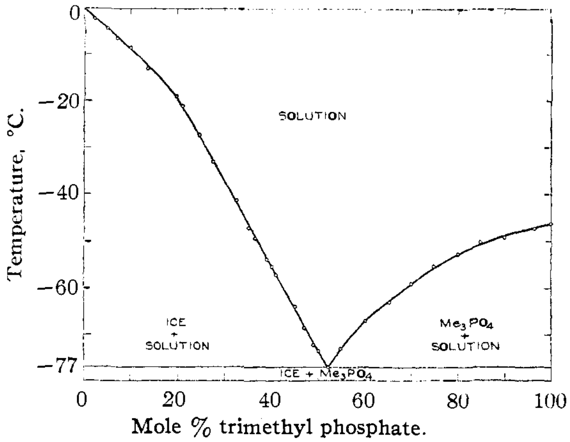

Fig. 1.—The system trimethyl phosphate–water.

Approximate freezing points of the various mixtures were first determined by supercooling several degrees below the anticipated freezing point and observing the maximum temperature rise obtained by seeding with a small amount of frozen solid of identical composition. After allowing the frozen fraction to melt, the mixture was again supercooled two-tenths to five-tenths of a degree below the approximate freezing point previously found, and seeded as before. The temperature gradient between the cooling bath and the ester–water mixture was controlled so that the change in freezing temperature due to the progressive freezing of the mixture was always less than 0.05° per minute. This allowed ample time to balance the potentiometer.

Discussion.—Mixtures ranging from about 35 to 80 mole per cent. of the ester were found to become decidedly viscous near their freezing points. Mixtures having compositions near that of the eutectic failed to freeze spontaneously even when cooled to −90°, and in such cases solid "seed" could be obtained only by seeding first with a small amount of the "alpha" solid ester.

The eutectic composition (52.0 mole % Me_3PO_4) was first estimated by extrapolation and then tested experimentally. The eutectic freezing point found was then checked by progressively freezing a 50.0 mole per cent. mixture which initially froze at −73.40° and fell to −77.00°, where the temperature remained constant until the mixture was practically frozen solid. This value agreed within 0.05° of that found for the extrapolated eutectic composition.

Summary

1. Freezing points of the system trimethyl phosphate–water have been studied.

2. The eutectic composition was found at 52.0 mole per cent. of the ester, with a freezing point of −77.0°.

3. Tabulated data, graphical representation and reference to experimental methods, and some discussion have been included.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dehydrogenation of Normal Heptane and Cyclohexane on Cerium, Vanadium and Thorium Oxide Catalysts*

BY RICHARD A. BRIGGS AND HUGH S. TAYLOR

In extension of our investigations on the dehydrocylization of normal heptane on chromium oxide catalysts, we have accumulated data on the aromatizing properties of the oxides of cerium, vanadium and thorium, published data being scanty and contained primarily in patents.[1,2,3,4] Moldavskii and Kamusher[5] investigated thorium oxide. In 1939, while this work was in progress, Koch[6] published data using narrow-boiling fractions of the product of the Fischer–Tropsch process, testing vanadium oxide.

Experimental Details

Apparatus.—The apparatus was essentially similar to that described in earlier work on chromium oxide catalysts.[7] In the final phase of the work the feed system for

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* Original manuscript received November 8, 1940.

[1] Wietzel and Pfaundler, U. S. Patent 1,910,910, May 1933; Convention Date, Nov. 1925.

[2] Mittasch, Pier, Wietzel and Langheinrich, U. S. Patents 1,913,940, 1,913,941, June 1933; Convention Date, Feb. 1926.

[3] Pier and Donath, U. S. Patent 1,975,476, Oct. 1934; Convention Date, Feb. 1926.

[4] Grosse and Morrell, U. S. Patents 2,124,566, 2,124,567, 2,124,583, 2,124,584, 2,124,585, 2,124,586.

[5] B. L. Moldavskii and H. D. Kamusher, *Compt. rend. Acad. Sci.* (USSR), **1**, 355 (1936).

[6] H. Koch, *Brennstoff-Chem.*, **20**, 1 (1939).

[7] S. Goldwasser and H. S. Taylor, THIS JOURNAL, **61**, 1260 (1939).

the hydrocarbon under study was patterned after that used by Hoog, Verheus and Zuiderweg.[8] This system of liquid feed proved to be very reproducible and constant for long periods of time.

Materials.—The normal heptane was the standard product of the California Chemical Company. Cyclohexane was of high grade prepared and purified by Professor John Turkevich of this Laboratory. The cerium oxide was a refined technical hydrated oxide. Analysis showed a trace of sulfur and iron. Ammonium metavanadate, C. P., was the source of the vanadium oxide. Activated alumina as a support was a commercial product (Alorco) of 10–14 mesh. Aluminum and thorium nitrates of reagent grade were the sources for the corresponding oxides.

Analyses.—The methods of analysis of gas and liquid products followed closely those described in our previous work on chromium oxide gel aromatization catalysts.[9]

Standard Procedure.—Except when otherwise noted the liquid was fed to 15 g. of catalyst at 2.45 ml. per hour. The rates of gas evolution at $t = 30$ and 120 minutes are recorded in the subsequent tabulations. The gas analysis was normally recorded on the sample collected after 120 minutes.

After each run the catalyst was regenerated by passing a 1:2 mixture of purified air and tank nitrogen over the catalyst mass for eight to ten hours and then reducing again with dry, oxygen-free hydrogen for eight to ten hours.

Preparation of Catalysts.—Catalyst 1, Cerium Oxide Gel: Ceric ammonium nitrate, 0.1 *N*, was precipitated with 0.1 *N* ammonium hydroxide added dropwise (3 drops per second) with vigorous stirring. The precipitate was washed, dried and heated in hydrogen to 450°.

Catalyst 2, Co-precipitated Cerium–Aluminum Oxides: Cerium ammonium nitrate and 0.1 *N* aluminum nitrate solution, to contain 4% CeO_2, was similarly precipitated with 0.1 *N* ammonium hydroxide, washed, dried and heated as in the previous case.

Catalyst 3, Rapidly Co-precipitated Cerium–Aluminum Oxides: A series of preparations ranging in cerium content from 2 to 10% were made with 1.5 *N* aluminum nitrate solutions and 1.5 *N* ammonium hydroxide.

Catalyst 4, This was identical with those of Catalyst 3 except that the gelatinous precipitate was more thoroughly washed.

Catalyst 5a, Cerium Oxide on Alumina: Twenty-four grams of activated alumina was immersed in 3.4 g. of cerium ammonium nitrate in 7 ml. of water and dried. The temperature was then raised to 400° during six hours in hydrogen, and reduced before use at 450° for twenty-four hours. Catalysts 5b, 5c and 5d were minor variants of this preparation. The final product in all cases contained 4% CeO_2.

Catalyst 6, Vanadium Oxide on Alumina: A solution of 3.86 g. of ammonium metavanadate in 10 ml. of water was made by adding enough oxalic acid to effect solution as a complex salt. To this 27 g. of activated alumina was added, dried at 100°, and decomposed at 300°. This yielded a 10% V_2O_5 catalyst. Catalysts of varying vanadium content were prepared according to this method.

Catalyst 7, Pure Vanadium Oxide: This was prepared according to the directions of Taylor and Yeddanapalli.[10]

Catalyst 8, Pure Vanadium Oxide: Ammonium metavanadate was heated at 200° and the resultant fine powder mixed with long-fibred asbestos.

Catalysts 9 and 10, Vanadium Oxide on Alumina with additional thoria (9) and alumina (10) deposits: Catalysts prepared as with Catalyst 6 were further impregnated with solutions of thorium and aluminum nitrates, respectively. Catalyst 9 contained 2% by weight of thoria based on the vanadium oxide–alumina mix. Catalyst 10 contained an equivalent molar concentration of alumina.

Catalyst 11, Vanadium Oxide in Aluminum Oxide Gel: Aluminum hydroxide was precipitated rapidly from a concentrated solution of nitrate and washed several times with distilled water. Ammonium metavanadate was stirred in until the mixture (15% V_2O_5) was as homogeneous as possible and the mixture was dried at 100°.

Catalyst 12, Thorium Oxide Gel: Thorium hydroxide was precipitated from 0.1 *N* solutions of the nitrate and ammonium hydroxide, added slowly.

Catalyst 13, Thorium Oxide on Alumina: A solution of 3.95 g. of thorium nitrate in 8 ml. of water was used to impregnate 28.5 g. of activated alumina.

Catalyst 14, Chromium Oxide on Alumina: A 10% chromium oxide catalyst was prepared from a solution of 4.97 g. of ammonium dichromate to which was added 27 g. of activated alumina.

Catalyst 15, Chromium Oxide on Alumina with Thorium Oxide Deposit: A sample of Catalyst 14 was impregnated further with a solution of thorium nitrate to furnish 2% by weight of the chromium–aluminum oxide mixture as thorium oxide.

Experimental Results

A selection of typical data on the behavior of cerium oxide catalysts toward heptane is given in Table I; for cyclohexane the data are in Table II. Typical data for 10% vanadium oxide on alumina are given in Table III, while Table IV shows the influence of catalyst composition with the same catalytic materials. Table V shows the effect of temperature on heptane dehydrogenation on thoria gels and supported thoria. Table VI shows a typical set of data on the dehydrogenation of cyclohexane on several of the catalysts studied with heptane. Table VII gives the results of extended tests during thirty-six hours on a 15% vanadium oxide–alumina gel (no. 11) catalyst at 490 and 510°.[11]

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(8) Hoog, Verheus and Zuiderweg, *Trans. Faraday Soc.*, **35**, 991 (1939).

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

(10) Taylor and Yeddanapalli, *Bull. Soc. Chim. Belg.*, **47**, 162 (1938).

(11) A detailed record of all the experimental results on these catalysts is to be found in the thesis of Richard A. Briggs, Princeton University, 1940. A copy of this thesis may be loaned through the Inter-Library Loan or micro-film can be obtained at cost on application to Hugh S. Taylor, Princeton University.

TABLE I

TYPICAL DEHYDROGENATION DATA FOR HEPTANE ON CERIUM OXIDE CATALYSTS

Cat. prepn.	Temp., °C.	Rate of gas evolution, cc./min. at *t* min. 30	120	Gas analyses, % Olef.	H_2	Satd.	Liquid analysis D^{20}_4	Olef.	Arom.
1	500	41	38	5.8	69.2	22.1	0.701	4.5	8.5
1	530	71	64	7.5	66.1	23.3	.713	7.8	16.1
2	555	64	74	15.4	54.9	25.8	.738	10.6	27.0
3	555	46	54	23.6	43.2	31.7	.697	10.2	5.7
4	555	45	56	16.5	50.2	29.8	.704	8.6	10.2
5a	555	49	61	26.5	39.5	30.4	.693	11.8	4.5

TABLE II

TYPICAL DEHYDROGENATION DATA FOR CYCLOHEXANE ON CERIUM OXIDE CATALYSTS

1	510	41	34	3.5	90.2	5.2	0.793	2.6	14.1
1	530	55	46	4.1	89.4	5.1	.801	2.6	22.3
5a	525	5	6	5.5	83.7	9.3	.780	1.2	1.3
5a	555	26	35	6.1	85.5	6.5	.785	4.8	4.2

TABLE III

TEMPERATURE EFFECT ON HEPTANE DEHYDROGENATION WITH 10% V_2O_5 ON ALUMINA

6	490	36	34	2.4	84.1	12.1	0.711	11.1	14.2
6	500	44	43	3.0	82.3	13.3	.725	11.7	20.6
6	510	52	56	3.4	80.9	14.6	.737	12.1	29.1
6	520	69	73	2.9	80.4	15.4	.756	10.1	38.9
6	530	88	91	2.9	79.7	15.4	.795	8.3	63.7

TABLE IV

EFFECT OF CATALYST COMPOSITION ON HEPTANE DEHYDROGENATION WITH V_2O_5 ON ALUMINA AT 510°

Cat. compn.									
2% V_2O_5	510	32	31	7.7	64.1	25.3	0.704	16.5	13.0
5%	510	49	57	4.4	76.1	17.8	.733	12.8	16.2
10%	510	52	57	2.5	81.5	14.5	.738	11.5	28.7
15%	510	75	74	2.8	83.2	12.1	.762	9.9	38.4
20%	510	69	61	2.9	82.4	12.5	.746	10.2	35.8
15%[a]	510	109	114	4.7	78.8	15.1	.820	7.2	75.6

[a] These data refer to Catalyst 11, vanadium oxide–alumina gel, the remainder to the preparations described as Catalyst 6.

TABLE V

TEMPERATURE EFFECT ON HEPTANE DEHYDROGENATION WITH ThO_2 GEL (CATALYST 12) AND DEPOSITED ThO_2 (CATALYST 13)

Cat. no.									
13 (5%)	525	19	24	21.4	40.4	34.3	0.688	8.4	0.2
13 (5%)	555	60	70	18.5	47.1	31.6	.714	15.3	10.3
13 (10%)	525	33	36	18.4	46.1	33.2	.693	12.4	0.6
13 (10%)	555	72	74	15.2	45.8	36.1	.723	11.7	16.3
12	525	38	29	14.5	58.4	23.6	.694	8.2	3.7
12	555	70	53	19.3	48.2	29.9	.702	14.4	7.2

TABLE VI

DEHYDROGENATION OF CYCLOHEXANE ON VARIOUS CATALYST PREPARATIONS OF VANADIUM AND THORIUM OXIDES

Cat. no. and compn.										
6	10% V_2O_5 on Al_2O_3	470	29	35	3.4	93.0	2.6	0.795	1.6	17.0
		490	49	58	3.8	90.7	3.6	.807	2.1	27.1
		510	76	81	4.1	89.3	4.3	.826	2.8	51.7
6	20% V_2O_5 on Al_2O_3	510	85	88	2.1	92.9	3.8	.833	3.2	59.8
7	Pure V_2O_5	510	54	17	1.8	90.0	6.2	.795	3.0	14.0
12	ThO_2 gel	555	51	42	2.4	91.2	5.6	.793	3.1	15.2
13	5% ThO_2 on Al_2O_3	555	44	59	3.7	86.5	9.2	.794	6.4	14.0
13	10% ThO_2 on Al_2O_3	555	49	71	3.4	85.6	9.1	.798	6.8	16.9

TABLE VII

HEPTANE DEHYDROGENATION ON VANADIUM OXIDE–ALUMINA GEL CATALYSTS

Gas Analyses					Liquid Analyses			
Cut at *t* hr.	Gas rate	Olef.	H_2	Satd.	Cut at *t* hr.	Sp. gr.	Vol. % Olef.	Vol. % Arom.
				T, 490°				
3	73	3.3	81.0	14.4	7	0.745	9.5	32.5
10	68	2.4	82.6	13.9	14	.745	9.4	32.7
21	51	3.0	81.5	13.7	21	.744	9.7	32.0
25	50	3.0	80.5	15.0	25	.733	9.8	26.0
30.5	49	3.0	79.8	15.4	30.5	.726	9.9	22.3
36	47	3.8	78.3	15.2	36	.724	10.2	20.4
				T, 510°				
0	106	2.4	78.1	17.8	6	.821	6.6	76.7
11	88	2.5	78.1	17.9	11.5	.799	8.4	62.6
14.5	87	3.0	78.0	17.6	15.5	.771	9.2	46.6
22	70	3.5	77.1	17.8	23	.763	10.3	42.4
29	61	4.6	75.1	18.5	30	.745	11.2	32.5
36	59	6.0	71.4	20.8	36	.737	12.3	29.1

Discussion of Results

Cerium Oxide Catalysts.—Dehydrogenation and cyclization of heptane both occur on these catalysts in the temperature range 480–530°. Cracking also occurs as indicated by the hydrogen content (~70%). Cracking yields hydrogen and a carbonaceous residue in addition to saturated and unsaturated hydrocarbons since the hydrogen collected is more than equivalent to the olefin-aromatic yield. From 2 to 10% of the heptane is cracked to hydrogen and carbon in the temperature interval studied, in addition to the gaseous hydrocarbons as cracking products. The yields of aromatics are small fractions of those claimed in the patent literature. Co-precipitated ceria–alumina catalysts give more olefins and saturated hydrocarbons than pure cerium oxide gel and have a much smaller rate of gas evolution. They, as well as the deposited catalysts, deteriorate less rapidly with time. With cyclohexane the rate of gas evolution is lower but the hydrogen content is higher than with heptane, due to a decrease in cracking with cyclohexane.

Vanadium Oxide Catalysts.—The 10% vanadium oxide on alumina is markedly superior to ceria. In the interval 470–530°, the hydrogen content is 80–84% and the toluene yield rises from 8.5 to 63.7%. An optimum concentration of vanadium oxide was obtained at 15%, lower contents giving lower toluene and more cracking. This points, as do the ceria results, to marked influence of the alumina on cracking. It suggests that in the 15% catalyst the alumina is effectively covered with vanadium oxide. Vanadium oxide–alumina gel catalysts are initially 50% better than the deposited catalysts and show long life as shown by Table VII. With cyclohexane, vanadium oxide shows marked dehydrogenating properties with less cracking than with *n*-heptane.

The data with both feed liquids indicate that vanadium oxide has good aromatizing properties. Direct comparison of 10% vanadium oxide with 10% chromium oxide on alumina at 510° indicates similar gas compositions but the aromatic contents of the liquids were 29 and 61%, respectively, with rates of gas evolution also in the ratio 1:2. Our data compare favorably with Koch's data on Kogasin gasoline,[6] but neither sets of data attain the conversions claimed in the patent literature.

Thorium Oxide Catalysts.—The data for thorium oxide with *n*-heptane prove conclusively that it is not a good catalyst for aromatization. None of our data compare with the claims set forth in the patent literature. Pure thoria gel is no better than the deposited catalysts. They are also poor agents for the dehydrogenation of cyclohexane.

From the scientific standpoint, the definite, if poor, dehydrogenating characteristics of thoria catalysts are of importance since hitherto these catalysts have been regarded as essentially dehydration catalysts. It is to be remarked that the dehydrogenation activity is manifested in a higher range of temperature than the dehydration activity and conforms in this respect to the behavior of alumina catalysts already discussed,[12] as to dehydration–dehydrogenation characteristics.

Summary

1. The aromatization of *n*-heptane and cyclohexane on ceria, vanadium oxide and thoria catalysts has been studied.

2. The influence of temperature, of mode of preparations, of deposition on supports and of reactant feed rate have been severally examined.

3. The order of aromatization activity is vanadium, cerium, thorium oxides.

4. Vanadium oxide is comparable with but inferior to chromium oxide.

5. Thoria, while possessing dehydrogenating activity, is a poor aromatization catalyst.

PRINCETON, N. J. RECEIVED JULY 24, 1941

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[12] H. S. Taylor, *Z. physik. Chem.*, Bodenstein Festschrift, 475 (1931).