[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Nickel–Chromic Oxide Catalysts for the Hydrogenation of an Oil[1]

BY J. C. W. FRAZER AND C. B. JACKSON

The use of "copper chromite" prepared by the decomposition of copper ammonium chromate as a catalyst for the hydrogenation of the $\rangle C{=}O$ group in organic compounds has been described.[2,3]

These catalysts were prepared by the addition of ammonium hydroxide to a solution of copper nitrate and ammonium dichromate followed by the thermal decomposition of the resulting copper ammonium chromate. A nickel catalyst for the hydrogenation of ethylenic linkages, prepared by the decomposition of nickel ammonium chromate, was found to be extremely active. In the course of the investigation it was found that the presence of small but definite quantities of compounds of sulfur, selenium or tellurium gave rise to an increased activity. The purpose of this paper is to describe catalysts so prepared and to give results indicative of their activity for the saturation of ethylenic linkages of an oil.

Experimental

Preparation.—Lazier[2] and Adkins and Connor[3] both prepare their metal–chromic oxide catalysts by the addition of ammonium hydroxide to a solution of the metal nitrate and ammonium chromate followed by filtration, drying and ignition of the precipitate. In this study it was found advantageous to precipitate the nickel ammonium chromate by the addition of ammonium hydroxide to a concentrated solution of nickel nitrate and chromic acid. Thus, one mole (290.0 g.) of $Ni(NO_3)_2 \cdot 6H_2O$ and one mole (100.0 g.) of chromic acid were dissolved in 250 cc. of water and 3 moles of ammonium hydroxide added all at once while stirring rapidly. The yellowish red precipitate was filtered off on a Büchner funnel and washed once with approximately 50 cc. of distilled water to remove the mother liquor. The precipitate was dried at 110° after which it had the empirical composition of $Ni_2O \cdot (NH_4)_2 \cdot (CrO_4)_2$. This nickel ammonium chromate was then decomposed as described by Adkins and Connor[3] for copper ammonium chromate. The decomposed material had the composition of $Ni_2Cr_2O_5$. The yield was 92 to 98% of theoretical. The reduction product of this material will be referred to as Catalyst 1 or as the non-promoted nickel–chromic oxide catalyst.

A catalyst was prepared as above except that nickel sulfate was used instead of nickel nitrate. The nickel ammonium chromate was washed five times with distilled water, dried and decomposed. The $Ni_2Cr_2O_5$ so formed was then washed with hot water until the filtrate gave only a faint test for $SO_4^=$. A series of catalysts was then prepared by incorporating a definite quantity of a sulfur compound into the solution of nickel nitrate and chromic acid before precipitation.

Small quantities of the non-promoted "nickel chromite" were suspended in solutions of nickel sulfate to determine if the promoter effect could be obtained by incorporation of the sulfur compound after decomposition of the nickel ammonium chromate. The procedure was to suspend the powder in the liquid and stir vigorously for the time specified. The $Ni_2Cr_2O_5$ was filtered off, washed with 50 cc. of distilled water and dried at 110°. Table I shows the extent of such treatment.

TABLE I

Catalyst no.	Moles $Ni_2Cr_2O_5$	Solution	Concn. $NiSO_4$ g./100 g.	Duration treatment, min.
10	0.25	H_2O	...	15
11	.25	$NiSO_4$	1.0	15
12	.25	$NiSO_4$	3.0	15

Further preparations of catalysts were made as described above except that selenium oxide or tellurium oxide in varying amounts were added to the solution of nickel nitrate and chromic acid before the addition of ammonium hydroxide.

Reduction.—The catalyst was reduced by heating in a stream of hydrogen in the usual way. The temperature of the furnace was raised at the rate of approximately 120° per hour until 350° was reached at which point the temperature was held for at least four hours. The temperature was then raised about 90° per hour until 540° was reached. This temperature was maintained for half an hour, after which the tube and contents were cooled to room temperature, still in a current of hydrogen. The hydrogen was then swept out by means of a current of carbon dioxide, and the catalyst poured quickly into a weighed quantity of oil. In all cases the reduced material was quite black and pyrophoric.

Testing the Catalysts.—The experimental basis for the comparison of the catalysts is the extent of saturation produced in an oil by hydrogenating under set conditions. In all cases, catalyst containing 0.633 g. of nickel was suspended in 300 g. of cottonseed oil and heated to 180° for thirty minutes in the presence of hydrogen in a high speed autoclave illustrated in Fig. 1. Milligan and Reid[4] have shown that the rate of hydrogenation is roughly proportional to the rate of stirring. In the autoclave illustrated, a speed of 42,000 r. p. m. was attained by the stirrer. Hydrogen was passed into the oil directly from a cylinder of electrolytic hydrogen and was not regulated other than to maintain an excess.

The iodine numbers (Wijs) of the hydrogenated fats were determined; the lowering of the iodine number is a direct measure of the amount of hydrogenation which has

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[1] Taken from a dissertation presented by C. B. Jackson to the Faculty of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Lazier, U. S. Patent 1,964,000.

[3] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[4] Milligan and Reid, *Ind. Eng. Chem.*, **15**, 1048 (1923).

taken place and hence of the activity of the catalyst. The test for each catalyst was duplicated and found to check within ±3 iodine numbers.

Table II gives the iodine numbers of the fats obtained by hydrogenating cottonseed oil under conditions described above with the various preparations of catalysts. The iodine number of the original oil was 110.9.

TABLE II

Catalyst no.	Preparation	Iodine number of hydrogenated oil
1	$Ni(NO_3)_2 + CrO_3 + 3NH_4OH$	32
2	$NiSO_4 + CrO_3 + 3NH_4OH$ (washed thoroughly)	22
3	No. 1 + 16 g. $NiSO_4 \cdot 6H_2O$ per mole $Ni(NO_3)_2$	12
4	No. 1 + 8 g. $NiSO_4 \cdot 6H_2O$ per mole $Ni(NO_3)_2$	8
5	No. 1 + 4 g. $NiSO_4 \cdot 6H_2O$ per mole $Ni(NO_3)_2$	4
6	No. 1 + 2 g. $NiSO_4 \cdot 6H_2O$ per mole $Ni(NO_3)_2$	16
7	No. 1 + 4 g. BaS per mole $Ni(NO_3)_2$	14
8	No. 1 + 2.5 g. H_2SO_4 per mole $Ni(NO_3)_2$	7
9	No. 1 + 4 g. $CuSO_4$ per mole $Ni(NO_3)_2$	14
10	No. 1 washed with H_2O	36
11	No. 1 washed with 1% $NiSO_4$ solution	11
12	No. 1 washed with 3% $NiSO_4$ solution	13
13	No. 1 + 16 g. SeO_2 per mole $Ni(NO_3)_2$	107
14	No. 1 + 8 g. SeO_2 per mole $Ni(NO_3)_2$	108
15	No. 1 + 4 g. SeO_2 per mole $Ni(NO_3)_2$	108
16	No. 1 + 2 g. SeO_2 per mole $Ni(NO_3)_2$	14
17	No. 1 + 1 g. SeO_2 per mole $Ni(NO_3)_2$	4
18	No. 1 + 0.5 g. SeO_2 per mole $Ni(NO_3)_2$	7
19	No. 1 + 16 g. TeO_2 per mole $Ni(NO_3)_2$	107
20	No. 1 + 8 g. TeO_2 per mole $Ni(NO_3)_2$	109
21	No. 1 + 4 g. TeO_2 per mole $Ni(NO_3)_2$	4
22	No. 1 + 2 g. TeO_2 per mole $Ni(NO_3)_2$	4
23	No. 1 + 1 g. TeO_2 per mole $Ni(NO_3)_2$	6
24	No. 1 + 0.5 g. TeO_2 per mole $Ni(NO_3)_2$	11

The Quantity of Promoter in the Catalyst.—The results given above indicate that the addition of a small quantity of sulfur, selenium or tellurium compound to the catalyst enhances the activity considerably. The actual quantity is quite small since some of the promoting element is removed with the mother liquor when filtering and washing the ammonium complex, and some is removed during the reduction period as hydrogen sulfide, hydrogen selenide or hydrogen telluride. Since compounds of sulfur, selenium or tellurium in smallest concentrations are usually considered to be quite poisonous to catalysts the selenium content of several of the selenium promoted nickel-chromic oxide catalysts was determined by the method of Robinson, Dudley, Williams and Byers.[5]

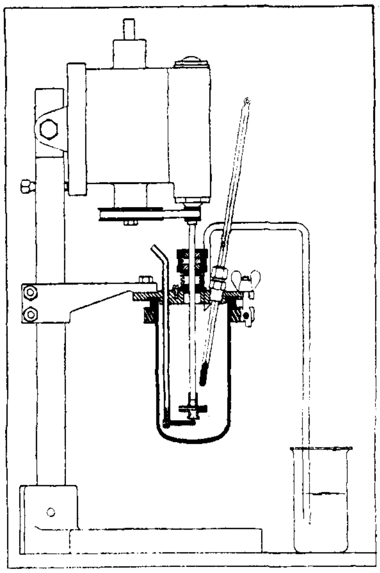

Fig. 1.—High-speed autoclave.

Table III gives the selenium content of four catalysts before and after reduction by hydrogen.

TABLE III

Catalyst	%Se before reduction	%Se after reduction
15	0.44	0.08
16	.31	.03
17	.28	.02
18	.25	.00

Discussion

The reduction of the material obtained by the decomposition of nickel ammonium chromate furnished a hydrogenation catalyst which is interesting in several respects. The catalyst is quite easy to prepare, requiring little or no washing. The nickel chromic oxide catalysts described have a theoretical nickel content of 43.5% which is considerably higher than the nickel content of the usual catalyst prepared by the precipitation of the hydroxide or carbonate on diatomaceous earth. Due to the fact that a definite chemical compound is formed in its preparation the activity of the catalyst can be easily duplicated within very narrow limits and this activity is considerably greater than that of catalysts prepared by usual methods. Hydrogenated fats obtained

(5) Robinson, Dudley, Williams and Byers, *Ind. Eng. Chem., Anal. Ed.*, **6**, 274 (1934).

by the prescribed test using catalyst prepared by the precipitation of nickel on kieselguhr[6] had an iodine number of 48 to 55, while under the same conditions of testing, the nickel–chromic oxide catalyst consistently gave hardened fats of iodine number of 29 to 35. With the promoted catalysts, using one of the promoting substances, sulfur, selenium or tellurium in its optimum concentration, it was possible to obtain, consistently, hardened fats of iodine number 2 to 7 under the same conditions as to concentration of catalyst, time, temperature and degree of agitation. It is a generally accepted fact that even the most minute quantities of compounds of sulfur, selenium or tellurium are extremely deleterious to the activity of hydrogenation catalysts, and especially so when those compounds are associated with the catalysts at high temperatures, as during the reduction. Such is true in higher concentrations as exemplified by catalysts 13, 15, 19 and 20 above. However, when the concentration is less there is actually an increase of activity over that of catalysts prepared in exactly the same way but with the strict exclusion of all traces of the so-called promoter elements. Further as the concentration is made still less the activity of the catalysts diminishes and approaches that of the unpromoted catalysts. The same degree of enhancement of activity is produced by each of the promoting elements sulfur, selenium and tellurium but at slightly different concentrations of each of the three due to the difference in solubility of the compounds in the mother liquor from the preparation of the nickel ammonium chromate. Catalysts 11 and 12 indicate that the promotion by a sulfur compound can be brought about by the addition of the sulfur compound after the decomposition of the nickel ammonium chromate and that it is not entirely necessary to have the sulfur compound incorporated at the time of the precipitation.

No explanation for the promotion of the activity of hydrogenation catalysts by substances usually considered to be virulent catalyst poisons can be offered now.

Summary

1. Catalysts composed of nickel and chromic oxide have been shown to be of high activity for the hydrogenation of an oil.

2. The use of small quantities of the compounds of sulfur, selenium and tellurium for the promotion of the activity of nickel–chromic oxide catalysts for the hydrogenation of an oil has been described.

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[6] Reid and Rather, THIS JOURNAL, 37, 2116 (1915).

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The Oxidation Potential of Thallous and Thallic Salts

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Introduction

The ease of oxidation of thallous to thallic salt varies greatly with the nature of the anion present. Thus thallous chloride in hydrochloric acid solution is much more easily oxidized than is thallous sulfate or thallous nitrate in solutions of sulfuric or nitric acid. This difference is due mainly to the fact that the thallic ion, which is the primary oxidation product of thallous ion, is more or less converted into a complex anion with a consequent displacement of the equilibrium conditions of the thallous–thallic ion reaction of oxidation. The extent of such complex-ion formation, and hence the magnitude of the effect, varies with the nature of the anion of the salt and acid present.

Spencer and Abegg[1] have studied this effect of complex-ion formation quantitatively by measuring the oxidation potential of the reaction of reduction of the thallic salt for the cases cited above. Later Grube and Hermann[2] made a more careful determination at 18° of the oxidation potential of thallic to thallous sulfate in sulfuric acid solution. They showed that the oxidation potential is nearly independent of the concentration of the sulfuric acid, and that, when referred to the molal hydrogen electrode, it varies with the ratio, $(\Sigma \text{Tl}^{+++})/(\Sigma \text{Tl}^{+})$, of the two salt concentrations, expressed as formula weights per liter, in accordance with the simple equation

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[1] Spencer and Abegg, *Z. anorg. Chem.*, 44, 379 (1905).

[2] Grube and Hermann, *Z. Elektrochem.*, 26, 291 (1920).