

The results are in agreement with the generally accepted mechanism for macropolymerization involving a free radical chain reaction. It has been suggested that, for polymerizations catalyzed by

benzoyl peroxide, the chain is initiated by free radicals formed by thermal decomposition of the catalyst.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Influence and Behavior of Thiophene on Aromatization Catalysts

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In view of the present interest in the cyclization and aromatization of petroleum hydrocarbons by catalytic means, it was considered important to investigate the influence of sulfur on this process. We record an investigation on two typical aromatization catalysts, chromium oxide and molybdenum oxide.

These substances were of especial interest since they have been shown to be active in removing sulfur compounds from gasoline and benzene. Orlov and Broun¹ investigated the removal of thiophene from gasoline by hydrogenation at 400° on catalysts of (1) molybdenum trioxide, (2) nickel, cobalt, aluminum and magnesium oxides in the proportions: 42:3:5:1, and (3) cobalt oxide, which were reduced in hydrogen before use. They found the nickel catalyst to be best, but in the light of the investigations of Elgin, Wilder and Taylor² (*vide infra*), they were apparently reporting on the activity before reaching the steady state, since they note that the catalyst rapidly lost activity and could not be regenerated.

Pease and Keighton³ investigated the efficiency of the removal of thiophene from benzene by hydrogenation. They found an equimolar mixture of cobalt sulfide-molybdenum oxide to be the most efficient. Further investigations by Pease and Munro⁴ showed that a cobalt sulfide-chromium oxide catalyst was as efficient as Keighton's best and that a chromium oxide gel although inactive at 200° gave complete removal at 400°.

I. G. Farbenindustrie A.-G. has patented a process for the desulfurization of crude oils by treatment with hydrogen at 300° and ten atmospheres pressure on a molybdenum oxide-zinc oxide catalyst.

Moldavskii and co-workers^{5,6} have studied molybdenum sulfide. They showed that at 450° benzene is not hydrogenated whereas thiophene is attacked. At 350°, 90% of the thiophene was already decomposed. They gave the mechanism: thiophene → thiophane → butyl mercaptan. The average velocity of hydrogenation and decomposition of thiophene was also investigated on the sulfides of cobalt, nickel, manganese, cadmium and copper.

In the present investigation, thiophene was chosen since it has been shown to be among the most difficult of such compounds to remove either catalytically or by the usual liquid phase treatments. Elgin,⁷ in a study of catalytic action on pure sulfur compounds in a naphtha carrier, found that, at the steady state, the ease of removal was in the order: mercaptan > alkyl sulfide > thiophene. The last was not removed at all after the initial poisoning of the catalyst unless hydrogen was added to the input gases. Faragher, Morrell and Comay⁸ found that solutions of thiophene showed no cracking at temperatures up to 870°. Other sulfur compounds, such as sulfides and disulfides, gave hydrogen sulfide, mercaptans, thiophene and elementary sulfur. Malisof and Marks⁹ investigated the further cracking of mercaptans and showed that they yield olefins and hydrogen sulfide. For example, butyl mercaptan gave butylene and hydrogen sulfide. This latter reaction is reversible and at lower temperatures, especially in the presence of catalysts, mercaptans can be obtained from olefins plus hydrogen sulfide.¹⁰

(5) Moldavskii and Prokopchuk, *J. Applied Chem.* (U. S. S. R.) **5**, 619 (1932).

(6) Moldavskii and Kumari, *J. Gen. Chem.* (U. S. S. R.), **4**, 298-306 (1934).

(7) Elgin, *Ind. Eng. Chem.*, **22**, 1290 (1930).

(8) Faragher, Morrell and Comay, *ibid.*, **20**, 527 (1928).

(9) Malisof and Marks, *ibid.*, **23**, 1114 (1931); **35**, 780 (1933).

(10) Sachanen, "Conversion of Petroleum," Reinhold Publishing Co., New York, N. Y., 1940, p. 97.

(1) Orlov and Broun, *Khim. Tverdogo Topliva*, **3**, 817-824 (1932).

(2) Elgin, Wilder and Taylor, *Ind. Eng. Chem.*, **22**, 1284 (1930); Elgin, *ibid.*, **22**, 1290 (1930).

(3) Pease and Keighton, *ibid.*, **25**, 1012 (1933).

(4) Pease and Munro, *ibid.*, **25**, 1013 (1933).

Experimental Details

Apparatus.—The apparatus consisted of: (a) a calibrated feed tube operated by means of a synchronous motor as described by Hoog, Verheus and Zuiderweg,¹¹ (b) a system for purifying and metering hydrogen for introduction to the catalyst chamber, (c) a catalyst chamber enclosed in a temperature controlled furnace, (d) a condenser and cold trap for liquid products, (e) a calibrated reservoir for collecting and measuring gas samples, (f) a gas analysis system. In addition, two devices for trapping out sulfur dioxide and hydrogen sulfide from the off-gas were used. With hydrogen as the carrier gas two absorbers containing 1 *N* sodium hydroxide were used. With heptane containing thiophene no hydrogen was used but the hydrogen produced in the dehydrogenation processes passed through the absorbent fluid after traversing a perforated disk which broke the gas stream into fine bubbles, facilitating absorption and assisting in the maintenance of a more constant pressure in the system. A spray trap was mounted above this absorber, and mild suction was applied to give a steady gas stream. The disk was made by embedding fine platinum wires in a Pyrex glass plate, and dissolving out the wire with aqua regia.

Procedure.—Unless otherwise noted the feed rate for liquid was 2.3 cc. of liquid per hour. The temperature, recorded in a thermocouple well placed near the middle of the catalyst charge, was regulated at $470 \pm 1^\circ$.

Analysis.—The sulfur content of the off-gas was determined as follows. To the contents of the absorber system two or three drops of bromine were added and the whole heated on a hot-plate for twenty minutes to oxidize as much sulfur to sulfate as possible in the alkaline medium. With relatively large amounts of sulfide collected, colloid sulfur formed on addition of bromine but disappeared on warming. The solution was next acidified with hydrochloric acid and the usual procedure of dehydration and removal of silica followed. The sulfate was then determined as barium sulfate.

A volumetric method for sulfur using cadmium sulfate as absorbent and titrating the cadmium sulfide iodometrically was found to be insufficiently precise as well as poorly adapted for determining sulfur dioxide in the oxidation stage.

The liquid products were of two types, (1) those in which a benzene solution of thiophene was the charging liquid, (2) those in which heptane, either pure or containing 0.5 mole % thiophene, was used. The benzene products were investigated for sulfur content only. In the products from pure heptane, specific gravities, unsaturates and aromatics were determined¹² and, when thiophene was present, the total sulfur was also determined.

In the benzene solutions thiophene could be determined in amounts as low as 0.0005% by weight using a colorimetric application of the indophenine reaction.¹³ The delicate color could not be observed with samples from heptane charging stock, since olefins in the product darkened

the acid layer. In the definitive experiments the A. S. T. M. Lamp method (A. S. T. M. No. D-90-29T) for total sulfur in oil products was used. Instead of the usual 5-ml. sample, one of 2-ml. was used, delivered from a specially calibrated Pyrex pipet. This lowered the accuracy but a reproducibility of 0.01% sulfur was possible, which is, however, some 5% of the thiophene initially present.

Gas analyses were carried out in a modified Orsat apparatus, with the usual liquid absorbents for carbon dioxide, unsaturates and oxygen, hydrogen and carbon monoxide being determined by combustion over copper oxide at 260° and the residue reported as saturated hydrocarbons.

Materials.—Chromium oxide gel of our standard type,¹² Catalyst A, and two supported catalysts were studied. A 10% chromium oxide catalyst, Catalyst B, was made by impregnating "Alorco" activated alumina with a solution of the calculated amount of ammonium bichromate. A 10% molybdenum oxide catalyst on alumina, Catalyst C, was prepared in a similar manner from ammonium molybdate. The charge of catalyst was 15 g. in all cases.

Commercial tank nitrogen and hydrogen were used, purified when necessary. Thiophene-free benzene and California Chemical Company heptane were used with additions of a synthetic thiophene from the Paragon Testing Laboratories, to yield, normally, 0.5% thiophene content as assayed by the sulfur lamp.

Experimental Results

Sulfur Removal.—In Table I are presented typical data on the removal of sulfur by the three catalysts. With Catalyst A the molar ratio of hydrogen to benzene was 1:1 with a liquid feed of 4.5 cc. per hour and with the supported catalysts, B and C, at the liquid feed of 2.3 cc. per hour it was 2:1. The normal molar ratio of benzene to thiophene was 1:0.005 with the exception of Run 10 in which the thiophene was 2.5-fold greater. With Catalyst A the thiophene in the product was determined by the indophenine reaction, with the two others by the lamp method.

TABLE I
CATALYTIC REMOVAL OF SULFUR FROM HYDROGEN-
THIOPHENE MIXTURES

Run no.	Catalyst	% Thiophene in product	Removal in %
7	A	<0.0005	100
10	A	≤ .001	99.9
14	A	< .0005	100
1	B	.000	100
3	B	.008	98.5
1	C	.003	99.5
3	C	.002	99.6

Table II shows the thiophene removal from heptane and the aromatic yield in a continuous run over twelve hours. The fall in this latter, the hydrogen-yielding process, indicates an initial molar ratio of hydrogen to thiophene of 1.9:0.005

(11) H. Hoog, J. Verheus and F. J. Zuiderweg, *Trans. Faraday Soc.*, **35**, 993 (1939).

(12) J. Turkevich, H. Fehrer and H. S. Taylor, *THIS JOURNAL*, **63**, 1129 (1941).

(13) Allen, "Commercial Organic Analysis," Churchill, London, 1927, p. 517.

with a fall in ratio with time approximately proportional to the aromatic yield.

TABLE II
CATALYTIC REMOVAL OF SULFUR AND AROMATIC YIELD FROM 1:0.005 *n*-HEPTANE-THIOPHENE MIXTURES ON CATALYST B

Run no.	Time, hr.	% Thiophene in product	Removal in %	Vol. % aromatic in product
H1	4	0.144	67	17.9
H2	8	.101	79	11.1
H3	12	.106	76	7.3

Distribution of Sulfur in Products.—The location of the sulfur removed was studied with Catalysts B and C. The gaseous effluent was passed through absorbers containing 1 *N* sodium hydroxide during runs and the subsequent regenerative oxidation and reduction. The hydrogen-benzene-thiophene ratio was 2:1:0.005. In the regenerative oxidation, nitrogen was first passed to displace hydrogen and hydrocarbon vapors and air then turned in to yield a mixture containing 5% oxygen. The contrast in the behavior of the two catalysts is shown by typical data cited in Tables III and IV.

TABLE III
CATALYTIC REMOVAL OF 0.5 MOLE % THIOPHENE FROM BENZENE ON CHROMIUM OXIDE ALUMINA CATALYST B

Run no. and recovery process	Time, hr.	Thiophene input, g.	Thiophene equivalent in off-gases, g.	Input recovered, %
B3A	4	0.0486	0.0062	3.1
B3B	8	.0992	.0668	33.8
B3C	4	.0494	.0512	26.0
Trap A	16		.0008	0.4
% Input recovered as decomposition products during hydrogenation				63.3
Oxidation A	4		0.0234	11.9
Oxidation B	4		.0010	0.5
Reduction A	4		.0026	1.3
Reduction B	4		.0039	2.0
Trap B	16		.0074	3.7
% Input recovered as decomposition products during oxidation-reduction				19.4
Total % input recovered as reaction products				82.7

In an additional experiment of this type the total recovery of product sulfur equivalent to thiophene input was 68.7%. The recovery of product sulfur during hydrogenation was 60% of the thiophene input.

After this initial experiment with molybdenum oxide-alumina a sixteen-hour hydrogen period, with 0.1878 g. thiophene input, gave only 0.3% recovery of product sulfur, equivalent to thiophene input, while the subsequent eight-hour oxidation and fourteen-hour reduction yielded

TABLE IV
CATALYTIC REMOVAL OF 0.5 MOLE % THIOPHENE FROM BENZENE ON MOLYBDENUM OXIDE-ALUMINA CATALYST C

Run no. and recovery process	Time, hr.	Thiophene input, g.	Thiophene equivalent in off-gases, g.	Input recovered, %
B4A	4	0.0503	0.0009	0.6
B4B	4	.0506	.0011	.7
B4C	4	.0471	.0011	.7
Trap A	16		.0007	.5
% Input recovered as decomposition products during hydrogenation				2.5
Oxidation	8		0.0219	14.8
Reduction	12		.0018	1.2
Trap B	20		.0008	0.6
Oxidation	8		.0152	10.3
Reduction	9		.0023	1.6
Trap C	17		.0002	0.2
% Input recovered as decomposition products during oxidation-reduction				28.7
Total % recovered as reaction products				31.2

52.1 and 23.4% recoveries, respectively, of such product sulfur. Tests of catalyst activity with pure heptane followed by catalyst regeneration still further increased the sulfur recovery so that upward of 80% of the thiophene input was accounted for, and this almost exclusively in the catalyst regeneration process, in marked contrast to the chromium oxide case. The highest amount of the sulfur input observed as decomposition products during the hydrogen-liquid feed was 2.5% of the input in any run with molybdenum oxide, while, with chromium oxide, the evolution of hydrogen sulfide in the hydrocarbon vapor stream remained greater than 50% even with catalysts at low efficiency. Also, with chromium oxide, the initial evolution of hydrogen sulfide is less than later, when the surface approaches saturation. In one experiment in which sulfur had thus been in part stored on the catalyst, the evolution of hydrogen sulfide was actually greater, during a four-hour period on stream, than was equivalent to the thiophene input in the same interval. With the molybdenum oxide catalyst the reverse is the case. The mass stores up sulfur compounds to such an extent that in the later runs a much higher percentage recovery takes place during the regeneration but not during the period of hydrocarbon feed.

A heptane-thiophene feed on the chromium oxide catalyst, B, showed 74.1% total recovery of product sulfur, 53% in the hydrocarbon stream, 21% in the regeneration process.

Catalyst Content in Sulfur and Aromatization Efficiency.—The liquid and gas yields from the dehydrocyclization of heptane on chromium oxide catalysts subjected to various pretreatments which leave sulfur residues in the catalyst are shown in Table V. Details of the catalyst pretreatment are shown in the footnotes to the table.

TABLE V

DEHYDROCYCLIZATION OF HEPTANE ON CHROMIUM OXIDE-ALUMINA CATALYST B PRETREATED WITH THIOPHENE-BENZENE VAPORS

H3A, B, C and D are runs with heptane. H3T1A, B and C are runs with heptane containing 0.5 mole % thiophene.

Run no.	d_{40}^*	Liquid Analyses, %		Gas yields %	
		Olefin	Arom.	cc./5 min. at 90 min.	H_2
H3A ^a	0.742	11.5	34.7	55	86
H3B ^b	.706	12.4	24.8	28	86
H3T1A ^c	.699	11.5	17.9	20 ^d	80
H3T1B ^d	.702	11.2	11.1		
H3T1C	.699	10.5	7.3		
H3C ^e	.714	12.6	23.2	30	91
H3D ^f	.727	11.1	37.8	40	88

^a Catalyst brought slowly to 470° overnight in hydrogen.

^b Catalyst subjected to 2 runs with C_4H_8S in C_6H_6 , each followed by regeneration, preceding H3B. ^c Regenerated between H3B and H3T1. ^d A, B and C were four hour cuts of twelve hour run No. H3T1. ^e Regenerated for seventeen hours between H3T1 and H3C. ^f Regenerated for twenty hours between H3C and H3D. ^g First twenty minutes of run only.

From the work of Taylor and Fehrer,¹⁴ it has been deduced that the slow stage in the process of reaction is the dehydrogenation of the heptane to heptene. Poisoning with sulfur materially reduces this activity, from 46.1% in H3A to 17.8% in H3T1C. There is also a somewhat greater effect of poisoning on the cyclization activity from 34.7% in H3A to 7.3% in H3T1C. The runs H3C and D showed that activity is gradually restored after thiophene treatment.

Molybdenum oxide shows a sharp contrast in behavior as is seen in Table VI. The activity in the initial run (H4A) may be somewhat low, as is often found, but after the treatment with thiophene the yields of aromatics are excellent.

Comparison of H4D and H4T1 indicates that the actual presence of thiophene in the charging liquid has little effect on aromatic yield as the fall in yield is accounted for completely on the basis of the normal fall in activity due to carbonaceous deposit.

The type of catalyst surface formed by treatment of molybdenum oxide surfaces with sulfur

(14) Taylor and Fehrer, *THIS JOURNAL*, **68**, 1387 (1941).

TABLE VI

DEHYDROCYCLIZATION OF HEPTANE ON MOLYBDENUM OXIDE-ALUMINA CATALYST C PRETREATED WITH THIOPHENE-BENZENE VAPOR

H4A, B, C and D are runs with straight heptane. H4T1 is a run with heptane containing 0.5 mole % thiophene.

Run	d_{40}^*	Liquid Analyses, %		Gas yields %	
		Olefin	Arom.	cc./5 min. at 90 min.	H_2
H4A ^a	0.726	9.1	20.9	57	91
H4B ^b	.803	9.9	64.1	90	88
H4CA ^c	.800	9.9	59.1	80	85
H4CB ^d	.761	10.9	37.6	70	87
H4CC	.745	10.5	35.1	65	
H4D ^e	.770	10.4	46.5	80	90
H4T1 ^f	.746	11.1	29.9	70	90

^a New catalyst, brought slowly to 470°, then reduced overnight. ^b Thiophene-benzene-hydrogen for twelve hours, followed by two regenerations, precedes H4B. ^c Thiophene-benzene-hydrogen for sixteen hours followed by one regeneration, precedes H4C. ^d A, B and C were one and a half hour cuts of 4.5-hour run No. H4C. ^e Thiophene-benzene-hydrogen for sixteen hours, followed by H4D without regeneration. ^f H4T1 followed H4D directly.

compounds is different from that produced from bulk molybdenum sulfide. Catalysts of this latter type are known as strong cracking catalysts, breaking carbon-carbon bonds. The hydrogen percentages show that our catalysts do not possess this marked cracking characteristic.

The differentiation between molybdenum sulfide catalysts and catalysts obtained from the supported oxide with sulfur-containing materials is confirmed by the work of Hall and Cawley.¹⁵ The results of the determination of the composition of gasoline products from high pressure catalytic hydrogenation of middle oils are given in Table VII.

TABLE VII

	MoO ₃ -Al ₂ O ₃ catalyst	Pelleted MoS ₂ catalyst
Aromatic hydrocarbons, % by weight	27	2
Naphthenic hydrocarbons	66	50
Paraffinic hydrocarbons	7	48

These results are of interest since the middle oils contained sulfur. It would be expected that the molybdenum oxide would be more or less converted to the sulfide. Yet the difference between the reaction paths each favor is very marked. On the supported catalyst 93% of the material was converted to cyclic hydrocarbons, naphthenic or aromatic, whereas the pelleted sulfide gave 48% paraffinic. The sulfide catalyst

(15) Twelfth Report, Committee on Contact Catalysis, National Research Council, John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 86-87.

thus exhibits considerable cracking activity. The results are of even greater interest in that unsupported molybdenum oxide catalysts have definite cracking characteristics on heptane as unpublished data from this Laboratory show. A typical gas yield from dehydrogenation of heptane on such unsupported molybdenum oxide shows: unsaturates 11%, saturates 47%, hydrogen 41%.

Summary

1. Chromium and molybdenum oxide catalysts admixed with hydrocarbons are highly efficient for the removal of thiophene at 470°. With chromium oxide the greater part of the sulfur input comes off as hydrogen sulfide during the course of passage of vapor, hydrogen being pres-

ent. With molybdenum oxide, on the other hand, only traces of hydrogen sulfide appear during the run and the bulk of the recovered sulfur comes out in the regenerative oxidation.

2. The sulfur from the thiophene has a profound poisoning effect on the aromatization activity of the chromium catalyst, a drop of about 60% in the aromatic yield being observed.

3. The aromatization activity of the molybdenum catalyst is considerably enhanced by the passage of sulfur-containing hydrocarbons. An increase in aromatic yield from 21 to 64% was observed under optimum conditions. Sulfur in excess of the optimum depresses the activity but not to its original value.

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The Silicon Carbide Electrode

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It has been claimed by Kamienski¹ that an electrode made of silicon carbide (carborundum) when dipped into a solution gives a potential which is almost independent of the presence of oxidizing or reducing agents. This observation was assertedly verified by Lifschitz and Reggiani,² and the use of silicon carbide as one member of a bimetallic electrode pair in potentiometric titrations has been described by these workers and a number of others.³ In view of the great practical and theoretical importance of such an ideally inert electrode, we have investigated the electrode properties of silicon carbide. The results unambiguously show that a properly made silicon carbide electrode behaves as an ordinary oxidation-reduction indicator electrode like platinum or gold.

Experimental

The electrodes were made from large fragments and single crystals of silicon carbide ranging in color from clear, pale green (almost colorless) to deep blue and jet black. No difference in behavior due to color was observed. A few electrodes were made from rods of pressed Carborundum granules. Most of the material was kindly supplied by the Carborundum Company of America, to which we

express our appreciation for its cooperation. The electrodes were constructed by sealing the crystals or short sections of rod to the open ends of glass tubes by means of de Khotinsky cement. Electrical contact between the inner surface of the crystal and the wire to the potentiometer system was assured by pouring a little mercury into the tube. The behavior of the electrodes in potentiometric titrations was studied by measuring their potential against a suitable reference electrode (calomel or quinhydrone) and comparing it with the potential of a bright platinum electrode in the same solution and measured against the same reference electrode. Potential measurements were made with a potentiometer set-up, using a galvanometer with a sensitivity of 28 megohms.

Titration were made of potassium iodide with permanganate and with ceric sulfate, of ferrous iron with permanganate, of titanous chloride with ferric chloride, and of hydrochloric acid with sodium hydroxide. A typical set of results is shown plotted in Fig. 1. All the results led to the same conclusion, that the silicon carbide electrode behaves as a noble metal electrode, adopting the potential of the solution into which it is placed. In well-poised systems the silicon carbide electrodes almost immediately assumed the potential of the platinum electrode to within one or two millivolts. At the equivalence points they gave pronounced potential leaps, but did not attain the equilibrium values as rapidly as the platinum. This makes possible the use of the platinum-silicon carbide pair as a bimetallic electrode system. The use of this pair is hardly to be recommended, however, because various silicon carbide electrodes gave markedly different potential breaks against platinum.

A few of the electrodes did not behave in the normal manner, but, as Kamienski claimed, they maintained ap-

(1) B. Kamienski, *Z. physik. Chem.*, **A138**, 345 (1928); **145**, 48 (1929).

(2) I. Lifschitz and M. Reggiani, *Gazz. chim. ital.*, **61**, 915 (1931).

(3) (a) Kahlenberg and A. C. Krueger, *Trans. Am. Electrochem. Soc.*, **56**, 201 (1929); (b) J. A. Atanasiu and A. J. Velculescu, *Z. anal. Chem.*, **85**, 120 (1931).