma}\,\theta^2_{H,\sigma} \\ &= \frac{k_{T,\tau}\,K_{T,\tau}\,K_{H,\tau}\,c_T\,c_{H_2}}{(1+\sqrt{K_{H,\tau}\,c_{H_2}} + K_{T,\tau}\,c_T + K_{B,\tau}\,c_B + K_{CH,\tau}\,c_{CH})^3} \\ &\quad + \frac{k_{T,\sigma}\,K_{T,\sigma}\,K_{H,\sigma}\,c_T\,c_{H_2}}{(1+\sqrt{K_{H,\sigma}\,c_{H_2}} + K_{T,\sigma}\,c_T + K_{THT,\sigma}\,c_{THT})^3} \qquad (1) \end{aligned}$$

The hydrogenation of cyclohexene on the τ sites is expressed as

$$\begin{aligned} r_{CH} &= k_{CH,\tau}\,\theta_{CH,\tau}\,\theta^2_{H,\tau} \\ &= \frac{k_{CH,\tau}\,K_{CH;\tau}\,K_{H,\tau}\,c_{CH}\,c_{H_2}}{(1+\sqrt{K_{H,\tau}\,c_{H_2}} + K_{T,\tau}\,c_T + K_{B,\tau}\,c_B + K_{CH,\tau}\,c_{CH})^3} \qquad (2) \end{aligned}$$

The net reaction rate for the disappearance of THT can be formulated as

$$\begin{aligned} r_{THT} &= k_{T,\tau}\,\theta_{T,\tau}\,\theta^2_{H,\tau} - k_{THT,\sigma}\,\theta_{THT,\sigma} \\ &= \frac{k_{T,\tau}\,K_{T,\tau}\,K_{H,\tau}\,c_T\,c_{H_2}}{(1+\sqrt{K_{H,\tau}\,c_{H_2}} + K_{T,\tau}\,c_T + K_{B,\tau}\,c_B + K_{CH,\tau}\,c_{CH})^3} \\ &\quad - \frac{k_{THT,\sigma}\,K_{THT,\sigma}\,c_{THT}}{(1+K_{T,\sigma}\,c_T + K_{THT,\sigma}\,c_{THT})} \qquad (3) \end{aligned}$$

Table. 1. Pre-Exponential Factors $K°$ for Adsorption Equilibrium Constants Used in Model 2

	$K°$ $m^3/mol \times 10^7$
CH	1.963
H	2.413
T	1.590

Due to the low concentration of THT, the second term on the right-hand side of Eq. 3 can be expressed as

$$\frac{k'_{THT,\sigma}\, c_{THT}}{(1 + K_{T,\sigma}\, c_T)} \tag{4}$$

where $k'_{THT,\sigma}$ is the adjusted rate constant for the disappearance of THT on σ sites.

Results and Discussion

The activity of the monolithic catalyst used was checked by running two slurry experiments, one with crushed monolithic catalyst and the other with a commercial pellet catalyst. It was shown that the monolithic catalyst is as active as the commercial one. No significant deactivation of the catalyst was observed during the period of this investigation.

In order to obtain the kinetic properties of the reactions, eleven experimental series were carried out in the monolithic catalyst reactor.

Due to the slowness of the reactions studied here, it was expected that mass transfer would not influence the overall reaction rates. This was investigated by running three experiments with different gas and liquid flow rates while keeping other conditions unchanged. The results of these experiments indicated no mass transfer effects.

The experimental data were fitted to the kinetic equations presented in the previous section, using concentrations as dependent variables and with the rate constants expressed as

$$k_{i,s} = k^{\circ}_{i,s} \exp\left[\frac{-E_{ai,s}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{5}$$

by nonlinear least-squares regression analysis. This way of writing the rate constant facilitates the parameter search and minimizes the influence of the correlation between the preexponential factor and the energy of activation. Furthermore, the equilibrium constants are expressd as

$$K_{j,s} = e^{\Delta S_j/R}\, e^{-\Delta H_{j,s}RT} = K^{\circ}_j\, e^{-\Delta H_{j,s}/RT} \tag{6}$$

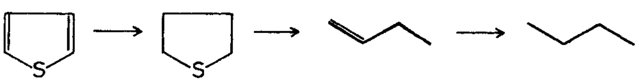

Figure 5. Thiophene HDS, final model.

In order to minimize the number of parameters used in the kinetic equations, the preexponential factors for the adsorption constants were fixed by calculating the entropies of adsorption. This step was necessary because of a very high correlation between parameters when the equilibrium constants were of the same form as Eq. 5. The values of ΔS were calculated by assuming that the chemisorbed species still have the vibrational and rotational degrees of freedom left. Thus the only contribution to ΔS was assumed to be the translational entropy (Adamsson, 1982). The translation entropy for a given gas phase molecule at the standard state can be calculated using the method of Sackur and Tetrode (Barrow, 1966). In our case the entropy of adsorption (from liquid phase to the catalyst surface) was then easily obtained by taking the loss of entropy due to condensation into account. The values of the preexponential factors used in all kinetic equations are given in Table 1.

The influence of butenes on the reaction rates was not taken into consideration due to their low concentration.

The kinetic equations tested involved 13 parameters altogether. A statistical analysis of the regression results obtained indicated very high correlation between parameters. In such a case any attempt to determine the parameters is meaningless.

However, relatively recently the theory of initial ring hydrogenation leading to THT has been advanced (Kemball and Dowden, 1981). Recent studies (Huckett et al., 1987; Spies and Angelici, 1987) support the proposal that thiophene is bound to the catalyst surface by a π-electron bond. This step leading to the formation of THT disrupts the aromatic stabilization of the thiophene ring. This evidence suggests a kinetic test of a dual site mechanism where the ring hydrogenation takes place on one site, τ, prior to the HDS of THT on another site, σ, Figure 5. Cyclohexene, butenes, thiophene, and hydrogen compete mutually for the hydrogenation sites. These assumptions result in the same equations as above, with $k_{T,\sigma}$, $K_{T,\sigma}$, and $K_{H,\sigma}$ being zero (no adsorption/reaction of thiophene and hydrogen on hydrogenolysis sites).

These equations (nine parameters), fit the experimental data very well, with all parameters being statistically significant. The residual analysis showed no trends. The numerical values of the calculated parameters with approximate 95% confidence intervals are given in Table 2. Figure 6 shows a typical experiment with the model curves. From this figure it is seen that the rate of reaction for both HDS and HYD is low during the first two hours. Hence the data from this period of time were not used in the regression analysis.

Table 2. Estimated Values of Parameters in Model 2 with Approximate 95% Confidence Limits

	ΔH, site τ J/mol	E_a J/mol	$k°$ mol/s · kg cat.
CH	$(-4.82 \pm 0.46) \times 10^4$	$(1.10 \pm 0.16) \times 10^5$	$(4.22 \pm 2.06) \times 10^{-3}$
H	$(-5.41 \pm 0.93) \times 10^4$	$(8.40 \pm 1.20) \times 10^4$	$(2.82 \pm 1.12) \times 10^{-3}$
T	$(-4.89 \pm 0.42) \times 10^4$	$(8.53 \pm 2.31) \times 10^4$	$(2.69 \pm 1.99) \times 10^{-3}$

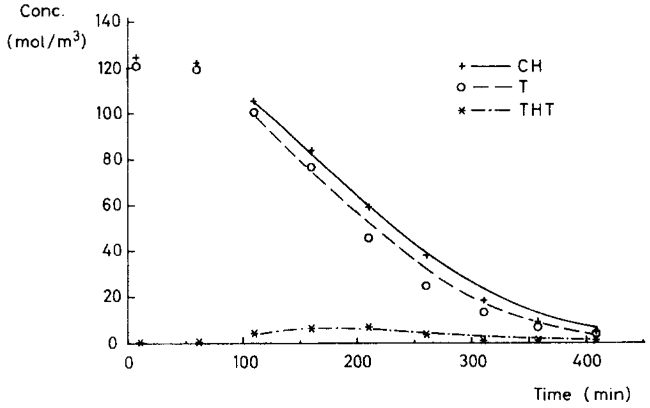

Figure 6. HDS of thiophene and hydrogenation of cyclohexene in a monolithic catalyst reactor.

+, O, *: observed concentrations
——, ---, -●-: model curves
H_2 pressure 40 bar, temp. 523 K

At this stage, an analysis based on the physicochemical interpretation of the parameters is necessary. Some thermodynamic constraints on the parameters are

a. Activation energies, rate, and equilibrium constants must be positive

b. For localized adsorption the entropy upon adsorption should decrease

c. Enthalpy of adsorption must be negative

Tables 1 and 2 show that the values of the fitted parameters cannot be rejected thermodynamically.

Thus, from a statistical point of view the regression results suggest the following reaction scheme: first a hydrogenation of the thiophene ring in competition with cyclohexene on one kind of site and then a further desulfurization on the second type of site.

In order to achieve more simplified reaction rates, simple power law models with Arrhenius-type rate constants, Eq. 5, were considered. These models are written as

$$r_{\mathrm{CH}} = k_{\mathrm{CH}}\, c_{\mathrm{CH}}^{\alpha_1}\, c_{\mathrm{H_2}}^{\beta_1}\, c_{\mathrm{T}}^{\delta_1} \tag{7}$$

$$r_{\mathrm{T}} = k_{\mathrm{T}}\, c_{\mathrm{CH}}^{\alpha_2}\, c_{\mathrm{H_2}}^{\beta_2}\, c_{\mathrm{T}}^{\delta_2} \tag{8}$$

$$r_{\mathrm{THT}} = r_{\mathrm{T}} - k_{\mathrm{THT}}\, c_{\mathrm{THT}}^{\gamma} \tag{9}$$

The empirical equations presented above were fitted to the observed data by nonlinear least-squares regression analysis. The values of parameters with approximate 95% confidence intervals are shown in Table 3. It should be noticed that in the empirical model presented, any additional term results in much higher parameter correlations without changing the residual sum of squares for the better.

A closer investigation of both models indicates that:

a. Hydrogen has low influence on the HDS/HYD selectivity

b. Cyclohexene and thiophene inhibit reaction rates of HDS and HYD, respectively

c. A comparison between the apparent energies of activation shows that the selectivity with respect to thiophene is favored by a low temperature ($E_{a,\mathrm{T}} < E_{a,\mathrm{CH}}$)

Table 3. Estimated Values of Parameters in Empirical Model with Approximate 95% Confidence Limits

	E_a J/mol	$k°$ mol/s · kg cat.
CH	$(9.21 \pm 1.76) \times 10^4$	$(9.77 \pm 5.51) \times 10^{-4}$
T	$(6.53 \pm 0.77) \times 10^4$	$(8.09 \pm 3.72) \times 10^{-4}$
THT	$(8.87 \pm 1.89) \times 10^4$	$(1.20 \pm 0.46) \times 10^{-2}$
	Exponents	
	α_1	0.95 ± 0.12
	α_2	-0.12 ± 0.09
	β_1	0.39 ± 0.25
	β_2	0.42 ± 0.23
	δ_1	-0.37 ± 0.08
	δ_2	0.52 ± 0.09
	γ	0.84 ± 0.06

The calculated values of the activation energies and heats of adsorption are in good agreement with the data reported in the literature (Vrinat, 1983; Van Parijs and Froment, 1986).

The effect of the diffusion limitation in the solid catalyst is estimated by the method of Weisz. For the reaction given in Figure 6, the Weisz modulus was calculated to be 0.32, which confirms the absence of an internal diffusion resistance.

Conclusions

The kinetic study of the hydrogenolysis of thiophene and hydrogenation of cyclohexane in a monolithic catalyst reactor supports the existence of two types of active sites, one for hydrogenation and one for sulfur elimination. Hydrogenolysis of thiophene requires thiophene ring hydrogenation (in competition with other unsaturated compounds) before a C-S bond cleavage takes place. The selectivity with respect to thiophene is favored at low temperature and is not dependent on the hydrogen pressure for the experimental conditions studied in this work.

The monolithic catalyst reactor is an excellent alternative for hydrotreatment processing due to its simplicity.

Acknowledgment

The financial support of the National Energy Administration of Sweden is gratefully acknowledged.

Notation

c_j = bulk concentration of component j, mol/m^3
$E_{ai,s}$ = energy of activation for reaction i, on site s, J/mol
$\Delta H_{j,s}$ = enthalpy change upon adsorption of component j on site s, J/mol
$k_{i,s}$ = reaction rate constant for reaction i, on site s, mol/s · kg catalyst
$k'_{\mathrm{THT},\sigma}$ = adjusted reaction rate constant for disappearance of tetrahydrothiophene on site σ, mol/s kg catalyst
$k_{i,s}^{\circ}$ = preexponential factor in reaction rate constant for reaction i, on site s, mol/s · kg catalyst
K_j° = preexponential factor in adsorption equilibrium constant of component j, m^3/mol
$K_{j,s}$ = adsorption equilibrium constant of component j, on site s, m^3/mol
r_i = rate of reaction i, mol/s · kg of catalyst
R = equation of state constant, J/mol · K
ΔS_j = entrophy change upon adsorption of component j, j/mol · K
T = absolute temperature, K
T_m = experimental mean temperature, K

Greek letters

α_i = apparent order of reaction with respect to cyclohexene in reaction i
β_i = apparent order of reaction with respect to H_2 in reaction i
δ_i = apparent order of reaction with respect to thiophene in reaction i
γ = apparent order of reaction with respect to tetrahydrothiophene
$\theta_{j,s}$ = fractional coverage of component j, on site s
τ = hydrogenation site
σ = hydrogenolysis site

Subscripts

B = butenes
CH = cyclohexene
H = hydrogen, dissociatively adsorbed
H_2 = molecular hydrogen
T = thiophene
THT = tetrahydrothiophene
i = reaction index
j = component index
s = site index

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