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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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

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).

TABLE II

REVIVIFICATION WITH NITROGEN–OXYGEN MIXTURES

O_2 concn., %	0.2	2.0	5.0	20.5 (air)
Hours for revivification	40	12	5	3

During the process water and carbon dioxide were evolved and the temperature of the gel rose markedly. The process of revivification involves, obviously, a cleansing of the catalyst surface by oxidation of heavy carbonaceous material deposited during a run and acting as poisons. The cycle of dehydrogenation, poisoning and revivification was repeated on a single catalyst a large number of times during this investigation without any observed over-all decrease in catalyst activity.

The Effect of Water Vapor.—The effect of 3% water vapor was studied by observing comparatively the rate of gas yield from heptane–3% nitrogen and heptane–3% water vapor charges. This amount of water vapor produced a decrease in gas yield to one-fifth that in the heptane–nitrogen charge. The poisoning was only temporary, the rate being restored toward normal when the introduction of water vapor was stopped. The water vapor induced the "cracking" of heptane since the hydrogen content of the gaseous product fell from 88 to 73%, the unsaturates rose from 1.4 to 9.3% and the saturated hydrocarbons from 8.5 to 14.4%.

The effect of lower amounts of water vapor can be seen from Table III in which are compared gas evolution and analyses of liquid products obtained in the first half hour of a run on a chromium oxide gel prepared by alcohol reduction with 0.0, 0.5 and 1.0% of water vapor in the charge. The retardation involves decrease of toluene and not of olefins.

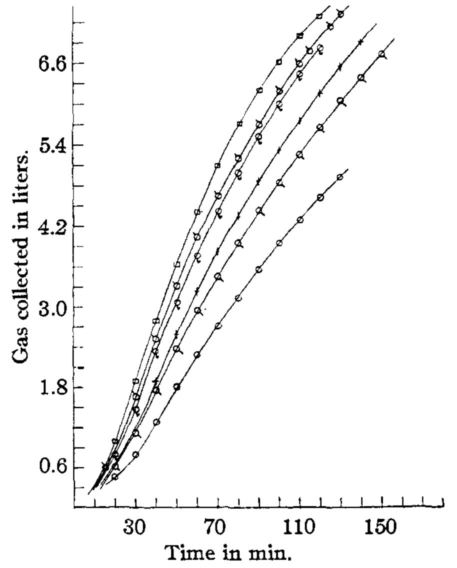

Fig. 1.—Influence of temperature on gas evolution from heptane on chromium oxide gel: ○, 476°; 🔍, 486°; ×, 496°; ♀, 506°; ɓ, 506°; □, 516°.

TABLE III

EFFECT OF WATER VAPOR ON HEPTANE DEHYDROGENATION AT 475°

Run	Water added, mole %	Rate of gas evolution cc./min. at *t* min. = 20	80	Liquid analyses d^{20}_4	Olefin, %	Aromatics, %
194	0	100	32	0.744	13.4	41.5
195	0.5	80	26	.739	13.5	37.6
196	1.0	68	15	.732	14.2	32.6

Influence of Temperature on Dehydrogenation Activity.—A series of experiments was carried out at 10° intervals from 476 to 526° and at larger intervals beyond these temperatures. Heptane was charged at 0.3 cc. of liquid per minute to 15 g. of standard gel catalyst with revivification before each run. Between 476 and 516° the rate of gas evolution approximately doubled as shown in Fig. 1, while the composition of the gaseous products was practically identical. A typical analysis showed: hydrogen, 90%; olefins, 2%; saturated hydrocarbon, 8%. The increase in dehydrogenation velocity over the range of temperature in question corresponds to an observed activation energy of 16.5 kcal.

Between 526 and 566° there is a further 60% increase in gas evolution. The reaction became less dehydrogenating, the second two liters of gas at 566° showing on analysis: H_2, 71.8%; olefins, 3.6%; saturated hydrocarbons, 19.7%. The surface became more rapidly poisoned. The catalyst was stable, intervening runs at 476° showing complete reproducibility.

At 586 and 626° higher rates of gas evolution were obtained with little tendency for the rate to fall. This was indicative of a change in reaction, dehydrogenation decreasing in favor of cracking reactions. The gaseous product at 626° analyzed: hydrogen, 13.8%; olefins, 51.3%; saturated hydrocarbons, 33.0%. The gel still retained its black vitreous appearance with no indication of sintering.

Summary

1. Chromium oxide gel has been found to be stable, when properly controlled, up to temperatures as high as 600°.

2. Dehydrogenation and aromatization of normal heptane is the predominant set of reactions up to 525°.

3. Conditions for revivification of spent chromium oxide gel catalyst have been defined.

4. Water acts as a transient poison for the dehydrogenation activity of the gel catalyst.

5. Transitions from black to green forms of chromium oxide gel catalyst have been found to represent states of oxidation of the catalyst and not active and inactive forms for the dehydrogenation and aromatization of liquid paraffins.

6. The glow phenomenon carried out in a nonoxidizing atmosphere, as in hydrogen or nitrogen, does not affect activity of the chromium oxide gel.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXI. Some Heat Capacity, Entropy and Free Energy Data for the Four Methylnonanes

BY GEORGE S. PARKS, THEO J. WEST AND GEORGE E. MOORE

The preparations and some physical properties of the four isomeric methylnonanes have been described by Calingaert and Soroos.[1] After the completion of their work, these investigators kindly loaned us samples of the compounds for our present study of the heat capacities at low temperatures and important thermodynamic properties derived therefrom.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[2] In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is probably less than 0.7%, except insofar as impurities in a sample may cause premelting at the upper temperatures of the crystals. The fortuitous errors were ordinarily under 0.25%; and this latter figure may also be considered our probable *relative* error in making comparisons among the decane isomers.

On an average about forty specific heat determinations in the temperature interval between 80 and 298°K. were made upon each of the methylnonanes. These results were then plotted on a large scale, a smooth curve through the experimental data was drawn, and specific heat values were read off from this curve for various even temperatures. For the sake of spatial economy and ease of comparison these derived values, rather than the more numerous experimental ones, are recorded in Table I. They and also the fusion data of Table II are expressed in terms of the *defined* conventional calorie[3] and with all weights reduced to a vacuum basis.

From the amount of premelting in the various fusion determinations we have obtained the following estimates of the purity of the compounds in mole %: 2-methyl, 99.1; 3-methyl, 99.7; 4-methyl, 99.3; and 5-methyl, 99.7.

Two of these methylnonanes, the 3-methyl and 4-methyl compounds, contain an asymmetric carbon atom and in these cases our liquid samples were really equimolal mixtures of the dextro and levo forms. On crystallization at low temperatures these liquids probably produce, like *d*-*l*-pinene,[4] a eutectic mixture of the *d* and *l* isomers. On this assumption we have estimated, with the aid of the data in Table II, that the freezing points of the pure 3-methyl and 4-methyl isomerides would really come at about 199 and 186°K., respectively.

With rather rapid cooling to the temperature of liquid air, the 4-methyl compound could be obtained readily as a glass; and we were able to make a series of measurements of the heat capacity of this undercooled, amorphous material. These results were similar to those obtained previously by the Nernst method with other glassy substances.[5] In this case they exhibit a sudden 75% rise in the temperature interval 109–122°. The specific heat values thus derived for the glass at the several even temperatures of the tabulation are given in the right branch of the fourth column

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[1] Calingaert and Soroos, THIS JOURNAL, 58, 635 (1936).

[2] Parks, *ibid.*, 47, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, 30, 47 (1926).

[3] The factor 1/4.1833 has been used in converting the international joule to this defined calorie.

[4] Ross and Somerville, *J. Chem. Soc.*, 2770 (1926).

[5] Parks, Thomas and Light, *J. Chem. Phys.*, 4, 64 (1936).