

Catalytic Exchange and Hydrogenolysis of Thiophenes and Related Heterocycles

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The exchange and hydrogenolysis (deuteriumolysis) of thiophene, 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene, furan, and γ -picoline were examined over a Mo/ γ -alumina catalyst. The exchange of thiophene, and γ -picoline were examined over γ -alumina, Mo/ γ -alumina and CoMo/ γ -alumina catalysts. Three types of exchange functions seem to exist in the last two catalysts, random exchange and multiple exchange on γ -alumina and α -exchange on Mo. Poisoning with picoline and water suppresses γ -alumina type exchange but not α -exchange and desulfurization. Multiple exchange is correlated with hydrogenation/dehydrogenation activity and α -exchange is correlated with desulfurization. π -Complex formation seems important in multiple exchange but methyl group exchange requires, in addition, heteroatom activation. The role of Co may be to facilitate surface hydrogen mobility and thereby decrease coke formation.

INTRODUCTION

Despite massive developmental accomplishments leading to elegant practical applications, fundamental mechanistic understanding of heterogeneous catalytic hydrogenolysis reactions is scarce. The experimental problems associated with potentially capricious catalyst character tend to undermine confidence in data and obscure mechanistic interpretation. Nevertheless, one commercially valuable hydrogenolysis reaction, hydrodesulfurization (HDS), has been examined in some detail. Frequently, thiophene has been used in such studies because of its presence in petroleum and its high activation energy for reaction.

Work reviewed through 1957 (1) reveals various opinions about the exact sequence of

steps involved in HDS of thiophene. One group favors ring saturation (hydrogenation) as the first process (2-4) and another supports ring opening to form 1-butadiene-thiol (5). More recently the theory of initial C-S bond cleavage leading to hydrocarbons and H₂S as the only desorbed products has been advanced (6-12). Concomitant exchanges between thiophene (13) and deuterium and pyridines (14) and deuterium have been examined on catalysts related to the commercial variety, and a series of studies examining catalyst composition, structure and reactivity have employed water and pyridine poisons to further elucidate mechanistic details (15-17).

Because of the available background information, the industrial importance of hydrogenolysis reactions and the dearth of

detailed molecular mechanistic understanding, we undertook exploratory experiments aimed at deciphering the nature of surface species involved in hydrodesulfurization. In fact we extended the studies somewhat to C-O and C-N bonds. In this paper, therefore, we report studies on the exchange and hydrogenolysis (deuterium-olysis) of thiophene, 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene and the exchange of furan and γ -picoline (4-methylpyridine).

EXPERIMENTAL

Apparatus

The experimental apparatus was similar to that previously described (18-22). The reaction/analytical train consisted of a stainless steel microreactor ($5.5 \times \frac{1}{4}$ in. i.d.), heated by a furnace (Lindberg, Heviduty types 54356A) and connected to a Varian 90-P gas-liquid chromatograph (GLC). Carrier gas (hydrogen or deuterium) entered the reactor through a pre-heat section of $\frac{1}{8}$ in. stainless steel tubing and passed into the GLC column (20 ft \times $\frac{1}{4}$ in. containing $\frac{1}{3}$ of its length as dioctylphthalate, $\frac{1}{3}$ as tricyanoethoxypropane and $\frac{1}{3}$ as Carbowax 4000, all 15% on 60-80 mesh Chromosorb W). Sample injection ports were located before the pre-heat section and after the reactor. The empty reactor did not catalyze HDS at 400°C. In a typical experiment a sample of catalyst was packed in the reactor between two glass wool plugs and heated to 400°C under flowing hydrogen for 12 hr. Before adjusting to reaction conditions several samples of thiophene (30-100 μ l total) were injected through the reactor to sulfide the catalyst. After adjusting to reaction conditions samples were injected through the reactor and GLC separated products were trapped for mass spectral and NMR analyses by condensation in liquid nitrogen cooled glass traps. With deuterium as a carrier gas negative GLC peaks revealed the presence of hydrogen; therefore, the minimum temperature of exchange could readily be detected.

Materials

Three different catalysts were tested. Catalyst A was a sample of molybdenum oxide on alumina pellets found in V. I. Komarewsky's old laboratory at Illinois Institute of Technology and manufactured by Edgal Corporation. Chemical analysis revealed 10.5% by wt Mo. It was crushed and material passing through a 60 mesh sieve was packed in the reactor. A pressure of 40 psi was required to maintain a 60 cc/min H_2 flow rate.

Catalyst B was a sample of activated γ -alumina extrudate (Girdler T-126) furnished by Chemetron Corporation. It was crushed and sieved to 60-80 mesh for use in the reactor. Catalyst C was a sample of 6% Cobalt molybdate on γ -alumina extrudate (2.5% Co, 13.5% Mo) furnished by Davison Division of W. R. Grace and Co. It was crushed and sieved to 60-80 mesh. A pressure of 10 psi H_2 or D_2 was required to maintain 60 cc/min flow rate for both Catalysts B and C.

Deuterium gas, 99.7% was purchased from Liquid Carbonic and Stohler. The thiophenes and furan were obtained from Matheson Coleman and Bell while γ -picoline (98%) was purchased from Aldrich Chemical Co. Furan was twice distilled and γ -picoline once distilled before use. The other compounds were used as received.

RESULTS

Molybdenum Oxide on γ -Alumina (Catalyst A)

Initially it seemed best to use a catalyst less complex than the commercial variety so that a comparison might reveal individual and/or synergetic effects of different components.

Following an initial 24 hr heating at 400°C under H_2 (60 cc/min) several samples of thiophene were injected over the catalyst. Since total conversion of thiophene initially occurred (butane and butenes but no H_2S passed through the gas chromatograph), the amount of catalyst used (1.8 g) was sufficient for every mole-

TABLE I
 PERCENT DEUTERATED SPECIES OF VARIOUS HETEROCYCLES EXCHANGED OVER MOLYBDENUM OXIDE-ON-GAMMA-ALUMINA CATALYST
 (1.8 g catalyst, 60 cc/min D₂ at 40 psi; 20 μl sample size)

	Thiophene			2-Methyl-thiophene			3-Methyl-thiophene			2,5-Dimethyl-thiophene			Furan			4-Picoline					
	200°C			300°C			200°C			200°C			200°C			260°C			200°C		
	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	
d ₀	27.6	38.0	6.3	.82	.09	1.8	14.1	8.0	5.6	2.5	1.0	2.2	30.4	34.2	31.1	34.3	1.0	(0.2)	11.9	(9.5) ^d	
d ₁	41.9	37.7	25.0	4.5	1.8	2.3	39.4	54.1	27.2	14.9	18.0	17.9	49.5	42.0	49.3	43.0	6.3	(2.1)	12.4	(5.5)	
d ₂	23.8	24.2	37.5	84.0	12.5	10.6	35.4	26.2	43.7	78.3	81.0	77.5	20.1	23.9	19.5	22.7	18.0	(8.8)	12.6	(6.8)	
d ₃	6.0	.03	25.0	10.3	39.3	29.8	10.6	8.3	23.5	4.4	—	2.1	—	—	—	—	28.0	(21.2)	13.0	(10.1)	
d ₄	.57	.05	6.3	0.2	46.3	55.4	—	2.5	—	—	—	0.3	—	—	—	—	26.0	(29.3)	14.8	(18.4)	
d ₅	—	—	—	—	—	—	—	.47	—	—	—	—	—	—	—	—	15.0	(24.8)	18.0	(24.9)	
d ₆	—	—	—	—	—	—	—	.37	—	—	—	—	—	—	—	—	5.0	(11.7)	8.3	(12.4)	
d ₇	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.6	(2.4)	9.2	(12.3)	
d _{avg}	—	1.15	—	2.04	—	3.3	—	1.42	—	1.85	—	1.8	—	.897	—	.884	—	—	3.4	(4.1)	

^a Random distribution calculated by binomial equation.

^b Mass spectral analysis at 10 V correcting for natural abundance of ²H and ¹³C.

^c After picoline poisoning.

^d Picoline desorbing with furan at 260°C (long residence on surface).

cule of thiophene to make surface contact. After many injections of thiophene the activity decreased to about 90% conversion at 400°C. At 200°C only a trace of conversion occurred. The latter temperature/conversion but not the former are in agreement with the work of Schuit and Lipsch (17) who found only about 40% thiophene conversion at 400°C over a commercial catalyst. In good agreement, however, Amberg and Owens found 100% conversion at 350°C and 1% at 186°C over another commercial catalyst. We did not attempt to determine the nature and percent of each of the hydrocarbon products.

The carrier gas was changed to D₂ and thiophene was passed over the catalyst at 160, 200 and 300°C. Large negative GLC peaks indicated the presence of hydrogen and, hence, massive exchange. Samples were collected and mass spectral analyses revealed deuterium distributions shown in Table 1. Similar to the findings of Kemball and Kieran (13) over MoS₂, dideterothiophene forms at the lower temperatures. At 300°C perdeuteriothiophene predominates. NMR analyses of the 200°C sample showed positions 2 and 5 to contain most deuterium. Because Amberg and Desikan (9) found-rate differences between thiophene and its two monomethyl derivatives, we examined the exchange of 2- and 3-methylthiophene and 2,5-dimethylthiophene at 200°C (Table 1). No hydrodesulfurization of the methylthiophenes occurred under these conditions and mainly 5-deutero-2-methylthiophene, 2,5-dideutero-3-methylthiophene and 3,4-dideutero-2,5-dimethylthiophene dominated. Minor amounts of deuterium enter α -methyl but not β -methyl. Furan was exchanged for comparison (no deuteriumolysis) and, although less exchange occurred, 2,5-dideuterofuran was the most exchanged species. 4-Picoline was exchanged at 200°C (no deuteriumolysis) and the temperature was then increased to re-examine furan at 260°C. Again no hydrogenolysis of furan occurred but the odor of 4-picoline was detected at the GLC exit. Mass spectral analysis of the 260°C exchanged furan simultaneously revealed the exchange pat-

tern of the contaminating 4-picoline (Table 1). This slowly eluted picoline contained more deuterium than that previously trapped; both patterns differed substantially from random distributions and NMR analysis of the initial sample suggested the following distribution: d₁ and d₂ contain deuterium at the 2 and 6 positions, d₃, d₄ and d₅ contain deuterium in the methyl group as well as positions 2 and 6 and d₆ and d₇ contain deuterium also at the 3 and 5 positions. These results are similar to some of those of Wells and Moyes for pyridine and 2-methylpyridine (14). When Catalyst A was removed from the reactor it was greyish-black indicating moderate coking.

γ -Alumina (Catalyst B)

Catalyst A was replaced with γ -alumina (Catalyst B) to determine its activity for exchange. After pretreatment with H₂ at 400°C for 12 hr. the carrier gas was switched to D₂. Injections of thiophene over the catalyst resulted in no negative hydrogen peak at 200°C and none at 300°C but when the temperature was increased to 400°C a broad negative peak signalled desorption of the hydrogen which had been exchanged out of the thiophene samples at 200°C and 300°C. Injections of thiophene at 400°C produced hydrogen peaks with long tails. Mass spectral analyses confirmed exchanged at both 200°C and 300°C as well as 400°C (Table 2) but the patterns are considerably different from those obtained over Catalyst A. In fact the occurrence of deuterated species higher than d₄ suggests the presence of saturated compounds. Several samples of γ -picoline were next injected over the catalyst and after it seemed that all of the picoline had desorbed two samples of thiophene were passed over the catalyst. The γ -picoline and thiophene mass spectral analyses are in Table 2. It turned out that a small amount of picoline eluted with the thiophene; not enough, however, was collected for a reliable mass spectral analysis. No desulfurization of thiophene was observed on catalyst B under any conditions.

TABLE 2
 PERCENT DEUTERATED SPECIES OF VARIOUS HETEROCYCLES EXCHANGED OVER
 GAMMA-ALUMINA CATALYST (1.5 g catalyst, 60 cc/min D₂ at 10 psi; 25 μ l sample size)

	Thiophene								4-Picoline	
	200°C		300°C		400°C		400°C		400°C	
	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^{b,c}	Ran. ^a	Exp. ^b
d ₀	6.5	10.6	3.3	13.7	.3	1.6	10.2	14.0	.01	0
d ₁	25.5	18.0	17.7	26.1	3.5	6.5	31.4	23.8	0.2	0
d ₂	37.5	38.7	35.8	17.1	18.2	29.0	36.2	42.3	1.5	0.6
d ₃	25.5	27.9	32.3	6.7	41.9	20.8	18.6	16.5	7.0	3.2
d ₄	6.0	4.8	11.0	32.3	36.1	31.4	3.6	4.0	18.2	16.7
d ₅	—	0	—	4.0	—	7.0	—	0	31.7	47.6
d ₆	—	0	—	0	—	3.8	—	0	29.0	26.0
d ₇	—	0	—	0	—	0	—	0	11.4	6.0
d _{avg}	—	1.98	—	2.30	—	3.10	—	1.74	—	5.13

^{a,b} Footnotes *a* and *b* same as in Table 1.

^c After picoline treatment.

Cobalt Molybdate on γ -Alumina (Catalyst C)

After the standard pretreatment in H₂ carrier gas, six samples (25 μ l each) of thiophene were passed over the catalyst at 400°C; approximately 80% thiophene conversion occurred in each case. The temperature was lowered and the minimum temperature for conversion was found to be 180°C. The carrier gas was changed to D₂ and exchanged thiophene samples were collected at 200°C and 300°C (Table 3). 4-Picoline was passed over the catalyst at 300°C and before it completely desorbed a sample of thiophene was injected and collected (Table 3). After all of the thiophene had desorbed, another sample of picoline was collected and analyzed (numbers in parentheses in Table 3). The carrier gas was changed back to H₂ and the catalyst flushed for 12 hr at 400°C to remove all traces of picoline. After changing back to D₂ the temperature was adjusted to 300°C and 25 μ l of D₂O was injected. Before the water had desorbed, a sample of thiophene was injected and collected. For comparison the experiment was repeated with H₂O. A characteristic hydrogen peak revealed exchange of H₂O; however, the exchange patterns of thiophenes in both experiments were very similar as shown in Table 3.

Adsorption

Although little effort was made to obtain quantitative data on catalyst retention of samples, the following qualitative observations were made: (1) retention increased at lower temperatures, (2) pronounced tailing of the butenes revealed their stronger adsorption on the catalysts than thiophene, (3) desorption seemed to be slower in D₂ than in H₂, (4) adsorption of the thiophenes decreased in the order 2,5 dimethyl > 2-methyl \geq 3-methyl > thiophene, (5) the extent of adsorption of thiophene and 4-picoline on the different catalysts decreased in the order B > A > C, and (6) on catalyst C at 300°C H₂O was retained 7 min compared to 3 min for thiophene and about 1 min for H₂.

DISCUSSION

Exchange Patterns

Comparing an exchange pattern to a random pattern aids mechanistic discrimination. For example, if the exchange pattern of thiophene matched the random pattern, it could be said that each hydrogen exchanged independently and with the same activation energy. Therefore, in the tables we have tabulated random distribu-

TABLE 3
 PERCENT DEUTERATED SPECIES OF VARIOUS HETEROCYCLES EXCHANGED OVER COBALT MOLYBDATE-ON-GAMMA-ALUMINA CATALYST
 (1.1 g catalyst, 60 cc/min D₂ at 10 psi; 25 μ l sample size)

	Thiophene												4 Picoline	
	200°C		300°C		300°C		300°C		300°C		300°C		300°C	
	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^b	Ran. ^a	Exp. ^{b,c}	Ran. ^a	Exp. ^{b,d}	Ran. ^a	Exp. ^{b,e}	Ran. ^a	Exp. ^{b,f}	Ran. ^a	Exp. ^b
d ₀	5.1	8.5	.4	.95	16.5	9.7	4.5	0.9	3.3	0	0.1 (.01)	0 (0) ^f	0 (0)	0 (0)
d ₁	22.5	15.3	6.9	7.5	37.6	39.6	21.0	10.0	17.7	8.0	1.1 (.2)	0 (0)	1.1 (.2)	0 (0)
d ₂	37.3	41.8	19.1	35.3	32.0	46.4	37.0	64.6	35.8	63.4	5.9 (1.5)	1.0 (1.4)	5.9 (1.5)	1.0 (1.4)
d ₃	27.5	27.9	42.2	40.8	12.2	4.3	29.0	21.6	32.3	24.3	16.5 (7.0)	3.9 (5.7)	16.5 (7.0)	3.9 (5.7)
d ₄	7.6	6.5	31.6	15.6	1.7	0	8.5	2.9	11.0	4.30	28.0 (19.2)	14.6 (16.2)	28.0 (19.2)	14.6 (16.2)
d ₅	—	—	—	.76	—	0	—	0	—	0	28.4 (31.7)	34.7 (32.7)	28.4 (31.7)	34.7 (32.7)
d ₆	—	—	—	0	—	0	—	0	—	0	16.0 (29.0)	26.3 (42.2)	16.0 (29.0)	26.3 (42.2)
d ₇	—	—	—	0	—	0	—	0	—	0	3.9 (11.4)	19.4 (1.9)	3.9 (11.4)	19.4 (1.9)
d _{avg}	—	2.1	—	3.01	—	1.45	—	2.16	—	2.25	—	4.40 (5.14)	—	4.40 (5.14)

^{a,b} Footnotes *a* and *b* same as in Table 1.

^c After picoline poisoning.

^d After D₂O poisoning.

^e After H₂O poisoning.

^f After long residence on surface.

tions for every case and would draw attention to the following points. At low temperatures, the exchanges on γ -alumina and cobalt molybdate catalysts show a tendency towards a random distribution. That a random distribution at 400°C on γ -alumina may be masked by multiple exchange (i.e., perdeutero) is shown by the pattern on the picoline-poisoned γ -alumina. At the higher temperature on Mo/ γ -alumina the pattern becomes more random as multiple exchange becomes dominant. The 3,4 positions in 2,5-dimethylthiophene are randomly exchanged as are the 2,5-positions in furan, which suggests stepwise exchange of the set rather than pair exchange. Presumably the 2,5-positions of thiophene are also randomly exchanged but with a lower activation energy and this accounts for the large amounts of d_2 in thiophene and 3-methylthiophene.

At 200°C the amount of d_2 decreases on the different catalysts in the order Mo/ γ -alumina > CoMo/ γ -alumina > γ -alumina. Especially at lower temperatures Mo/ γ -alumina favors exchange of only the 2,5-positions of thiophene and resembles furan exchange at 200°C. These facts suggest a difference between Mo/ γ -alumina and the other two catalysts. This difference seems to be related to the multiple exchange function.

Multiple exchange is favored at the higher temperatures and decreases on the different catalysts in the same order as d_2 at 200°C. That two catalytic functions exist on each catalyst, but to different extents, is revealed by the effects of poisoning by picoline and water. Both inhibit multiple exchange and enhance (relatively) dideutero-exchange when it is allowed (on catalysts A and C). Since pyridines do not affect desulfurization as greatly as hydrogenation (10, 17), it seems reasonable to relate multiple exchange to hydrogenation but not desulfurization. Specifically, the multiple exchange (and hence hydrogenation/dehydrogenation) activity seems to predominate on γ -alumina while desulfurization is obviously a function of the Mo. Strong support for this comes from Kemball's exchange of thiophene on MoS₂; little

multiple exchange and hydrogenation occur (13).

Mechanistic Considerations

Clearly the easiest process for all of the heterocycles to follow on the Mo containing catalysts is α -exchange. This confirms previous conclusions that the adsorption may occur via the heteroatom (14, 17). Multiple exchange and desulfurization seem to require about the same activation energies in our experiments. The poisoning experiments, however, show they are not steps in the same sequence but probably occur on different reaction sites.

At least three different reaction sites seem to exist. On γ -alumina a site for low activation energy random exchange is present as is a site for multiple exchange/hydrogenation requiring higher activation energy. Picoline poisoning eliminates the latter sites which, presumably, are strongly acidic (10). On the Mo containing catalysts an additional function seems to exist, specific to α -exchange and desulfurization. Picoline poisoning on these catalysts seems not to destroy these abilities while retarding the γ -alumina multiple exchange/hydrogenation ability. Water seems to enhance dideutero-exchange at the expense of random and multiple exchange. Therefore, it seems that water poisons both functions of γ -alumina. Schuit, for example, found water poisoning had a small effect on desulfurization and a larger effect on butene hydrogenation (17). It seems, therefore, that dideutero-exchange and desulfurization are related. It appears, also, that hydrogenation/dehydrogenation sites and multiple exchange sites are related. This apparently contradicts Schuit's conclusion that hydrogenation and desulfurization occur on the same site at high temperatures (17). Schuit also observed hydrogen adsorption below 200°C and rationalized butene hydrogenation at that temperature by assuming interaction with molecular gaseous H₂. We observed thiophene exchange at 200°C which suggests that although no vacant sites exist for hydrogen adsorption at that temperature, a hydrogen acceptor can take hydrogen (deuterium)

from the surface and make space for gaseous hydrogen (deuterium) to adsorb. Disproportionation might also be considered as a possibility.

A plausible reaction sequence would be (1) adsorption at the heteroatom, (2) random α -exchange by a "rocking" motion, and (3) rupture of the carbon-heteroatom bond. We cannot clearly distinguish between an addition-abstractation and an abstractation-addition mechanism for α -exchange and desulfurization (13, 14). Through another pathway, (4), multiple exchange, random exchange and hydrogenation occur. These may involve π -complexes (14, 22) on γ -alumina. Where ring π -electron density is highest, picoline, the possibility for π -complexing increases and multiple exchange is large. Where ring electron density is lowest, furan, no multiple exchange occurs. Flat adsorption in a π -complex would also bring methyl groups close to the surface.

Methyl exchange occurs when methyl is α or γ but not β to the heteroatom. This is most pronounced in the picolines. Wells and Moyes found methyl exchange in α -picoline but not in β -picoline (14). We find methyl exchange in γ -picoline. Although these results were obtained over different catalyst systems their resemblance to methyl group acidities in picolines is inescapable. It seems therefore that, at least in the case of picolines, the ability to form a π -complex is not the only necessary criterion for methyl group exchange. Methyl group activation by the heteroatom seems also to be a necessary factor. To a much lesser extent methyl exchange occurs in the α -methyl thiophenes but here the heteroatom does not increase lability of methyl hydrogens.

Coking

If desulfurization, a hydrogen-consuming reaction, occurs on Mo (or molybdenum sulfide) and hydrogenation/dehydrogenation occurs on γ -alumina, then a hydrogen deficiency at Mo could result in dehydrogenation of adsorbed hydrocarbons on nearby γ -alumina leading to coke. Since γ -alumina strongly retains exchanged hy-

drogen in contrast to the other two catalysts, it seems possible to ascribe to Co [or cobalt aluminate (16)] the role of facilitating surface hydrogen mobility and, hence, decreasing the possibility of coke formation.

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