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Exchange and Desulfurization of Thiophene over Synthetic and Commercial Co/Mo Catalyst Systems

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Thiophene was desulfurized and exchanged with deuterium over laboratory-synthesized Co/γ-Al_2O_3, Mo/γ-Al_2O_3, and Co–Mo/γ-Al_2O_3 catalysts and over commercial Co–Mo/γ-Al_2O_3 catalysts. Magnetic properties of the Co/γ-Al_2O_3 catalysts were measured, desulfurization activities of all catalysts were measured, and the deuterium exchange patterns of the desorbed thiophenes were measured. For Co/γ-Al_2O_3, no clear correlation was found between magnetic properties and desulfurization activity, but a crude correlation was found between percent d_2 and desulfurization. For molybdenum-containing catalysts, desulfurization activity was high and accompanied by random exchange. Also d_2 was high. For the commercial catalysts high d_{av} generally correlated with high desulfurization activity. The results can be rationalized on the basis of a modified Komarewsky mechanism.

INTRODUCTION

Hydrogen–deuterium exchange has been used by several investigators for mechanistic investigation. Kieren and Kemball (*1*) first determined that molybdenum disulfide catalyzes the exchange of thiophene preferentially in the α-positions. Later we found that cobalt–molybdenum on γ-alumina catalyzes three kinds of exchange in thiophene (*2*). Two of them are random exchange and multiple exchange caused by alumina, and the third is α-exchange caused by molybdenum. We correlated multiple exchange with hydrogenation/dehydrogenation activity and correlated α-exchange with desulfurization. These correlations supported Desikan and Amberg's (*3*) theory of two different catalytic sites on cobalt–molybdenum desulfurization catalysts. They also supported the Komarewsky mechanism (*4–9*), which involves C–S bond breakage as the first step. However, they did not support the Kolboe mechanism (*10*), which involves an intramolecular hydrogen shift and was supported by Heineman and coworkers (*11*). Recently we extended our thiophene investigations to cobalt-on-γ-alumina, molybdenum-on-γ-alumina, and cobalt–molybdenum-on-γ-alumina catalysts. During the course of these investigations we noticed unique exchange patterns for thiophene desorbing from different cobalt–molybdenum-on-γ-alumina catalyst systems. Because unique exchange patterns might be characteristic of catalyst activity, we examined exchange patterns from a variety of catalysts. In this paper we report the results of these experiments.

EXPERIMENTAL

Catalyst Preparation

Four series of catalysts, Co/γ-Al_2O_3, Mo/γ-Al_2O_3, Mo–Co/γ-Al_2O_3, and Co–Mo/γ-Al_2O_3, were prepared for this work. An alumina support (E. 5015) supplied by Pro Catalyse, France, was used for all preparations. Physical analysis of this alumina revealed a surface area of 216 m^2/g and a total pore volume of 0.473 ml/g.

The Co/γ-Al_2O_3 series (Table 1, Catalyst Nos. 1–10). The alumina support was impregnated with cobalt, using solutions of cobalt(II) acetate (analytical grade, Fluka AG Chemische Fabrik, Switzerland) and cobalt(II) nitrate (analytical grade, E. Merck Ag, W. Germany). The method was

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TABLE 1

The Catalyst Samples Prepared using 25 g of the Alumina Support

Catalyst No.	Source of Co(II)	Amount taken (g/50 ml H_2O)	% Co adsorbed	% Mo adsorbed
(a) The Co/Al_2O_3 series				
1	nitrate	0.50	0.42	0
2	nitrate	1.0	0.75	0
3	nitrate	2.15	1.22	0
4	nitrate	4.31	1.79	0
5	nitrate	5.99	2.30	0
6	nitrate	7.20	2.80	0
7	acetate	1.00	0.86	0
8	acetate	2.52	1.76	0
9	acetate	3.99	2.31	0
10	acetate	4.49	3.95	0
(b) The Mo/Al_2O_3 series				
11	acetate	2.61	0	7.80
12	acetate	4.21	0	9.0
13	acetate	7.36	0	12.93
14	acetate	9.20	0	14.33
(c) The $Mo–Co/Al_2O_3$ series				
15	nitrate	5.12	1.29	7.80
16	nitrate	5.12	1.29	9.0
17	nitrate	5.12	1.28	12.93
18	nitrate	5.12	1.29	14.33
(d) The $Co–Mo/Al_2O_3$ series				
19	nitrate	1.0 nitrate 5.5 molybdate	0.75	12.1
20	acetate	1.0 acetate 5.5 molybdate	0.86	12.74
E_1	Cobalt Molybdate		0.20	0.74

similar to that employed by Tomlinson *et al.* (*12*). In each impregnation the support (25 g) first was suspended in the impregnating solution (50 ml) by stirring for 92 hr. Then it was filtered under vacuum and dried for 2 hr under flowing air at 110°C. Finally the samples were calcined under a flow of dry air (30 liters/hr) at 500°C for 3 hr. The concentrations of solutions and the percentages of cobalt absorbed by the support were determined by atomic absorption in each case and are shown in Table 1.

The Mo/γ-Al_2O_3 series (Table 1, Catalyst Nos. 11–14). Ammonium heptamolybdate (analytical grade, E. Merck AG., W. Germany) was used for the preparations of this series. The method of preparation was the same as in the Co/γ-Al_2O_3 series and analyses of the individual samples are presented in Table 1.

The Mo–Co/γ-Al_2O_3 series (Table 1, Catalyst Nos. 15–18). To prepare this series, the Mo/γ-Al_2O_3 catalysts were impregnated with cobalt nitrate (see Table 1).

The Co–Mo/γ-Al_2O_3 series (Table 1, Catalyst Nos. 19–20). This series was prepared by impregnating two of the Co/γ-Al_2O_3 samples with ammonium heptamolybdate. A special experimental sample, designated E_1, was prepared by impregnating the alumina support with a solution of cobalt molybdate (analytical grade, K & K Laboratories, Inc., Calif.). Due to the very low solubility of cobalt molybdate in water, very little molybdenum was deposited on the support even after five successive impregnations.

Nine commercial catalysts were used in this work. They are listed in Table 2.

Physical Measurements

Magnetic measurements. The magnetic susceptibilities of catalyst samples 1–10 (Table 1) were determined at room temperature by the Faraday method. The determinations were made on a Newport Instruments Variable Temperature Gouy Balance System calibrated with cobalt mercury thiocyanate (*13*). From their magnetic susceptibilities the magnetic moments of the cobalt ions were calculated. Correcting for the diamagnetic contributions of alumina and Co^{2+} to the moments are as follows:

	Diamagnetic susceptibility (10^6erg $Oe^{-2}mole^{-1}$)	Ref.
Co^{2+}	−12	(*15*)
Al_2O_3	−0.3	(*18*)

TABLE 2

The Commercial Catalysts

Catalyst	Suggested Application	% Co	% Mo
C_1	HDS, HDN, & Hydrogenation of lights and mid-distillates	3.8	16.0
C_2	HDS of light & heavy petroleum feeds	2.2	18.0
C_3	HDS of light & mid-distillates	3.1	15.0
C_4	HDS of light & mid-distillates	2.8	12.0
C_5	HDS of light & heavy petroleum feeds	4.0	13.0
C_6	HDS of light & mid-distillates	2.4	9.8
C_7	Desulfurization of gaseous feeds	1.5	11.3
C_8	Desulfurization of light to mid-distillates	2.2	11.5
C_9	HDS of light & heavy petroleum feeds (with drawn from market)	3.0	14.3

Surface area and pore size distribution measurements. Surface areas and pore size distribution were measured on the commercial catalysts and the alumina support prior to impregnation. These measurements were obtained with a Carlo Erba Sorptomatic apparatus at liquid-nitrogen temperature in an atmosphere of pure nitrogen. In addition the cumulative surface area and the pore volume of pores having radii less than 150 Å were calculated by the method of Crauston and Inkley (*15*). The average pore radius was calculated in the range of 0–150 Å. All of these data are shown in Table 5.

Pulse Experiments

The experimental apparatus has been described previously (*4*). In a typical experiment 0.2 g of catalyst (crushed and sieved to 60–80 mesh) was packed in the reactor between two glass-wool plugs and heated to 400°C under flowing hydrogen (97% H_2, 2.5% methane, and 0.5% C_2–C_4 hydrocarbons from the Tehran Refinery) overnight. Then 500 μl of thiophene (99% pure, Fluka AG Chemische Fabrik, Switzerland) was injected through the reactor to sulfide the catalyst. Next the system was adjusted to reaction conditions, the carrier/reactant gas was changed to deuterium (99.7% pure, Matheson Gas Products), and samples of thiophene were injected. The desorbed thiophene was then trapped for mass spectral analysis by condensation in liquid-air-cooled glass traps.

Activity Tests

Activity tests were carried out in a pressurized continuous-flow reactor system described previously (*16*). Catalysts were sulfided with a 25% solution of carbon disulfide in *n*-heptane as before (*16*). A 12% solution of thiopene in *n*-heptane was employed for the HDS reactions, which were carried out under the following conditions: LHSV, 4.5 liters/liter/hr; GHSV, 400 liters/liter; pressure, 30 atm; temperature, 300°C. Each catalyst was run for a week and samples were taken every day to assure the maintenance of steady-state conditions. Thiophene desulfurization activity (average value of thiophene converted to hydrocarbon) for each catalyst was determined from three consecutive samples taken during steady-state conditions.

Analyses

Gas chromatography. Conversions of thiophene to hydrocarbons in the activity tests were determined by gas chromatography with a Varian Model 920 gas chromatograph. The gas chromatography column was 10 ft × $\frac{1}{4}$ in. and contained 15% iso-octadecene on 60- to 80-mesh Chromosorb-P. It was used at 70°C with a hydrogen flow rate of 60 ml/min at 40 psig.

Mass spectrometry. Deuterium distributions of recovered substrates in the pulse experiments were determined by mass spectrometry. A Varian Model MAT CH-5 single-focusing 90° magnetic sector mass spectrometer was used. All spectra were run at constant ion pressure and an ionizing voltage of 11–70 eV. Parent peak regions were scanned at low electron voltage (determined by running standard thiophene) to eliminate any hydrocarbon fragments. The peak heights of each deuterated compound were accurately measured and deuterium distributions calculated according to previously reported procedures (*2*).

RESULTS

1. Magnetic Measurements

Results of the magnetic measurements on the Co/γ-Al_2O_3 catalysts are shown in Table 3. Initially the magnetic moments rise as the amounts of cobalt increase. This rise is attributed to the increasing proportion of octahedrally coordinated cobalt relative to the tetrahedrally coordinated form (*17*). Following the initial rise at about 1% cobalt (catalyst No. 3 in Table 3) the magnetic moments start to decrease. This decrease is due to the presence of diamagnetic Co^{3+} ions formed by aerial oxidation of Co^{2+} ions during calcination of the catalysts. Finally a second maximum occurs in the magnetic moments at about 2.3% cobalt (catalyst No. 5 in Table 3). This arises for samples prepared from both cobalt(II) nitrate and acetate (see catalyst No. 9 in Table 3).

TABLE 3

Magnetic Properties of the Co/Al_2O_3 Catalysts

Catalyst No.	Co (wt%)	Molar susceptibility (10^6g/emu)	Magnetic moment (μ_B)
Prepared from cobalt nitrate			
1	0.42	0.19	4.03
2	0.75	0.64	4.20
3	1.22	1.69	4.77
4	1.79	2.16	4.39
5	2.30	3.08	4.54
6	2.8	2.72	3.89
Prepared from cobalt acetate			
7	0.86	1.09	4.77
8	1.76	1.99	4.27
9	2.31	3.19	4.60
10	3.95	4.56	4.15

Impregnation with cobalt(II) acetate gives catalysts with slightly different magnetic properties from those prepared from cobalt(II) nitrate. At the lower cobalt concentrations the catalysts prepared from cobalt(II) acetate have higher magnetic moments (see catalysts Nos. 2 and 7 in Table 3). This indicates a higher proportion of octahedral cobalt(II). At high cobalt concentrations (about 2.5%) the samples prepared from cobalt(II) acetate also have higher magnetic moments (compare catalysts Nos. 9 and 10 with catalysts Nos. 5 and 6) indicating less oxidation to cobalt(III).

2. Pulse Experiments

Results from the deuterium exchange of thiophene over catalysts 1–20 (Table 1) and over the commercial catalysts (Table 2) are shown in Table 4. In addition thiophene exchanges were also run over the alumina support, the alumina support impregnated with small amounts of cobalt molybdate (before and after calcination), cobalt molybdate, and cobalt aluminate.

Very little exchange occurs over the lat-

TABLE 4

Results of Deuterium Exchange Experiments at 300°C on the Commercial[a] and Prepared[b] Co/Al_2O_3, Mo/Al_2O_3, $Mo\text{–}Co/Al_2O_3$, and $Co\text{–}Mo/Al_2O_3$ Catalysts

(0.2 g catalysts, 60 cm^3/min D_2 at 60 psi, 5 μl sample size)

Catalyst	1		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
d_0[c]	31.1[d]	(23.3)[e]	5.1	10.6	23.1	8.7	9.5	5.0	5.5	31.7	9.8	13.6	6.4	7.5	5.9	4.4	1.4	1.3	2.7	11.4	5.0
d_1	31.9	(41.0)	15.6	19.7	30.3	35.4	15.4	9.4	14.7	34.7	24.6	16.1	11.8	23.6	12.7	18.2	12.2	6.4	12.2	24.0	19.3
d_2	24.3	(27.0)	27.4	31.1	31.3	37.1	33.1	22.4	29.8	27.5	45.5	39.6	36.9	42.9	40.5	50.2	45.9	31.2	37.1	36.6	39.2
d_3	10.0	(7.9)	26.7	23.9	11.8	18.8	24.4	31.8	29.6	5.4	16.4	21.1	26.3	21.0	28.9	20.2	29.0	36.8	30.7	20.4	27.9
d_4	2.8	(0.9)	25.2	14.7	3.6	0.0	17.7	31.4	20.5	0.7	3.7	9.6	18.6	5.0	12.0	7.0	11.6	24.3	17.4	7.6	8.7
d_{av}[f]	1.22		2.51	2.12	1.42	1.66	2.25	2.72	2.45	1.09	1.80	1.97	2.39	1.93	2.28	2.07	2.37	2.76	2.48	1.90	2.16

Catalyst	Cobalt molybdate	Cobalt aluminate	Alu-mina support	$CoMoO_4/Al_2O_3$[g] (uncalcined)	$CoMoO_4/Al_2O_3$[g] (calcined
d_0[c]	77.7	87.0	18.4	30.2	30.3
d_1	17.3	8.3	34.4	28.4	26.8
d_2	5.8	5.0	31.3	24.8	22.3
d_3	0.8	0.2	12.6	11.9	13.6
d_4	0.0	0.0	3.2	4.8	7.1
d_{av}	0.27	0.18	1.48	1.33	1.40

Catalyst	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
d_0	3.6	12.4	1.8	15.5	6.5	2.2	33.5	22.4	23.0
d_1	14.4	22.3	7.3	12.9	7.3	7.0	37.6	37.9	27.4
d_2	51.1	36.6	46.4	36.0	35.0	26.2	27.8	35.2	34.2
d_3	24.4	21.1	30.7	21.2	30.7	34.6	1.4	4.2	12.3
d_4	6.6	7.7	13.9	14.4	20.6	29.9	0.2	0.3	3.1
d_{av}	2.16	1.90	2.47	2.06	2.52	2.83	0.96	1.22	1.45

[a] See Table 2.

[b] See Table 1.

[c] Deuterated thiophene; e.g., d_0 represents thiophene containing no deuterium, d_1 containing one deuterium, d_2 two, etc.

[d] Percent deuterated thiophene species after deconvolution of mass spectrum; see Ref. (*2*).

[e] Random distribution calculated from binomial expansion of $(H + D)^4$; such random distributions for other results may be calculated by computing vaules for H and D from d_{av} as follows: H is (4 minus d_{av}) divided by 4, D is 1 minus H.

[f] Average number of deuteriums per thiophene molecule.

[g] Catalyst E_1; see Table 1.

ter two catalysts (Table 4), and the molybdate compound exhibits somewhat greater and more random exchange than the aluminate. In contrast to previously reported results of exchange of thiophene over a different alumina catalyst (*2*), deuterated species containing more than four deuterium were not detected over our alumina support (Table 4). Even so, the exchange pattern supports our previous suggestion (*2*) of exchange sites existing on γ-alumina catalyst.

3. Pore Diffusion

We considered the possibility that pore diffusion might modify the results of the exchange experiments, and, therefore, we carried out surface area and pore size measurements on some of the commercial catalysts (Table 5). If pore diffusion were a problem, we would expect thiophene to remain in small pores longer than in larger pores and, as a result, expect multiple exchange to be greater in smaller pores. However, catalysts C_1 and C_4 in Table 5, which have similar average pore radii, exhibit different exchange patterns (Table 4), while catalysts C_5 and C_6, with widely different average pore radii, exhibit very similar exchange patterns. In fact C_5, with the smaller average pore radius, exhibits less rather than more multiple exchange. We suggest, therefore, that pore diffusion modification of these exchange patterns is not as important as other factors.

TABLE 5

Results of Surface and Pore Measurements Carried Out on Some Commercial Catalysts

Catalyst[a]	BET surface area (m^2/g)	Total pore volume (ml/g)	Average pore radius (Å)
C_1	318	0.64	35
C_4	270	0.50	31
C_5	215	0.48	21
C_6	165	0.65	75

[a] See Table 2.

4. Activity Tests

The results of the activity tests carried out for catalysts 1–20 (Table 1) and the commercial catalysts (Table 2) are shown in Table 6. Catalyst C_5 showed considerable cracking activity in addition to desulfurization. However, it is possible to diminish this cracking activity while still maintaining the HDS activity at the 100% level by diluting the catalyst bed with glass beads (*18*). Each activity experiment was run for about 7 to 10 days. During this period the activity of all catalysts reached an equilibrium value. However, the activity of the laboratory-prepared catalysts started to decrease from their equilibrium values toward the end of each run, but we did not attempt to determine the life of each individual catalyst. On the other hand the commercial catalysts were more stable even though some of them had lower equilibrium activities than the synthetic catalysts.

These activity tests show first that the activity order for the prepared catalysts was Mo–Co/γAl_2O_3 ≅ Co–Mo/γ-Al_2O_3 > Mo/γ-Al_2O_3 > Co/γ-Al_2O_3. Second, this order confirms the general belief that cobalt is not the desulfurization species in this type of catalyst (*2, 3, 19*). And, finally, in agreement with previous observations (*2*) the unimpregnated alumina support (Table 6) exhibits negligible activity.

DISCUSSION

1. The Alumina Support Impregnated with Cobalt Molybdate

The exchange pattern of thiophene over the alumina support is nearly random (Table 4). Upon impregnating the support with small amounts of cobalt molybdate the random character of the exchange diminishes ($CoMoO_4$/γ-Al_2O_3, uncalcined, Table 4) and the desulfurization activity increases (Table 6). Calcination of this catalyst produces very small effects on the exchange patterns but almost doubles the activity. We conclude, therefore, that structural changes in the cobalt and molybdenum are

TABLE 6

Percent Thiophene Desulfurized at 300°C, over the Commercial[a] and the Prepared[b] $Co/\gamma\text{-}Al_2O_3$, $Mo/\gamma\text{-}Al_2O_3$, $Mo\text{–}Co/\gamma\text{-}Al_2O_3$, and $Co\text{–}Mo/\gamma\text{-}Al_2O_3$ Catalysts

Catalyst No.	% Thiophene converted	Catalyst No.	% Thiophene converted	Catalyst No.	% Thiophene converted
$Co/\gamma\text{-}Al_2O_3$		$Mo\text{–}Co/\gamma\text{-}Al_2O_3$		Commercial	
1	50.1	15	100	C_1	98.3
2	7.5	16	100	C_2	87.3
3	19.2	17	100	C_3	99.4
4	34.1	18	100	C_4	95.0
5	31.5	$Co\text{–}Mo/\gamma\text{-}Al_2O_3$		C_5	100 (plus 12% cracking)
6	26.1	19	97.2	C_6	90.2
7	4.8	20	97.5	C_7	51.6
8	38.5	Alumina support	0.61	C_8	88.0
9	9.4				
10	19.5	$CoMoO_4/\gamma\text{-}Al_2O_3$[c] (before calcination)	28.5	C_9	70.6
$Mo/\gamma\text{-}Al_2O_3$					
11	71.1	$CoMoO_4/\gamma\text{-}Al_2O_3$[c] (after calcination)	54.5		
12	72.4				
13	98.5				
14	82.7				

[a] See Table 2.

[b] See Table 1.

[c] Catalyst E_1; see Table 1.

more important for activity than for exchange. We also conclude that the active desulfurizing species in the $Co\text{–}Mo/\gamma\text{-}Al_2O_3$ catalysts is probably not simple cobalt molybdate but may be related to it.

2. *State of Cobalt*

Magnetic measurements are of limited value in providing information about the state of cobalt in the Co/Mo catalyst systems. Calculations, based on such measurements, cannot be carried beyond a certain point because of interference of diamagnetic Co^{3+}. Therefore, the second maximum in the magnetic moments of the $Co/\gamma\text{-}Al_2O_3$ catalysts is (catalyst No. 5, Table 3) not understandable by magnetic measurements alone. However, on the basis of our exchange data some tentative statements can be made about the state of the cobalt. First the percent of octahedral cobalt gradually increases from catalyst 1 to 3 and this corresponds with an increase of d_2 formation (Table 4). Therefore d_2 formation in the thiophene exchange reaction may be correlated with octahedral cobalt in the $Co/\gamma\text{-}Al_2O_3$ catalysts. Second, in contrast, catalyst No. 5 shows a large amount of d_1 and d_2 formation while its exchange pattern is closer to random than any other (Table 4). But random exchange has previously been observed over a $Co/\gamma\text{-}Al_2O_3$ catalyst containing mostly Co^{3+} ions (*2*). Therefore, we suggest that catalyst No. 5 contains Co^{2+} mostly in the octahedral state, giving rise to large d_2 formation, and enough Co^{3+} to produce random exchange. The ratio of Co^{2+} (octahedral) to Co^{3+} must be large so that despite the diamagnetism of the latter, the catalyst shows a high magnetic moment (Table 3).

Finally, different values of magnetic moments have been reported for $Co/\gamma\text{-}Al_2O_3$ catalysts containing this same range of cobalt content but on a different alumina support (*17*). Thus it appears that different aluminas accept cobalt in different forms. This may account for the desirability of one alumina preparation over another.

The Co/γ-Al_2O_3 catalysts prepared from cobalt acetate show exchange patterns different from their matching pairs in the nitrate series. Such differences might be due to shift differences in the magnetic properties (Table 3) resulting from some carbonaceous species deposited on the catalyst surface during calcination of the acetate ion. For example, the exchange activity of catalyst 7 peaks toward d_3 and d_4 in contrast to its matching catalyst in the nitrate series, catalyst 3, for which d_2 formation is maximum. Similar differences occur for catalyst pairs 8,4 and 9,5. On the other hand, catalyst 10 shows an exchange trend similar to that of its nitrate counterpart, catalyst 6.

Catalysts 1, 4, 5, and 8 exhibit the highest desulfurization activities in the Co/γ-Al_2O_3 series. But there does not seem to be any clear correlation between desulfurization and magnetic properties. Only a crude correlation occurs between desulfurization and percent d_2. If catalyst 10 is excluded, the d_2 goes through a maximum at catalysts 5 and 6 as desulfurization increases. Apparently good desulfurization activity requires a certain ratio of tetrahedral to octahedral cobalt. The presence of some Co^{3+} does not interfere with desulfurization as long as the required ratio of tetrahedral/octahedral Co^{2+} exists.

3. Molybdenum Catalysts

The exchange patterns from the Mo/γ-Al_2O_3 catalysts peak toward d_2 formation (Table 4, catalysts 11–14). This same pattern was observed for a different Mo/γ-Al_2O_3 catalyst at 200°C rather than 300°C (*2*). This difference might be the result of the different alumina supports involved.

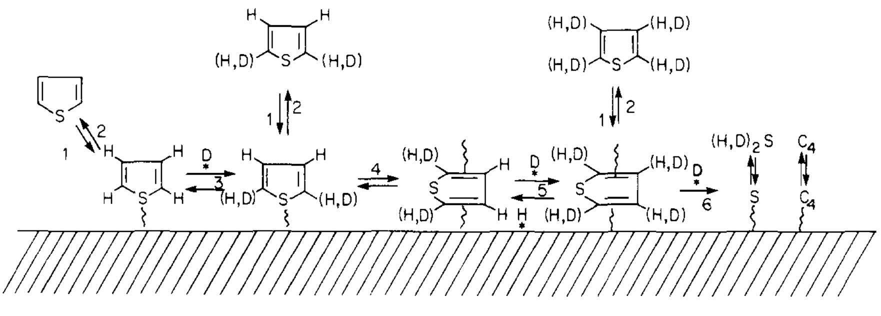
Molybdenum deposited on a Co/γ-Al_2O_3 catalyst greatly increases desulfurization activity (compare catalyst pairs 19,2 and 20,7 in Table 4). It also maximizes the exchange pattern toward d_2, brings it closer to randomness, and lowers the d_{av} (the average number of deuteriums per molecule). The additional presence of molybdenum, therefore, seems to increase random exchange at the expense of multiple exchange (greater than random amounts of d_4) on Co/γ-Al_2O_3 alone. On the other hand, cobalt impregnated on the molybdenum-containing catalysts seems to enhance the effects of molybdenum (compare catalyst pairs 11,15; 12,16; 13,17; and 14,18 in Table 4). For the two lower concentration Mo catalysts (11 and 12) the effect of Co is dramatic in two respects. Dideutero species are increased well above random and desulfurization is increased. In contrast, for the two higher concentration Mo catalysts the effect of Co is less. However, this is because d_2 and desulfurization were already large on the Mo catalyst.

The exchange patterns for the commercial catalyst fall into three categories. The first pattern resembles the cobalt-on-molybdenum catalysts (15–18) and is exhibited by commercial catalysts C_1–C_4. It is characterized by a volcano-shaped peak with a maximum at d_2. The second pattern is exhibited by C_5 and C_6 and is characterized by large d_{av} with higher than random amounts of d_2 and, especially, d_4. Both of these sets of catalysts exhibit high desulfurization activity. The third pattern is exhibited by C_7–C_9 and contains low d_{av}.

It is difficult to correlate exchange patterns with desulfurization activity, but reference to Table 6 generally indicates that catalysts C_1–C_6 are of the higher activity type. More specifically, d_{av} of 1.9 or higher generally corresponds with good desulfurization activity.

4. Mechanistic Considerations

Higher d_{av} values, which correspond to good desulfurization activity, are a result of some multiple exchange. This suggests flat adsorption of thiophene molecules on the surface. Flat adsorption appears to be necessary for desulfurization (*2*, *9*), so higher d_{av} values appear to correlate with good desulfurization activity. Greater than random amounts of d_2 and d_4, which are found for nearly all the molybdenum-containing catalysts (Table 4), suggests two exchangeable sets with an energy barrier separating them. Such an exchange pattern can be rationalized on the basis of a modified Komarewsky mechanism (*5*):



We suggest that the results over Co/Mo catalysts arise from an energy barrier order of 6 > 4 > 2 > 3 ≈ 5. Over certain Co/Mo catalysts the barrier at 6 is lower and greater desulfurization activity occurs, but because the order may become 4 > 2 > 6 > 3 ≈ 5, less d_3 and d_4 and more d_2 are obtained. Poor HDS catalysts of Co/Mo type seem to have the barrier at 4 much higher than other barriers, so d_1 and d_2 appear, but only little d_3 and d_4.

Certain Mo/γ-Al_2O_3 catalysts show appreciable desulfurization activity, but the relative heights of the energy barriers are not so obvious. The addition of cobalt to these catalysts invariably increases desulfurization activity, i.e., lowers the barrier at 6. However, the exchange patterns remain similar and suggest a concomitant lowering of the other barriers.

The correlation between d_{av} and desulfurization over the Co/Al_2O_3 catalysts is opposite to that of the Co/Mo catalysts. That is, higher desulfurization activity is found for lower d_{av}. In these cases the relative proportions of octahedral and tetrahedral Co^{2+} and Co^{3+} may play important roles since the d_{av} of catalysts 2 through 4 go through a minimum with increasing cobalt concentrations. Examination of the deviation of the patterns from randomness sheds some light on the problem. With the exceptions of catalysts 5 and 10 cobalt catalysts have lower d_2 and higher d_4 than random. This suggests a lower barrier at 4 than on Mo/Al_2O_3 catalysts, and possibly a process leading directly to multiple (d_4) exchange.

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