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Catalytic Hydrodesulfurization of Thiophene Studied by the Reversed-Flow Gas Chromatography Technique

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The new technique of reversed-flow gas chromatography was applied to a reaction of industrial importance, namely the catalytic hydrodesulfurization of thiophene. The catalysts were cobalt–molybdenum oxides supported on four different types of commercial aluminas. With the aid of the new technique, total fractional conversions of the reactant to products (*n*-butane and butenes), rate constants, and Arrhenius activation parameters were easily determined. For the three most active catalysts, the rate-determining step at temperatures below 500 K is the chemical reaction on the catalyst surface. Above 500 K the rate is diffusion- or adsorption-limited. For the less active catalyst the chemical reaction is the rate-determining step in the whole range of temperatures studied. The catalytic activity was found independent of the Na_2O content of the aluminas, as well as their pore volume and specific surface area. The results were found in good agreement with those determined by other techniques.

INTRODUCTION

The demand for fuel oil of extremely low sulfur content is growing steadily due to efforts to prevent air pollution. Obtaining this fuel oil requires hydrodesulfurization (HDS) of liquid petroleum fractions or of its residuums. Such HDS operations are in widespread use in the petroleum refining industry, and can be considered to be the most important chemical reactions presently practiced. Undoubtedly, the HDS of thiophene is the most representative HDS reaction of the petroleum fractions and its residuums. Substantial work on this reaction has been published (*1–11*). Thiophene and its simple alkyl homologs have been desulfurized at atmospheric and higher pressures over a wide range of catalysts and temperatures.

The main object of the present paper was to apply the new technique of reversed-flow gas chromatography to the kinetic study of this important reaction, using catalysts supported on various aluminas. A Greek alumina was included to see whether the catalyst prepared from that has a comparative activity with those produced from other commercial aluminas.

Reversed-flow gas chromatography (RFGC) is a new method for studying the detailed kinetics of surface-catalyzed reactions (*12–18*), and other related phenomena (*19–25*). This method serves to determine reaction rates in the whole range of conversions; from these rates true rate constants for catalytic reactions can be calculated. After a preliminary communication (*12*) and a general theoretical analysis (*13*), in which the relevant mathematical equations were derived, the method was used to study the dehydration of alcohols (*14*), the deamination of primary amines (*15*), the oxidation of carbon monoxide (*16*), the hydrogenation of propene (*17*), and the cracking of cumene (*18*).

The method has been also used successfully to determine gas diffusion coefficients in binary and ternary mixtures (*19–21*), adsorption equilibrium constants (*22*), rates of drying of catalysts (*23*), rate coefficients for evaporation of liquids (*24*), and critical volumes of gases (*25*). A review on the RFGC method will soon appear (*26*).

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In all catalytic studies mentioned above (*12–18*) the pulse method for introducing the reactant(s) was employed. However, an essential point in comparing catalytic activities is the method of testing, and therefore the application of RFGC with a continuous feeding of the reactants to the catalyst (continuous flow) is justified, since the treatment of the experimental data and the calculation of rate constants from the reversed-flow chromatograms are different from those used with the pulse method.

EXPERIMENTAL

Materials. The catalysts' supports were Greek alumina from Aluminium Hellas A.G., and three other aluminas from Houdry Katalysatorenwerke (Ho 415, Ho 417, Ho 425). $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ analytical reagent from Mallinckrodt Chemical Works and $Co(NO_3)_2 \cdot 6H_2O$ purum p.a. from Fluka A.G. were used for the catalysts' preparation.

Thiophene purum from Fluka A.G. was used as reactant, while the products were verified by using *n*-butane "practical" from Fluka A.G. and butenes (≥99.9%) from Matheson Gas Products.

The carrier gas was hydrogen (99.99%), and this, together with the hydrogen sulfide used for the sulfation of catalysts, was purchased from Linde A.G. (Greece).

The chromatographic material was 20% Carbowax 20 M on Chromosorb P, acid-washed, 60–85 mesh.

Preparation of catalysts. The catalysts used were prepared by the classical dry impregnation method of the aluminas with aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ first, and then with solutions of $Co(NO_3)_2 \cdot 6H_2O$. The quantity of the active phase, expressed as MoO_3, was 14% (w/w), while the deposited promoter, after the catalysts' calcination, was 3% (w/w) Co_3O_4. Finally, the catalysts were sulfided with a mixture of H_2S (15%) and H_2, for 4 h and a flow rate of 0.55 $cm^3\ s^{-1}$.

The specific surface areas and the pore volumes of the aluminas used were measured by a sorptometer (Perkin–Elmer Model 212D). They are given in Table 1 together with their content in Na_2O. The measurements were made before and after heating the catalysts at 873 K for 6 h to remove the adsorbed water.

Apparatus. The experimental setup for the application of the RFGC technique is generally very simple. A conventional gas chromatograph is modified as reported (*13*) to include a catalytic chromatographic column if there is only one reactant strongly adsorbed on the catalyst surface. In the case of two gaseous reactants, neither of which is retained in the catalyst bed for a long time, but they are eluted together with the products, a diffusion column is used to arrange a continuous feed of reactant(s) into the catalytic bed (*16*). In the present work the apparatus of Fig. 1 was employed. This is an improved arrangement which has already been described (*26*). A Pye–Unicam Series 104 gas chro-

TABLE 1

Some Properties of the Aluminas Used for the Preparation of Catalysts

Alumina	Na_2O (% w/w)	Pore volume, $cm^3\ g^{-1}$		Specific surface area, $m^2\ g^{-1}$	
		Before heating	After heating[a]	Before heating	After heating[a]
Houdry Ho 415	0.7	0.5	0.5	160	123
Houdry Ho 417	0.1	0.5	0.48	300	150
Houdry Ho 425	0.01	0.5	0.46	150	171.3
Commercial Greek	0.275	0.1	0.5	—	122.5

[a] At 873 K for 6 h.

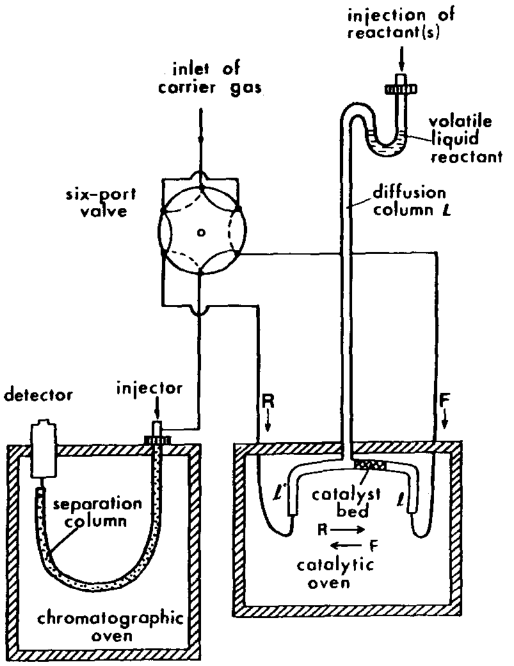

FIG. 1. Experimental setup to study the catalytic hydrodesulfurization of thiophene by the reversed-flow gas chromatography technique.

matograph, with a flame ionization detector, was modified as shown. The catalyst (0.05 g) was in a short section of the sampling column $l' + l$, while the remaining part of this column was empty. It was inside an oven, which kept constant the working temperature. The feed of the catalyst with the reactant thiophene (0.5 cm^3 of liquid placed in the upper section of the diffusion column) was achieved by the diffusion flux of the thiophene vapor inside the diffusion column L (80 cm × 2-mm i.d.). The separation column (6 m × 2-mm i.d.) had been filled with 20% Carbowax 20 M on Chromosorb P, and was kept at a constant temperature (395 K) with the aid of the chromatographic oven.

Procedure. With the carrier gas hydrogen (0.103 cm^3 s^{-1}) flowing in direction R (solid lines in the six-port valve) the catalyst is heated at 547 K for 20 h. During this period the retention times of the reactant thiophene and the products *n*-butane and butenes in the chromatographic column are found by injecting the pure substances into the separation column. Subsequently, the catalyst is heated at the working temperature for 2 h with the hydrogen flowing alternately in both directions R and F. The thiophene is introduced into the diffusion column L at the injection of reactant(s) point and the whole system is allowed to run for 20 h for establishment of the catalyst's steady state. Then, the flow is reversed (from the R- to the F-direction) by means of the valve and the detector records various positive and negative frontal boundaries, and some "sample peaks." This is illustrated in Fig. 2.

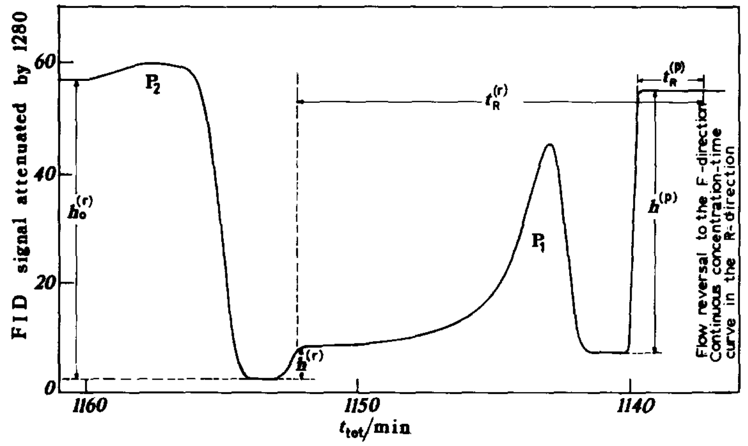

FIG. 2. Frontal boundaries and sample peaks obtained by reversing the carrier gas flow from R- to F-direction, during the hydrodesulfurization of thiophene over Co_3O_4–MoO_3–Al_2O_3 catalyst, at 507 K.

After a certain time for the reestablishment of the continuous chromatographic signal, the flow of the carrier gas is reversed again to the R-direction. New frontal boundaries and sample peaks, similar to those of Fig. 2, are recorded. This procedure is repeated many times at the same temperature, which means that one can easily make many measurements of the catalytic activity in the catalyst's steady state.

RESULTS AND DISCUSSION

The General Chromatographic Equation

The general mathematical equation describing the elution curve in the RFGC method is (*20, 26*)

$$\begin{aligned} c = {} & c_1(l',t_0 + t' + \tau) \cdot u(\tau) \\ & + c_2(l',t_0 + t' - \tau) \cdot [1 - u(\tau - t')] \\ & \quad \cdot [u(\tau) - u(\tau - t'_{\mathrm{M}})] \\ & + c_3(l',t_0 - t' + \tau) \cdot u(t_0 + \tau - t') \\ & \quad \cdot \{u(t - t')[1 - u(\tau - t'_{\mathrm{M}})] \\ & \quad - u(\tau - t')[u(\tau) - u(\tau - t'_{\mathrm{M}})]\}, \end{aligned} \tag{1}$$

where c is the concentration of the solute substance at the detector, which is analogous to the height of the elution curve, t_0 is the total time from the injection of the reactant, t' is the time interval of backward flow, t is the time from the last restoration of the carrier gas flow to the original direction, and $\tau = t - t_{\mathrm{M}}$, t_{M}, and t'_{M} being the gas hold-up times of the substances on the columns with lengths l and l', respectively.

This chromatographic equation contains on the r.h.s. three concentration terms c_1, c_2, and c_3. They all refer to the point l', i.e., at the junction of the columns L and $l' + l$ (cf. Fig. 1), but to different values of the time variable, namely $t_0 + t' + \tau$, $t_0 + t' - \tau$, and $t_0 - t' + \tau$, respectively. Each of these concentration terms is multiplied by a combination of unit step functions u, so that it appears in a certain time interval and vanishes in all others. There are various specific cases of Eq. (1) depending on the relative values of t_0, t', t, t_{M}, and t'_{M}. The most interesting of these arise when the duration of the backward flow t' is (a) *greater than the sum* $t_{\mathrm{M}} + t'_{\mathrm{M}}$ and (b) *smaller than both* t_{M} and t'_{M}.

In case (a), which is used here, the term c_3 vanishes and Eq. (1) becomes

$$\begin{aligned} c = {} & c_1(l',t_0 + t' + \tau) \cdot u(\tau) \\ & + c_2(l',t_0 + t' - \tau) \\ & \quad \cdot [u(\tau) - u(\tau - t'_{\mathrm{M}})]. \end{aligned} \tag{2}$$

This predicts that $c = 0$ for $\tau < 0$, i.e., $t < t_{\mathrm{M}}$, while for $\tau \geq 0$ or $t \geq t_{\mathrm{M}}$ two functions are recorded as a sum $c_1 + c_2$. The first is $c(l',t_0 + t')$ shifted forward by τ. This continues uninterrupted as the first term on the r.h.s. of Eq. (2) shows. In the other function c_2 the total time $t_0 + t'$ is shifted backward by τ, and this function vanishes when $\tau \geq t'_{\mathrm{M}}$ or $t \geq t_{\mathrm{M}} + t'_{\mathrm{M}}$. Thus a "sample peak" is predicted in the interval $t_{\mathrm{M}} \leq t \leq t_{\mathrm{M}} + t'_{\mathrm{M}}$, positioned on top of the otherwise continuing chromatographic curve.

Reversing now the carrier gas flow to the original direction, and so on, keeping the time between any two successive reversals greater than $t_{\mathrm{M}} + t'_{\mathrm{M}}$, two series of peaks are recorded. These are called F-peaks when the gas flows to the one direction (forward), and R-peaks when it flows to the other direction (reverse). Equation (2) describes both of them, provided that no delay would occur in the separation column (cf. Fig. 1). In the presence of the latter, however, all frontal boundaries and sample peaks are shifted by the retention times t_{R} of the various substances in the separation column.

If the concentrations c_1 and c_2 depend on a rate process taking place at the junction of L and $l' + l$, the rate coefficient of this process can be determined either from the sample peaks (their height or their area under the curve), or from the heights of the various frontal boundaries (positive or negative, cf. Fig. 2). In the present work the latter height h was used and this measures the concentration $c_1(l',t_0 + t' + \tau)$ at $t = 0$, i.e., at $\tau = t - t_{\mathrm{M}} = -t_{\mathrm{M}}$. Thus, $c_1 = c_1(l',t_0 + t' - t_{\mathrm{M}})$. Since the sum $t_0 + t'$ is the total time, t_{tot}, from the injection of the reactant and t_{M} is negligible compared to that, we can write

$$h \simeq c_1(l', t_{\mathrm{tot}}). \tag{3}$$

For a detailed explanation it is necessary, except of the experimental curve given in Fig. 2, to draw the theoretical elution curve predicted by Eq. (2). This is given in Fig. 3. With the hydrogen (carrier gas and reactant) flowing in direction R, the separation column and the branch l of the sampling cell contain reactant and products with concentrations $c^{(r)}$ and $c^{(p)}$, respectively, while the sampling branch l' is empty of any substance. After time $t_R^{(p)}$ (which is the retention time of the products in the separation column) from the reversal of the carrier gas flow to the F-direction, a negative frontal boundary appears with height $h^{(p)} \simeq c^{(p)}$. For time t'_M, which is the gas hold-up time in the sampling branch l', the elution curve is due only to the reactant still remaining in the separation column, but after this time new products appear, contained in the sampling branch l and passing through the catalyst. These products create the sample peak P_1. Comparison of this peak with the experimental one given in Fig. 2 shows that the actual peak is lower in height and broader than that predicted theoretically. This may be due to various slow processes, e.g., adsorption or diffusion, taking place when the products contained in l pass through the catalyst, before their arrival to the detector.

After time $t_R^{(r)}$ (which is the retention time of the reactant thiophene in the separation column) a new negative frontal boundary appears with height $h^{(r)}$, which measures the concentration of the reactant thiophene after passing through the catalyst bed. The elution curve then remains at the zero point for time t'_M, after which a new sample peak P_2 appears "sitting" on the ending baseline. This baseline has a height $h_0^{(r)}$, which measures the concentration of thiophene before its passing through the catalyst bed.

A second reversal of the carrier gas flow from F- to R-direction creates new frontal boundaries and sample peaks. This, however, is a more complicated process since the reactant thiophene passes through a catalyst which had been without reactant feed for some time. For this reason we did not use the chromatograms obtained when the direction of the carrier gas flow was reversed from F- to R-direction. All our experimental results were based on the simple reversals of the carrier gas flow from R- to F-direction.

Calculation of the Rate Constants

A single reversal of the carrier gas flow gives the total fractional conversion of the

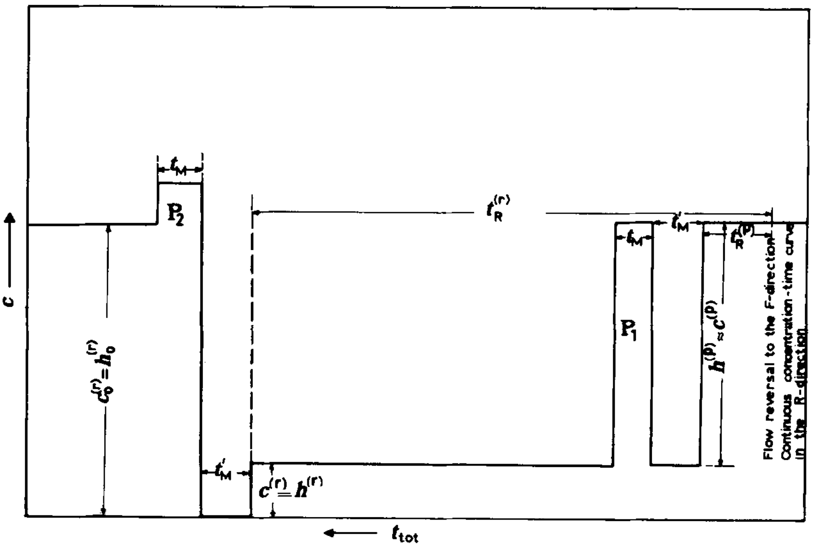

FIG. 3. Theoretical elution profile for the conditions of Fig. 2.

reactant to products:

$$x = \frac{h_0^{(r)} - h^{(r)}}{h_0^{(r)}}. \qquad (4)$$

This sampling process is repeated many times in the catalyst's steady state giving various values of x with a small deviation from each other. In Table 2 we give the mean values of x, obtained from four to seven samplings at different t_{tot} in the steady state. The (±) values listed with $\bar{x}$ are standard deviations, and their small magnitude is an indication that inhibition of the reaction by H_2S produced from thiophene is negligible, since there is a continuous flow of reactant through the catalyst and the samplings were made at times widely apart from each other. The absence of inhibition by H_2S is not unexpected, because all catalysts were sulfided before use, as reported under Experimental. In view of the above, first-order kinetics with respect to thiophene can be assumed, as was also done by others (*10*).

TABLE 2

Mean Fractional Conversions, $\bar{x}$, and Rate Constants, k, for the Hydrodesulfurization of Thiophene over Four Catalysts Supported on Various Aluminas, at Various Temperatures

Alumina	T (K)	$10^2\bar{x}$	10^3k ($m^3\ kg^{-1}$ cat. s^{-1})
Houdry Ho 415	464	23 ± 6	0.5 ± 0.1
	484	56 ± 1	1.68 ± 0.05
	503	89 ± 2	4.4 ± 0.4
	525	95.7 ± 0.4	7.1 ± 0.2
	545	97.4 ± 0.3	8.4 ± 0.3
Houdry Ho 417	466	17 ± 3	0.35 ± 0.07
	485	20 ± 1	0.46 ± 0.03
	505	33.0 ± 0.6	0.84 ± 0.02
	527	58 ± 2	1.9 ± 0.1
	547	80 ± 2	3.5 ± 0.2
Houdry Ho 425	466	16.9 ± 0.4	0.356 ± 0.009
	485	45 ± 2	1.16 ± 0.07
	497	70 ± 2	2.7 ± 0.2
	507	89.1 ± 0.6	4.7 ± 0.1
	546	98.1 ± 0.2	9.0 ± 0.2
Commercial Greek	466	22 ± 1	0.47 ± 0.02
	484	56 ± 2	1.66 ± 0.09
	505	82.4 ± 0.6	3.58 ± 0.07
	521	92.1 ± 0.4	5.6 ± 0.1
	544	96.8 ± 0.1	7.68 ± 0.07

Rate constants for the hydrodesulfurization of thiophene at various temperatures are also given in Table 2. The equation relating the rate constant k with the fractional conversion of the reactant to products is derived as follows. The specific rate of reaction r_m (in mol/kg cat · s) is given by the relation

$$r_m = \frac{dx}{d\tau_m} = \frac{dx}{d(1/v_m)} = \frac{dx}{d(W/v)}, \qquad (5)$$

where

τ_m = space time of the reactor

v_m = the reactor's space velocity (mol/kg cat · s)

v = feed rate (mol/s)

W = catalyst's weight (kg).

Integration of Eq. (5) gives

$$\int_0^W d\left(\frac{W}{v}\right) = \int_0^x \frac{dx}{r_m}. \qquad (6)$$

Since during an experiment the feed rate v is kept constant, Eq. (6) gives

$$\frac{W}{v} = \int_0^x \frac{dx}{r_m}. \qquad (7)$$

The feed rate is given by the product $v = \dot{V}c_0$, where $\dot{V}$ is the volume flow rate (m^3/s), and c_0 is the concentration of thiophene at the entry of the catalytic bed (mol/m^3).

Assuming a first-order reaction with respect to thiophene, $r_m = kc$, where k is the rate constant (in m^3/kg cat · s), Eq. (7) becomes

$$\frac{W}{\dot{V}c_0} = \int_0^x \frac{dx}{kc_0(1 - x)} \qquad (8)$$

or

$$k = \frac{\dot{V}}{W} \ln \frac{1}{(1 - x)}. \qquad (9)$$

To calculate actual reaction rates r_m at the entry of the bed, it is only necessary to multiply the rate constants by the concentration c_0 of thiophene. The latter can be found from the characteristics of the reactant

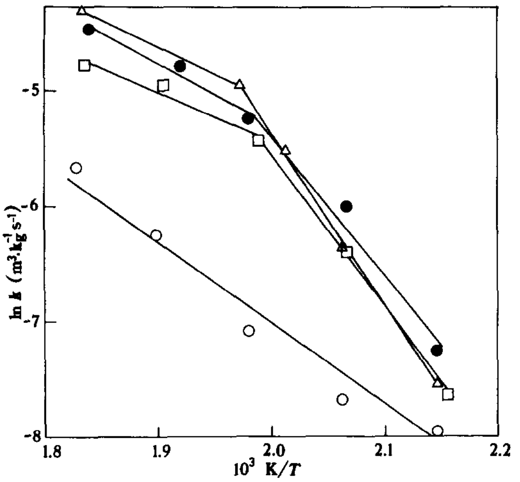

FIG. 4. Arrhenius plots for the hydrodesulfurization of thiophene over Co_3O_4–MoO_3–Al_2O_3 catalysts. Aluminas: (○) Ho 417, (□) Ho 415, (△) Ho 425, and (●) commercial Greek. The two latter plots have the ordinate shifted down by 0.4 units, i.e., the −5 should be read −5.4, etc.

feeding arrangement (cf. Fig. 1) as was done in another study (*24*). Since rate constants are more fundamental for a chemical reaction than reaction rates, only the first are reported in Table 2. In Eq. (9) one must use the corrected volume flow rate at the catalytic bed temperature and pressure. This correction can be easily made by the relation

$$\dot{V} = \dot{V}_{\text{meas}} \frac{T_1}{T_2} \cdot \frac{p_2}{p_1}, \qquad (10)$$

where $\dot{V}_{\text{meas}}$ is the measured flow rate, and the subscripts 1 and 2 refer to the bed and the environment, respectively.

Arrhenius Parameters

The Arrhenius plots for all catalysts used are given in Fig. 4. With the exception of the catalyst supported on alumina Houdry Ho 417, the remaining three catalysts give two straight lines on these plots. This is not a rare phenomenon (*27*) in the catalytic reactions and can be due to two reasons. First, to diffusion phenomena, and a chemical reaction being diffusion-limited at relatively high temperatures. Second, to the small surface coverage at high temperatures, lowering the true activation energy by the heat of adsorption of thiophene ΔH_a (a negative quantity) and giving an apparent activation energy:

$$E_a^{\text{app.}} = E_a^{\text{true}} + \Delta H_a. \qquad (11)$$

Activation energies and frequency factors for two temperature ranges (lower and higher than 500 K) are given in Table 3. The E_a listed show that, at temperatures lower than about 500 K, the rate-determining step is the chemical reaction on the catalyst surface, while at temperatures higher than 500 K the E_a values appear smaller than those expected (except for the catalyst supported on alumina Houdry Ho 417). If this were due to diffusion limitations, the apparent E_a values would be expected in the region 10–15 kJ mol^{-1}. Since the values found by us at high temperatures are all higher than 35 kJ

TABLE 3

Activation Energies (E_a) and Frequency Factors (A) for Two Temperature Ranges, Together with Heats of Adsorption (ΔH_a) for the Hydrodesulfurization of Thiophene over the Four Catalysts Used

Alumina	E_a, kJ mol^{-1}		ln A		ΔH_a (kJ mol^{-1})
	$T < 500$ K	$T > 500$ K	$T < 500$ K	$T > 500$ K	
Houdry Ho 415	110	35	21.0	3.0	75
Houdry Ho 417	62	—	7.9	—	—
Houdry Ho 425	125	38	24.3	3.6	87
Commercial Greek	101	44	18.6	4.9	57

mol^{-1}, the heat of adsorption of thiophene must be involved at high temperatures.

Thus, from Eq. (11) the heats of adsorption can be calculated as

$$\Delta H_a = E_a^{\mathrm{app.}} - E_a^{\mathrm{true}} = E_a^{\mathrm{high}\ T} - E_a^{\mathrm{low}\ T}. \tag{12}$$

These values are also given in Table 3.

Comparison of the Catalysts

The rate constants of Table 2, the Arrhenius parameters of Table 3, and the Arrhenius plots of Fig. 4 show that the activity of the catalyst prepared from the Greek commercial alumina is comparative with that of the two catalysts having as supports the Houdry aluminas Ho 415 and Ho 425. No correlation between catalytic activity and Na_2O content or specific surface area or pore volume of the aluminas seems to exist. For instance, the catalyst prepared from alumina Houdry Ho 417, which has the same pore volume as the other three, and Na_2O content or specific surface area (after heating) between the commercial Greek and the Houdry Ho 425 aluminas (cf. Table 1), was found to be considerably less active than those prepared from the other two aluminas.

Finally, we tried to compare the catalytic activity as determined by the RFGC method, with that found by other researchers using different techniques. This is not an easy task since most workers simply measure fractional conversions of the reactant to products and no kinetic parameters are involved as was done here. Owens and Amberg (*5*) found an apparent activation energy for the hydrodesulfurization of thiophene over "cobalt–molybdate" catalyst of 104.6 kJ mol^{-1}. This value is in fairly good agreement with the activation energies determined here (cf. Table 3) for the three most active catalysts at temperatures lower than 500 K.

Thomas *et al.* (*10*) studied the hydrodesulfurization of thiophene over a catalyst containing 18.6% w/w MoO_3 on γ-Al_2O_3 Ketjen 000-1.5E, with pore volume 0.51 $\mathrm{cm}^3\ \mathrm{g}^{-1}$ and specific surface area 213 $\mathrm{m}^2\ \mathrm{g}^{-1}$. They found a rate constant at 673 K equal to 1.05×10^{-3} m^3 thiophene converted · $(\mathrm{mol\ metal})^{-1}\ \mathrm{s}^{-1}$. Multiplying this value by 1.2922 mol metal/kg cat. gives 1.3568×10^{-3} m^3 thiophene converted · kg^{-1} cat. s^{-1}. Dividing the last number by 0.062, since the gas phase contained 6.2 mol% thiophene in hydrogen, the rate constant k comes out as $2.2 \times 10^{-2}\ \mathrm{m}^3\ \mathrm{kg}^{-1}$ cat. s^{-1} at 673 K. In the present work, the rate constant for the catalyst prepared from the Greek alumina at 673 K (calculated by using the Arrhenius parameters of Table 3) is $5.1 \times 10^{-2}\ \mathrm{m}^3\ \mathrm{kg}^{-1}$ cat. s^{-1}, i.e., only 2.3 times larger than that of Thomas *et al.* (*10*).

The final conclusion of this study is that the detailed kinetics of catalytic hydrodesulfurization reaction, which is very important for the oil refining industry, can be studied with simplicity and accuracy using the new RFGC technique. One other obvious conclusion is that one can prepare active hydrodesulfurization catalysts with MoO_3 (14% (w/w)) and Co_3O_4 (3% (w/w)) using commercial Greek alumina.

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