[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# Chromium Oxide Gel Catalysts for Dehydro-cyclization of *n*-Heptane

BY JOHN TURKEVICH, HAROLD FEHRER AND HUGH S. TAYLOR

We record in the following various alternative methods of preparation of chromium oxide gels and their characteristics in the dehydro-cyclization of *n*-heptane.

## Experimental Details

**Catalyst Preparations. I. The Standard Gel.**—This was prepared by slow precipitation with 0.1 *N* ammonium hydroxide of chromium nitrate solutions in the dilutions and with the technique detailed by Kohlschütter.[1]

**II. Gel from a Chromium Oxide Jelly.**—100 grams of $Cr(NO_3)_3 \cdot 9H_2O$ and 33 g. of ammonium acetate were dissolved in 625 g. of water. The solution was heated to boiling for a brief interval and cooled to room temperature. A solution of 90 cc. of concentrated ammonium hydroxide in 250 cc. of water was then added with stirring and the whole slowly warmed on a water-bath, whereupon a strong, homogeneous jelly was formed. This jelly was cut into cubes and partially dried at 50–60° for twelve hours. The cubes were then washed by decantation with distilled water until nitrate and ammonium ions had been removed. The cubes were then heated at 50–60° to a hard, black vitreous material, which before use was raised slowly in temperature with further elimination of water and finally held overnight at 300°.

**III. Gel from Chromic Acetate.**—Two types of acetate preparations were studied; one which was green in color gave a light green, gelatinous precipitate which seemed to offer no especial advantages over the standard gel preparation. A black chromium acetate gave black jellies.

(a) Concentrated ammonium hydroxide was added to a boiling solution of 75 g. of black chromium acetate in 500 cc. of water with vigorous stirring until the solution was alkaline. A purplish-black precipitate was deposited which set to a jelly on cooling. This was washed by decantation until peptization of the chromium oxide was occurring. The product was filtered, dried for fifteen hours at 120° and raised slowly in temperature to 350° during twenty-four hours. The catalyst was black and friable.

(b) To 100 g. of black chromium acetate in 500 cc. of water, 100 cc. of concentrated ammonium hydroxide was added, with stirring at 28°; no precipitation occurred but the mass, after standing for twelve hours, set to a stiff black jelly. Washing by decantation showed incipient peptization after ten decantations. The catalyst dried as previously to 350° gave a hard, black product different from Preparation IIIa.

(c) The variation in this procedure from IIIb lay in a ten-fold dilution of the chromium acetate. A bluish precipitate was completely deposited. It dried down after washing to a hard, shiny black product.

**IVa. Amorphous Chromium Oxide by Reduction of Chromic Acid.**—The preparation of amorphous chromium oxide by the alcoholic reduction of chromic acid was reported by Traube.[2] We have developed this into a method of preparation of an active catalyst for dehydrocyclization of heptane. To 160 g. of chromium trioxide in two liters of water, eight 10-cc. portions of ethyl alcohol were added with shaking at five-minute intervals. The preparation became dark brown in color, heat was evolved, and precipitation of chromium oxide was evident after the first addition of alcohol. After the addition of all the alcohol the mixture was allowed to stand for four hours and the 80 cc. alcohol was added as before. The mixture was then boiled under reflux for sixteen hours. The dark chocolate precipitate thereby produced appeared unchanged after further reflux for twenty-four hours with 40 cc. more alcohol. After filtration, washing and drying at 120° the product was bluish-black in color.

Traube records that his product shows the characteristic glow phenomenon (Feuererscheinung) and our preparations behaved similarly in air, the product having a bright green color and negligible catalytic activity. If the preparation is heated very slowly (1° per minute) in a current of nitrogen until a temperature of 350° is reached, a temperature rise associated with the "glow" phenomenon sets in. The catalyst can then be raised slowly in temperature to 600° without great loss of activity and it maintains its black color.[3]

**IVb. Reduction of Chromic Acid by Sugar.**—A solution of 80 g. of chromic acid in 500 cc. of water was treated with a sucrose solution containing 12.75 g. in 25 cc. of water. After an induction period a violent evolution of gas occurred. When the reaction subsided the mixture was evaporated to dryness on a steam-bath and dried at 110°.

**IVc. Reduction of Chromic Acid by Oxalic Acid.**—A similar solution of chromic acid was treated with 113 g. of oxalic acid in 200 cc. water. The solution was added in portions over a day and the product was then evaporated to dryness, yielding 102 g. of black product which remained black even if heated to red heat.

**IVd. Reduction with Varying Amounts of Oxalic Acid.**—Eight portions each containing 40 g. of chromic acid in 250 cc. of water were reduced with different amounts of oxalic acid, 0, 12.6, 25.2, 37.8, 50.4, 63, 75.6 and 88.2 g., respectively. The first three did not give workable products. The remainder gave black products showing increasing activity to a maximum with the addition of 75.6 g. of oxalic acid. The material dried at 110° was used after heating in a stream of nitrogen to 470° followed by reduction for at least four hours in hydrogen.

**V. Crystalline Chromium Sesquioxide.**—This was prepared according to the directions of Schiff[4] by heating in

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[1] H. W. Kohlschütter, *Z. physik. Chem.*, **170A**, 300 (1934); *Z. anorg. allgem. Chem.*, **220**, 370 (1934).

[2] M. Traube, *Ann.*, **66**, 109 (1848).

[3] We wish to acknowledge with thanks the coöperation of members of the M. W. Kellogg Company's research staff in working out some of the details of this preparation and for the use of their observations on the influence of nitrogen on the "glow" phenomenon.

[4] Schiff, *Ann.*, **106**, 114 (1858).

TABLE I

DEHYDRO-CYCLIZATION OF *n*-HEPTANE ON CHROMIUM OXIDE CATALYSTS

| Catalyst | Temp., °C. | Rate of gas evolution in cc./min. at *t* min. = 20 | 60 | Hydrogen content of gas, % | $d_4^{20}$ | Liquid analyses Olef., wt. % | Arom., wt. % | Liquid feed used analysis, cc. |
|---|---|---|---|---|---|---|---|---|
| I | 475 | 70 | 58 | 91 | 0.717 | 15 | 15 | 0–40 |
| II | 425 | 19 | 12 | 96 | .689 | 6.5 | 8 | 0–23 |
|  | 475 | 60 | 40 | 94 | .707 | 15 | 13 | 0–30 |
| IIIa | 490 | 50 | 29 |  |  |  |  |  |
| IIIb | 475 | 48 | 35 | 95 | .714 | 12.8 | 25.5 | 0–10 |
| IIIc | 475 | 50 | 29 | 94 |  |  |  |  |
| IVa | 450 | 51 | 41 | 95 | .714 | 13.3 | 23.1 | 0–10 |
|  | 475 | 100 | 40 |  | .743 | 13.4 | 41.5 | 0–10 |
|  |  |  |  |  | .713 | 13.6 | 24.3 | 10–20 |
| IVb | 475 | 39 | 27 |  | .697 | 3.7 | 7.0 | 0–50 |
| IVc | 475 | 87 | 50 |  | .720 | 9.0 | 18.0 | 0–45 |
| IVd (max) | 475 | 42 | 27 |  | .708 | 7.9 | 12.1 | 0–24 |
| V | 475 | 3 | 1 |  |  | 0.4 | 0 | 0–36 |

a furnace equal weights of potassium dichromate and sodium chloride in a crucible, covered with a layer of sodium chloride. On cooling the product was washed free from chloride and chromate ions. The product was mixed with glass wool and heated *in situ* in hydrogen to 470°.

**Apparatus and Procedure.**—The apparatus used for the dehydrogenation reaction consisted of (1) gas trains for supplying and metering pure nitrogen, oxygen and hydrogen, (2) a heptane feed system, (3) a vaporizer, (4) a catalyst chamber and (5) means for collecting and sampling liquid and gaseous products at constant pressure.

In an experiment approximately ten minutes were required to produce steady state conditions due to the endothermic nature of the reaction and the temperature and flow-rate adjustments necessary. After this initial period, the feed rate could be kept constant within 2–3% and the working pressure controlled to 0.5 mm. Temperatures could be kept constant to ±1°.

**Analyses.**—Gas analyses were carried out for olefins, hydrogen and saturated hydrocarbons.

The analysis of the liquid samples involved (a) the pycnometric determination of specific gravity, (b) the Hanus method[5] of determination of the percentage of olefin hydrocarbons and (c) the Kattwinkel method[6] of absorption in sulfuric acid for the determination of the percentage of olefins plus aromatic hydrocarbons.

**Standard Procedure.**—For comparative purposes on different gel preparations heptane was passed over 15 g. of catalyst at a rate of 0.3 cc. per minute at 475°, for periods up to one hundred twenty minutes. Because of the initial period of adjustment the first reliable data are obtained after the first ten minutes. Accordingly, in Table I the rate of gas evolution is recorded after twenty and sixty minutes. The hydrogen percentage in the gas and the olefin and aromatic contents of the liquid are also given. The last column designates the part of the charge which gave the liquid product analyzed. Before each experiment the catalyst was submitted to a standard revivification technique involving flushing with pure nitrogen then with nitrogen plus 5% of oxygen for at least five hours, then with pure nitrogen, with hydrogen and finally with pure nitrogen.

Experiments with a catalyst of type IVa, prepared by alcohol reduction, for the dehydrogenation alternately of cyclohexane and of heptane with and without intermediate revivification showed that the dehydrogenation of cyclohexane shows no fall in activity during a run and does not affect a subsequent aromatization of heptane. On the other hand, in heptane dehydrogenation a fall in activity steadily occurs and this cuts down catalyst activity for subsequent dehydrogenation of cyclohexane.

## Summary

1. As alternatives to the preparation of chromium oxide gel by slow precipitation with dilute ammonia from dilute chromium nitrate solutions three methods of preparation have been studied: (a) the formation from a jelly, (b) precipitation as gel from chromic acetate, (c) reduction of chromic acid by alcohol and other organic reducing agents.

2. The activities of the four catalyst types have been examined as to dehydrogenation–cyclization activity toward normal heptane and as to the composition of the liquid product in olefins and aromatics.

3. Catalysts obtained by alcohol reduction of chromic acid possess high activities and are readily prepared in bulk.

4. Partial reduction of chromic acid with

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[5] H. C. Sherman, "Methods of Organic Analysis," The Macmillan Company, New York, N. Y., 1929, p. 153.

[6] R. Kattwinkel, *Brennstoff-Chem.*, **8**, 353 (1927); *C. A.*, **22**, 3039 (1928).

oxalic acid gives products of high aromatizing activity and readily prepared.

5. Reduction of chromic acid by sugar solutions gives only moderately active products.

6. The diminution in activity with time in the aromatization of heptane reduces the activity of the catalyst for dehydrogenation of cyclohexane.

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# Thermal Stability, Poisoning, Revivification and Reactivity of Chromium Oxide Gel Catalysts for Dehydro-cyclization

BY DONOVAN J. SALLEY, HAROLD FEHRER AND HUGH S. TAYLOR

We record, in the following, studies on the stabilization of chromium oxide gel catalysts to dehydrogenation at temperatures as high as 625°, together with data on the poisoning and revivification of the catalysts during use.

**The Binding of Water in Chromium Oxide Gel.**—Quantitative measurements have been made of the removal of water from gels in the temperature interval 300–550°. A 10-g. sample of Burwell's chromium oxide gel no. 5[1] was studied. It was reduced for sixty hours *in situ* with hydrogen while the temperature was slowly raised to 300°. The gel tube was then sealed off from all but the evacuating system and the gel was evacuated at 300° for twenty-four hours. No pressure built up in the system during an eight-hour period at 300° after pumping was discontinued.

The gel was then evacuated with mercury vapor and Sprengel pumps, in a definite temperature interval, and any water removed was condensed in a water trap at −180°. Pumping was continued until a pressure of no more than 1–2 mm. built up after isolating the gel from the pumps for eight hours. The water trap was then weighed and collected gases also measured. The data obtained are shown in Table I.

TABLE I

DESORPTION OF WATER FROM CHROMIUM OXIDE CATALYST

| Temp. interval, °C. | Time of evacuation, hr. | Water vapor removed, cc., N. T. P. | Hydrogen removed, cc., N. T. P. |
|---|---|---|---|
| 300–350 | 20 | 116 | 2.2 |
| 350–400 | 22 | 127 | 0.1 |
| 400–450 | 24 | 99 | .1 |
| 450–475 | 48 | 127 | .1 |
| 475–508 | 24 | 27 | .1 |
| 508–550 | 45 | 6 | ... |

Thus, 0.35 mole of water per mole of chromium oxide can be removed between 300 and 550° from a gel even after previous exhaustive evacuation at 300°. Negligible amounts of hydrogen are removed above 350° from such a gel but a definite amount is desorbed in the 300–350° interval. During the whole treatment there was no evidence of the "glow" phenomenon and the material retained both its black lustrous appearance and normal catalytic activity.

**Further Evidence of Gel Stability.**—The "ruggedness" of a standard gel catalyst was also shown by treatment of a 7.5-g. sample heated during forty-five minutes in hydrogen to 475°, then in one hour to 548° and then after one hour further to 612° with hydrogen continuously passing. After this treatment abrupt replacement, at 500°, of hydrogen by a nitrogen stream containing 5% oxygen, followed by a hydrogen stream each change giving a temperature rise of 30° did not decrease normal activity. The experiments indicate that color of the gel is not a sufficient criterion of a harmful glow phenomenon, the black color being indicative of an oxidized surface, the green color that of a reduced surface. A harmful "glow" phenomenon is obtained by rapid rise of temperature in presence of oxygen with an unstabilized gel structure.

**Catalyst Revivification.**—A progressive decrease in dehydrogenating activity with length of run and a corresponding decrease in the yield of aromatics in the liquid product occurs during dehydrocyclization. Flushing the catalyst with pure nitrogen or with pure hydrogen does not restore activity. By passing mixtures of nitrogen and oxygen over the poisoned catalyst for various times the original activity was completely restored. The gas stream was passed rapidly over the catalyst and only a portion of the oxygen content was used in the revivification process. The minimum time required for revivification varied with the oxygen content as shown in Table II.

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[1] R. L. Burwell, Jr., and H. S. Taylor, THIS JOURNAL, 58, 697 (1936).