Study of Catalysts for Cyclohexane–Thiophene Hydrogen Transfer Reactions

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The effect of adding various promoter metals to cobalt–molybdenum–alumina on the cyclohexane–thiophene (donor–acceptor) reaction was investigated. It was found that most of the transfer of hydrogen from cyclohexane to thiophene is indirect, i.e., cyclohexane dehydrogenates and the hydrogen formed reacts with thiophene to effect hydrodesulfurization. From this study it was found that the direct hydrogen transfer reaction is promoted by adding Cr, V, Ti, Zr, Zn and Sn to the reference catalyst, whereas, after a certain level, addition of more cobalt has an inhibiting effect. Chromium has the strongest promoting effect for cyclohexane dehydrogenation, whereas, zinc addition resulted in the greatest promotional effect for thiophene hydrogenolysis. Deuterium tracer experiments were conducted and from these studies it was found that the relative transfer rates from cyclohexane and hydrogen were in agreement with those estimated from kinetic data for various hydrogen partial pressures.

INTRODUCTION

Due to the high cost of hydrogen, conserving it in processes which consume it and increasing its formation in processes which produce it are important research objectives. Since many feedstocks processed with hydrogen contain molecules with excess hydrogen, one obvious way to conserve hydrogen is to utilize this excess by dehydrogenation and/or direct hydrogen transfer from such "donor" molecules to the hydrogen deficient or hetero atom-containing molecules which must be hydrogenated. A process using this concept has been used for several years. It is Autofining, developed by British Petroleum in the 1950's (1). This process uses fluorided CoMo on alumina at about 400°C and 2000 kPa (300 psig) H_2 to desulfurize straight-run distillates (to about 0.1% sulfur). Recently Doyle reported (2) on the use of hydrogen donor reactions to effect desulfurization. Model reactions, such as thiophene–tetralin, thiophene–decalin and tetralin–benzothiophene were evaluated using a variety of catalysts (mainly homogeneous). The more salient conclusions were: donor desulfurization of both model compounds and real feeds are very effective and allows reactions to be carried out under fairly mild conditions, the best overall catalyst is cobalt molybdate, and it appears that the mechanism involves dehydrogenation of the donor then reaction of the hydrogen with the sulfur acceptor. Doyle also cited prior art involving hydrogen donor molecules in the desulfurization of various distillate fractions (3), in coal liquefaction processes (4) and in the thermal cracking of resids (5).

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This paper reports information obtained on the cyclohexane–thiophene (donor–acceptor) reaction and the effect on this reaction of adding various potential promoter metals to cobalt molybdate.

EXPERIMENTAL

Apparatus

The catalysts were charged (0.5 g/run) into a quartz U-tube reactor which had an inside diameter of 10 mm. It was held in a large furnace and maintained at 350°C for sulfiding or 425°C for hydrogen transfer experiments. In order to meter low flows accurately, two Brooks electronic flow controllers were placed in the flow lines (one each for H_2 and He). These controllers were quite linear and reproducibly metered flows of 1 cm^3/min H_2 and 9 cm^3/min He at atmospheric pressure. The catalysts were first presulfided at 350°C by passing 1.4 μl/min (0.4 SCCM) thiophene in 20 SCCM H_2 over them for 2 hr. A mixture of 10:1 cyclohexane:thiophene (2.8 μl/min) was then injected into the carrier gas (0.6–4.8 SCCM H_2 + 5.6–9.8 SCCM He, 10.4 SCCM total) through a heated, septum-sealed port using a gastight syringe driven by a Sage pump. The flow of hydrogen was required to prevent rapid deactivation of the catalyst. In order to even out pulses from the pump, a 100 cm^3 holding chamber was located just downstream from the inlet port. A nearly constant conversion level was reached after about 4–5 hr and it was after this time that the rate constant values were determined.

Products were analyzed by gas chromatography. The product gases were sampled from a $\frac{1}{4}$ cm^3 loop directly onto a column of 15% Carbowax 20M plus diisodecyl terephthalate on 60/80 mesh Chromosorb Q ($\frac{1}{8}$ in. × 8 ft SS). The column was operated at 70°C with a carrier flow of 20 cm^3/min He. A good separation of cyclohexane, benzene, thiophene, and C_4 hydrocarbons (total) was obtained in 10 min. A

small shoulder on cyclohexane, probably cyclohexene, was not resolved and was ignored. The sensitivity of the FID detector for each component was assumed to be proportional to the number of carbons in each. This assumption seems to be reasonably accurate from comparisons of total C_4 vs C_6 content with those of starting mixtures. The peak areas were integrated online by a Perkin–Elmer computer system, and the peak area data together with flow rates were converted to rate constants and hydrogen balances using a Wang 700B programmable calculator.

The catalyst used in the deuterium tracer study was 3% Co, 8% Mo, 5.4% Cr on gamma-alumina. It had a surface area of 139 m^2/g. All experiments using a mixture of thiophene, cyclohexane-d_{12} and hydrogen were made at 425°C and 100 kPa (1 atm) with 0.5 g of catalyst, 2.8 μl/min of 10:1 cyclohexane:thiophene injected into 10–20 cm^3/min flow of 1–40% H_2 in He. Products from the reaction were passed through a glass sampling loop cooled in liquid nitrogen. The loop was then placed in front of the gas chromatograph column and the trapped products were flashed onto the column. Each of the peaks was trapped separately in a collection manifold at the exit of the chromatograph. The separate fractions were run through the column several times, until they were free of other components, and then were analyzed on a mass spectrometer. The light hydrocarbon fraction was further separated into various components, mainly 1- and 2-butenes and butane, on a silver nitrate–benzyl cyanide column. The trans-2-butene peak was collected for mass spectrometric analysis, after a preliminary run showed it to have essentially the same deuterium content as the other butenes.

The mole fractions of deuterium (number) isomers were calculated from the mass number peak intensities. After ^{13}C corrections, the peak intensities for each mass were corrected in descending order from

the peaks for the perdeutero and mono-hydro species, which need no correction. The cracking corrections were made by measuring the cracking pattern of the undeuterated compound to determine the percentage loss of one, two, three, or four hydrogens from the parent ion. Then a statistical factor, assuming random cracking (all C–H bonds identical), and an isotope effect correction (approx $(2)^{\frac{1}{2}}$ for each deuterium substitution, thus D_2 loss $2\times$ slower than H_2 loss) for deuterium versus hydrogen loss were used to calculate the percentage losses of H, D, H_2, HD, D_2, H_3, H_2D, HD_2, D_3, H_4, H_3D, H_2D_2, HD_3, or D_4 from each of the parent ions. A Wang computer program was written for each of the compounds analyzed; it corrected all of the peak intensities and calculated the mole fractions of each isomer, the total deuterium content, and the mole fractions for a completely equilibrated system.

Using the measured cyclohexane deuterium content and assuming natural abundance ($x_D = 0.00015$) for the deuterium content of the hydrogen and thiophene, the total flows of H atoms and D atoms were calculated for each condition. A carbon and sulfur balance was calculated assuming no loss to the catalyst, that the flame ionization detector was a perfect carbon counter, and that all sulfur not present in thiophene was present as hydrogen sulfide. From the product composition determined by the gas chromatograph, and deuterium contents measured for thiophene, benzene, cyclohexane, and butenes, a complete hydrogen atom and deuterium atom balance was calculated, with the final assumption that hydrogen gas and hydrogen sulfide had the same deuterium contents. Neither of the latter could be accurately determined independently.

Procedures

After line-out at the standard condition, conversions at other H_2 flow rates were measured. The conversions were converted to pseudo-first order rate constants using $k = [-\ln(1 - x)]F/V$, where x is the fractional conversion, V is the catalyst volume (cm^3) and F is the total flow rate (cm^3/sec). A value of 0.5 cm^3 was taken for all of the catalysts. The constant k, in units of s^{-1}, is only a convenient function which is readily calculated from conversion data. The actual rate expression is undoubtedly quite complex. Since the con-

TABLE 1

Variation of Desulfurization and Dehydrogenation Rate Constants with Hydrogen Pressure[a]

	Desulfurization			Dehydrogenation		
	$k_{HDS}{}^0$ (s^{-1})	k_H (atm^{-1}s^{-1})	r	k_{DH} (s^{-1})	k_H (atm^{-1})	r^*
2Co11Mo	0.013	0.47	0.993	0.033	2.2	0.992
5Co8Mo	0.007	0.34	0.994	0.021	3.0	0.995
9Co8Mo	0.010	0.28	0.994	0.018	3.9	0.995
3Co8Mo5Ti	0.010 (0.062)	0.74 (0.74)	0.995 (0.993)	0.052 (0.047)	1.8 (3.8)	0.996 (0.981)
3Co8Mo5.4Cr	0.048 (0.059)	0.74 (0.58)	0.999 (0.999)	0.082 (0.085)	1.9 (2.2)	0.999 (0.999)
3Co8Mo9.1Zr	0.065	0.75	0.999	0.018	1.3	0.987
3Co8Mo5.3V	(0.048)	(0.43)	(0.998)	(0.035)	(7.1)	(0.996)
3Co8Mo11.6Sn	0.066	0.44	0.999	$\leqslant 0.006$	—	—

[a] Cyclohexane:thiophene = 10:1 at 425°C, 100 kPa; r = correlation coefficient for $k_{HDS} = k_{HDS}{}^0 + k_H(H_2)$; r^* = correlation coefficient for $(k_{DH})^{-1} = (k_{DH}{}^0)^{-1}[1 + K_H(H_2)]$. Values in parentheses are for runs with drier feed and are corrected as in Table 2.

versions, defined simply as

$$x_{DH} = \frac{\text{benzene area}}{\text{(benzene + cyclohexane) areas}},$$

and

$$x_{HDS} = \frac{C_4\text{(butane + butenes) area}}{\text{(}C_4 + \text{thiophene) areas}},$$

were usually small, the first order fit to the data was good for a given ratio of H_2, thiophene, and cyclohexane.

After about two-thirds of the data reported here were obtained, the molecular sieves used to purify hydrogen and helium gas were changed for fresh ones. Immediately, a decrease in dehydrogenation activity and an increase in desulfurization activity was noted. We presume that this is an effect due to the water content of the reactant stream, but have no direct evidence. The cyclohexane and thiophene were not dried carefully. The question of selective inhibition is one which we have not yet investigated further. What we have done is to correct all of the data obtained in the last set of experiments by constant factors. The factors were obtained from data for one of the catalysts run under both sets of conditions. These data are noted in the tables.

Materials

Cyclohexane (99%, Chem Samp Co) and thiophene (99+%, gold label, Aldrich) were used without further purification. A small quantity of heavier component (~0.5%) was noted in the thiophene but not identified. Cyclohexane-d_{12} was obtained from Diaprep, Inc.; mass spectrometric analysis showed its isotopic purity to be 98.0% deuterium.

Catalysts were made by impregnation of aqueous metal salts by the incipient wetness technique. The base catalyst was 3.27% Co–8.73% Mo made by impregnating a commercial gamma-alumina support to the point of incipient wetness with an aqueous solution of cobalt nitrate and ammonium molybdate. This was followed by drying at 250°C for 10 hr and an additional 10 hr at 535°C. To this CoMo/Al_2O_3 were added various metals by impregnation of aqueous solutions of metal salts (usually as nitrates, except titanium which was added as the chloride). After these metals were added the catalysts were dried the same way as cited above for the base. Table 2 gives the compositions of the catalysts in this series. Their surface areas varied from 120 to 150 m²/g.

RESULTS

One of the first variations in the reaction conditions evaluated was an increase in the inlet hydrogen partial pressure. The data were correlated well for several catalysts by the equation:

$$k_{HDS} = k_{HDS}^0 + k_H(H_2).$$

Values for k_{HDS}^0, k_H, and the correlation coefficient are given in Table 1. The limiting value at zero hydrogen pressure, k_{HDS}^0, was taken as that for direct hydrogen transfer to thiophene from cyclohexane. The magnitude of this reaction is small, and not greatly different from one catalyst to another. Most of the difference appears in the term dependent on hydrogen pressure, $k_H(H_2)$.

The dehydrogenation rate constant, on the other hand, was inhibited by hydrogen. A simple Langmuir-type inhibition expression was tested:

$$(k_{DH})^{-1} = (k_{DH}^0)^{-1}(1 + K_H(H_2)).$$

The high correlation coefficients found (Table 1) indicate that it is fairly accurate at low hydrogen pressures. Direct hydrogen transfer should not be inhibited by hydrogen, so that a general form applicable for expressing k_{DH} is

$$k_{DH} = \frac{k_{DH}^0}{1 + K_H(H_2)} + k_{HDS}^0 \left(\frac{\text{thiophene}}{\text{cyclohexane}}\right).$$

TABLE 2

Rate Constants for C_6H_{12} Dehydrogenation, C_4H_4S Hydrogenolysis at 425°C, 100 kPa

Catalyst composition (wt%)	k_H (atm^{-1} s^{-1})	k_{HDS}^0 (s^{-1})	k_{HD}^0 (s^{-1})	k_{DH}^t (s^{-1})
2Co11Mo	0.47	0.013	0.033	0.034
3Co8Mo[a]	0.49	0.030	0.019	0.022
3Co8Mo2Co	0.34	0.007	0.021	0.021
3Co8Mo6Co	0.28	0.010	0.018	0.019
3Co8Mo6.6Co	0.35	0.007	0.020	0.020
3Co8Mo11.6Sn	0.44	0.066	$\leq$0.006	$\leq$0.010
3Co8Mo5.3V[a]	0.43	0.048	0.035	0.040
3Co8Mo9.1Zr	0.75	0.065	0.018	0.024
3Co8Mo6.8Zn	0.80	0.061	0.030	0.036
3Co8Mo5.4Cr	0.74	0.048	0.082	0.086
3Co8Mo5.4Cr[a]	0.58	0.059	0.085	0.090
3Co8Mo5Ti	0.74	(0.010)	0.052	0.053
3Co8Mo5Ti[a]	0.74	0.062	0.047	0.053

[a] Observed k_H, k_{HDS}^0 reduced 40%, k_{DH}^0 increased 50% (see text). Constants defined in Table 3.

With this method of evaluating constants a study was undertaken to see if various transition metals added to a reference cobalt molybdenum–alumina catalyst resulted in significant changes of any of these constants.

In Table 2 data are given for a series of cobalt–molybdenum–alumina catalysts with added metal oxides, i.e., Co, Ti, V, Cr, Zn, Sr, and Sn, for the simultaneous cyclohexane dehydrogenation, thiophene desulfurization, and cyclohexane–thiophene hydrogen transfer reactions at 425°C, 100 kPa. The same data, normalized to a sample surface area of 100 m², are shown in Table 3.

In these tables, the constant k_H refers to thiophene hydrogenolysis by molecular hy-

TABLE 3

Rate Constants[a] for Cyclohexane–Thiophene Reactions over CoMo/Alumina at 425°C, 100 kPa[b]

Catalyst	k_H (atm^{-1} s^{-1})	k_{HDS}^0 (s^{-1})	k_H/k_{HDS}^0 (atm^{-1})	k_{DH}^0 (s^{-1})	k_{DH}^t (s^{-1})	k_d/k_t
3Co8Mo[c]	0.65	0.040	16	0.025	0.029	7
3Co8Mo5Ti[c]	1.00	0.084	12	0.063	0.072	8
3Co8Mo6.8Zn	1.21	0.092	13	0.045	0.054	5
3Co8Mo9.1Zr	1.01	0.088	11	0.024	0.032	3
3Co8Mo5.4Cr	1.03	0.067	15	0.115	0.120	19
3Co8Mo5.4Cr[c]	(0.81)[d]	(0.082)[d]	10[d]	(0.118)[d]	(0.125)[d]	16
3Co8Mo5.3V[c]	0.75	0.084	9	0.061	0.070	8
3Co8Mo11.7Sn	0.60	0.090	7	0.008	0.014	1
3Co8Mo6Co	0.40	0.014	29	0.026	0.027	2
3Co8Mo6.6Co	0.50	0.010	50	0.030	0.032	3

[a] $k_{HDS} = k_{HDS}^0 + k_H(H_2)$; $k_{DH} = k_{DH}^0[1 + K_H(H_2)]^{-1}$; $k_{DH}^t = k_{DH} + k_{HDS}^0$ (thiophene)/(cyclohexane); $(k_d/k_t) = k_{DH}$(cyclohexane)/k_{HDS}^0(thiophene).

[b] Corrected to total area = 100 m²/g.

[c] Corrected as in Table 2.

[d] After 6 days (deuterium tracer experiment).
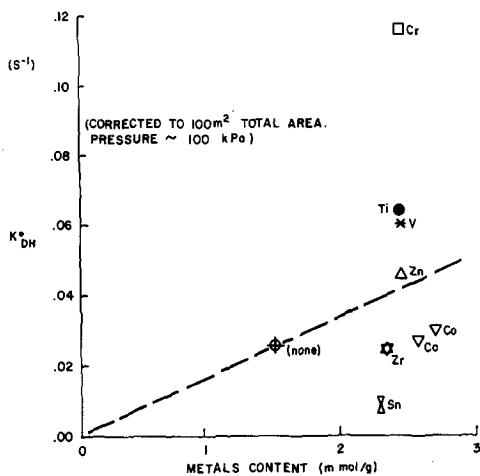
FIG. 1. Effect of added metals on dehydrogenation activity of 3% Co 8% Mo/Al₂O₃ catalysts at 425°C.

drogen, $k_{HDS}{}^0$ to the thiophene hydrogenolysis by cyclohexane, i.e., k_{HDS} at zero H_2 pressure, $k_{DH}{}^0$ to the dehydrogenation of cyclohexane to yield molecular hydrogen, $k_{DH}{}^t$ to the total rate of cyclohexane conversion, and k_d/k_t to the relative cyclohexane dehydrogenation and hydrogen transfer rates. The ratio of hydrogen transfer from molecular hydrogen to that from
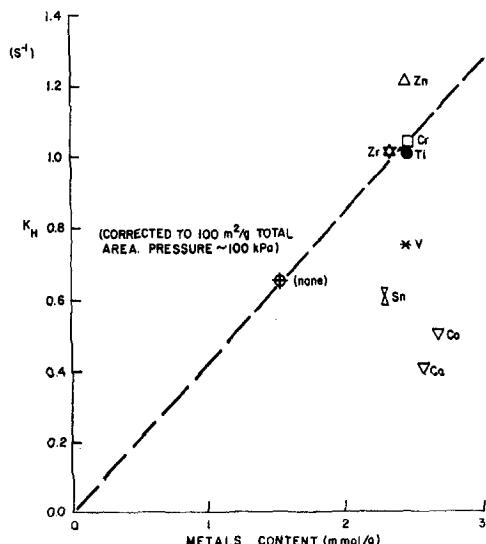

FIG. 2. Effect of added metal (to 3% Co, 8% Mo/Al₂O₃) on HDS activity at 425°C.
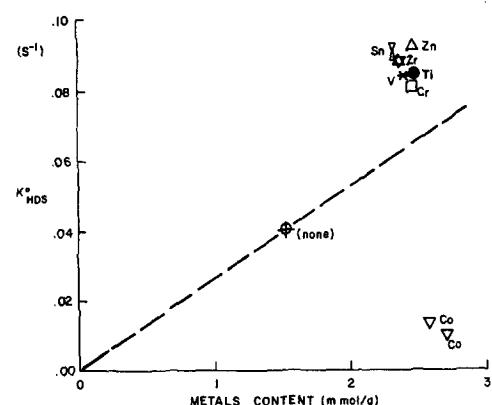
FIG. 3. Effect of added metals on direct hydrogen transfer. Cyclohexane–thiophene over 3% Co 8% Mo/Al₂O₃ catalysts at 425°C.

cyclohexane is about unity at a hydrogen partial pressure of 10 kPa (0.1 atm). Since the cyclohexane transfer appeared to be zero order for higher pressures, this ratio increases with hydrogen pressure until it reaches a limiting value when the transfer from molecular hydrogen is also zero order, i.e., when the surface is nearly saturated with H_2.

The ratios of cyclohexane dehydrogenation to molecular hydrogen relative to hydrogen transfer to thiophene (last column in Table 3) are mostly greater than unity, indicating that indirect hydrogen transfer is probably the predominant pathway for thiophene hydrogenolysis by cyclohexane. The ratio decreases as the hydrogen partial pressure increases and dehydrogenation is inhibited, but then most of the hydrogenolysis is by the added hydrogen.

Figures 1, 2 and 3 show the variation of $k_{DH}{}^0$, k_H and $k_{HDS}{}^0$ with total metal content of various promoted cobalt molybdenum alumina catalysts. The data in these figures permit a ranking of the effectiveness of the added metals for influencing these rate constants. The straight line in these figures is drawn from the origin through the point representing the value obtained from a 3% Co–8% Mo alumina catalyst. Extension of the line beyond that point indicates where

TABLE 4

Deuterium Contents of Products from $(C_4H_4S + C_6D_{12} + H_2)$ over $CoCrMo/Al_2O_3$ at 425°C

$P(H_2)$ (kPa):	11	3	1	3
t^a (s):	2.7	1.5	0.8	2.6
			$x_D{}^b$	
Cyclohexane (0.980 initially)	0.9775	0.9783	0.9777	0.9773
Thiophene	0.1934	0.1921	0.1868	0.2930
Benzene	0.2512	0.3807	0.3584	0.3709
Butenes	0.1786	0.1836	0.1526	0.2591
$H_2 + H_2S$ (by difference)	(0.18)	(0.20)	(0.23)	(0.42)
Total	0.70	0.80	0.87	0.87
Total excluding cyclohexane	0.19	0.22	0.23	0.37

^{a} t = superficial contact time = catalyst vol (cm³)/flow rate (cm³/s).

^{b} x_D = atom fraction deuterium.

rate constants should occur if the total metal content were increased at the same cobalt–molybdenum ratio.

In Table 4, the deuterium contents of the products are shown for the reaction of thiophene, hydrogen, and cyclohexane-d_{12} over $CoCrMo/Al_2O_3$ at 425°C and at several flow rates and hydrogen pressures. The change in the composit on of the cyclohexane reactant was quite small, but measurable. The product gas contained deuterium from the dehydrogenation of the

TABLE 5

Observed vs Equilibrium Deuterium Atom Distributions^a

	Cyclohexane			Thiophene			
	Obsd	Eq	Diff	Obsd	Eq	Diff	
d_{12}	0.7447	0.7431	+0.0016	0.4252	0.4231	+0.0019	d_0
d_{11}	0.2206	0.2233	−0.0027	0.4027	0.4059	−0.0032	d_1
d_{10}	0.0312	0.0307	+0.0005	0.1465	0.1460	+0.0005	d_2
d_9	0.0033	0.0025	+0.0008	0.0241	0.0233	+0.0008	d_3
d_8	0.0000	0.0001	−0.0001	0.0012	0.0013	−0.0001	d_4
	($x_D = 0.9775$)			($x_D = 0.1934$)			
	Benzene			Butenes			
d_6	0.0054	0.0002	+0.0052	0.2129	0.2070	+0.0059	d_0
d_5	0.0155	0.0044	+0.0111	0.3535	0.3603	−0.0068	d_1
d_4	0.0447	0.0334	+0.0113	0.2673	0.2744	−0.0071	d_2
d_3	0.1222	0.1331	−0.0109	0.1232	0.1194	+0.0038	d_3
d_2	0.2559	0.2975	−0.0416	0.0429	0.0324	+0.0105	d_4
d_1	0.3390	0.3547	−0.0157	0.0000	0.0056	−0.0056	d_5
d_0	0.2167	0.1762	+0.0407	0.0000	0.0006	−0.0006	d_6
	($x_D = 0.2512$)			($x_D = 0.1786$)			

^{a} $C_4H_4S + C_6D_{12}$ over $CoCrMo/Al_2O_3$ at 425°C. [$P(H_2) = 11$ kPa, $C_4H_4S/C_6D_{12}/H_2 = 1:10:20$ $x_D = 0.7$]. Obsd = observed mole fractions; $x_D = \sum_{i=0}^{j} i(x_{di})/j$ = deuterium atom fraction; Eq = mole fractions at equilibrium (random); Diff = (Obsd − Eq) values.
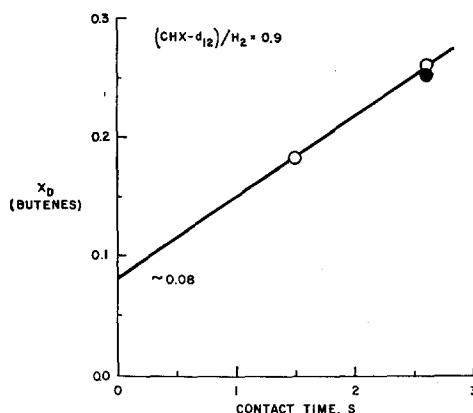
FIG. 4. Butene deuterium content vs contact time. Thiophene and cyclohexane-d_{12} at 425°C over CoCrMo/Al$_2$O$_3$.

cyclohexane. However, this was not present entirely as D_2; a fair amount of HD indicated that mixing occurred. The thiophene recovered from the products was extensively exchanged. It contained almost as much deuterium as the hydrogen, indicating that it was nearly equilibrated. The product benzene and butenes were extensively exchanged.

The unconverted cyclohexane had a slightly lower deuterium content than the starting material. Comparing the observed deuterium distribution in the cyclohexane with that calculated for an equilibrium (random) distribution, the mole fractions found for the starting material were within ±0.0005 for each species (d_8–d_{12}). But the recovered cyclohexane was deficient in the d_{11} isomer, while the recovered thiophene was deficient in the d_1 isomer by almost the same amount (Table 5). The differences

between observed and equilibrium distributions indicate that exchange is not completely stepwise (two H or D atoms may be exchanged at a time) or direct (dehydrogenation to cyclohexane and hydrogenation to dihydrothiophene may occur reversibly).

In the absence of exchange, the relative rates of thiophene hydrogenolysis by hydrogen and cyclohexane might be estimated from the deuterium contents of the butene, butane, and hydrogen sulfide products. With exchange, only a very crude estimate can be made by extrapolating the deuterium content to zero contact time as shown in Fig. 4. At roughly equal cyclohexane-d_{12} and H$_2$ partial pressures of 3 kPa, the limiting deuterium content in the butenes is 0.64D/molecule.

If it is assumed that the rate determining steps involve addition of one hydrogen molecule and that subsequent hydrogenation to stable products by H$_2$ is rapid, then one would expect 2D/molecule in the butene product from cyclohexane-d_{12} hydrogen transfer to thiophene. Correcting for an isotope effect of two (Table 6) for deuterium vs hydrogen, the transfer rates are the same for cyclohexane and hydrogen at 3 kPa. This is lower than the 10 kPa hydrogen pressure for equal rates which is estimated from the kinetic data, and indicates a lower direct transfer rate for cyclohexane to thiophene. In view of the many assumptions and the paucity of data the agreement is not bad, but it is possible that only part of the hydrogenolysis at zero hydrogen inlet pressure is actually direct.

TABLE 6

Rate Constants[a] for Thiophene HDS and Cyclohexane Dehydrogenation on CoCrMo/Al$_2$O$_3$

Cyclohexane	k_{HDS}^0	$k_H(H_2)$	k_{DH}^0	$(K_H H_2)$	$k_H(H_2)/k_{HDS}^0$
C$_6$H$_{12}$	0.10	0.95	0.057	2.1	10
C$_6$D$_{12}$	0.11	1.08	0.026	1.3	10
(Ratio)	(0.9)	(0.9)	(2.2)	(1.6)	1.0

[a] Rate constants (s^{-1}) at 425°C, (H$_2$) = 1 atm. Constants (uncorrected) as defined in Table 3.

In Table 6, a comparison of cyclohexane and cyclohexane-d_{12} dehydrogenation and hydrogen transfer to thiophene is shown. There is a normal deuterium isotope effect of 2.2 on dehydrogenation at 425°C, while the effect on hydrogen transfer appears slightly inverse. That may be due to a coupling between desulfurization and dehydrogenation, since the ratio of hydrogen transfer to hydrogenolysis by H_2 is constant. A coupling which gives this effect is inhibition of thiophene hydrogenolysis by the benzene product from cyclohexane dehydrogenation.

Some experiments with a 1:1 (wt%) mixture of cyclohexane:thiophene were made for comparison with the 10:1 mixture used for most of the experiments reported here. The intercept and slope for the variation of desulfurization rate constant with hydrogen pressure were both smaller with the higher thiophene partial pressure, as expected for inhibition by thiophene (and product H_2S). The variation in cyclohexane dehydrogenation rate constant with hydrogen pressure was almost the same for the two mixtures, but the rate constants were much higher for the higher thiophene partial pressure (and lower cyclohexane partial pressure). The absolute rate of benzene formation was unchanged.

DISCUSSION

The model donor–acceptor reaction cyclohexane–thiophene was chosen because it proceeds with more difficulty than most other such systems which have been studied, such as tetralin–thiophene. It was hoped that this model reaction would be more sensitive to catalyst change. The closest analogous model system to cyclohexane–thiophene is decalin–thiophene, which has been reported by Doyle (2). For that reaction $Mo(CO)_6$ was used as the catalyst and no desulfurization occurred, whereas, using tetralin as the donor resulted in 55% desulfurization. The reactions were conducted at 300°C for 16 hr using an auto-

clave. In that work it was pointed out that the donor process becomes more favorable at higher temperatures, whereas in direct hydrodesulfurization the reaction becomes less favored. Thus, it was realized that rather severe conditions would be required in the cyclohexane–thiophene reaction. It was also found early in the experimental work that a low inlet partial pressure of hydrogen was needed to prevent catalysts from rapidly becoming deactivated with coke at the high temperature used. The technique used to estimate the contribution due to direct hydrogen transfer from cyclohexane to thiophene was to extrapolate k_{HDS} to zero hydrogen pressure. According to the data in Table 1, this contribution is small, which is in agreement with Doyle's conclusion (2). He suggested that the mechanism of donor–acceptor reactions does not involve a concerned transfer of hydrogen from donor to acceptor, but instead involves "freed" hydrogen via donor dehydrogenation which reacts with the acceptor to effect desulfurization.

The data presented in this paper show that the direct hydrogen transfer reaction can be enhanced by adding various metals (1.0 mmol/g) to the reference 3% Co–8% Mo–alumina catalyst. As shown by the data in Fig. 3, all of the metals evaluated, with the exception of additional cobalt, promoted direct hydrogen transfer. This was a significant increase in that the k_{HDS}^0 value more than doubled, whereas with cobalt, there was a fourfold decrease. This decrease with added cobalt was not unexpected based on a similar finding by others (6). It has been proposed (7) that the tendency to occupy tetrahedral positions by cobalt and other ions is an important factor in making a metal cation a promoter. Once the required amount of cobalt is added to give this promotion additional cobalt could go on as cobalt oxide, covering the active surface and deactivating the catalyst.

The largest promotional effect was noted in dehydrogenation activity where chromium addition resulted in approximately a sixfold increase in k_{DH} as shown by the data in Fig. 1. The data in Fig. 2 show that zinc provided the greatest enhancement of thiophene hydrogenolysis closely followed by chromium, titanium and zirconium.

The following is a summary of these results:

Direct H transfer (k_{HDS}):
   (Cr, V, Ti, Zr, Zn, Sn) > none > Co
Cyclohexane dehydrogenation (k_{DH}^0):
   Cr > (Ti, V, Zn) > (Zr, Co, none) > Sn
Thiophene hydrogenolysis by H_2 (k_H):
   Zn > (Cr, Ti, Zr) > (V, Sn, none) > Co
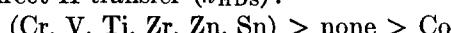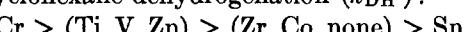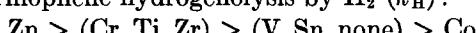
Experiments conducted with deuterated cyclohexane and thiophene using a chromium promoted, cobalt molybdenum–alumina catalyst were done in an attempt to obtain more information about the direct hydrogen transfer reaction. However, the deuterium exchange was very fast and prevented any precise estimates of the relative amounts of direct hydrogen transfer from cyclohexane and hydrogen to thiophene. A rough estimate of the relative rates for deuterium transfer from cyclohexane to thiophene and hydrogen transfer from H_2 to thiophene was made by extrapolating the butene deuterium content to zero contact time as shown in Fig. 4. The rate of transfer from H_2 was about the same as from cyclohexane at 3 kPa, in agreement with the relative values of k_H (H_2) and k_{HDS}^0.

The data in Table 5 show that there is a deficiency in C_6HD_{11}, compared to a random distribution, and a striking similarity was observed for the thiophene distribution when arranged in reverse order, i.e., it is deficient by about the same amount in the d_1 species. This is evidence that the transfers occur not only one at a time but also in pairs. For cyclohexane, it suggests that part of the exchange may take place via dehydrogenation to cyclohexene, or at least that a disadsorbed species is formed which

has lost two hydrogens. For thiophene, a partially hydrogenated species may be formed, such as
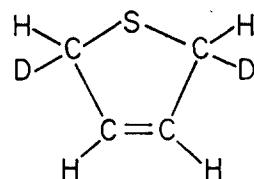
The product deuterium distributions were nearly equilibrated, especially the C_4's. This can only occur if the products exchange much faster than they are formed. Otherwise, products formed at the front of the bed will have distributions different from those at the end of the bed. The benzene product shows the greatest deviations from an equilibrium distribution. Although it exchanges rapidly, the average deuterium content is so far removed from that of the benzene formed initially that equilibrium is not reached.

The exchange rates for the compounds involved were estimated by assuming reversible first order reactions and an accessible pool of H and D atoms—the entire pool for cyclohexane, which exchanges slowest, and the H and D atoms excluding cyclohexane for the other components. The exchange constant values were 0.006, 0.9, 1.2, and 1.0 s^{-1} for cyclohexane, benzene, thiophene and butenes, respectively. The exchange rates for the unsaturated molecules were all about the same and about 200 times faster than the exchange rate for cyclohexane. Cyclohexane exchange requires a carbon–hydrogen bond breaking, which is less favorable; the factor of 200 at 425°C corresponds to an extra 30 kJ/mol (7.5 kcal/mol) in the energy barrier for reaction. The estimated contact time for exchange of 1 deuterium atom/molecule was less than 1 s for the unsaturates, and about 1 min for cyclohexane.

In conclusion from the research reported in this paper, it has been found that the direct hydrogen transfer from cyclohexane

to thiophene over CoMo/alumina is slow compared to hydrogenolysis by H_2 at moderate pressures. Under conditions such that cyclohexane dehydrogenation is fast, cyclohexane hydrogenolysis of thiophene will occur indirectly via dehydrogenation and subsequent hydrogenation of thiophene. This conclusion supports Doyle's proposed mechanism for such reactions. The direct hydrogen transfer reaction can be catalyzed by adding various transition metal promoters to the reference cobalt molybdenum–alumina catalyst. The addition of more cobalt results in a sharp decline in the rate of this direct transfer reaction, which is in agreement with reports by DeBeer et al. (6) and Schuit and Gates (7). Relative transfer rates from cyclohexane and hydrogen estimated by deuterium tracer experiments are in accord with those estimated from kinetic data for variation in hydrogen partial pressure.

ACKNOWLEDGMENTS

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