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John Turkevich

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Magnetic Studies of Chromium Oxide Catalysts

JOHN TURKEVICH

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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The magnetic susceptibility of active chromium oxide gel and "glowed" inactive chromium oxide was measured from liquid air temperature to 444°C and no difference in magnetic behavior was noted. Activated adsorption of hydrogen does not markedly affect the magnetic susceptibility of the active gel catalyst. The interaction of chromic nitrate with ammonia, filtration, and drying results in a chromium oxide intermediate in oxygen content to Cr_2O_3 and CrO_3 . Revivification of the catalyst by oxygen treatment results in a similar chromium oxide. Mechanism for the preparation of an active chromium oxide catalyst and a structure for such an oxide have been proposed.

CHROMIUM oxide gel obtained by slow interaction in dilute solution of chromic nitrate and ammonia has been found to be an efficient catalyst in various hydrogenation-dehydrogenation reactions of hydrocarbons. This gel catalyst is unstable with respect to crystalline chromic oxide and reverts to the latter undergoing "the glow phenomenon." The crystalline chromic oxide so obtained is inactive for reactions for which the gel form is active.¹ Differentiation between the two forms by chemical analysis is complicated by the fact that it is difficult to distinguish between the oxygen held in the water of hydration and the oxygen associated directly with the chromium atom due to a valence of chromium greater than three. It was therefore thought of interest to see whether the differences in catalytic properties between the gel and the crystalline form reflected itself in differences in magnetic characteristics. A magnetic study was also made of substances obtained at various stages of the preparation of standard chromium oxide gel catalyst.

MATERIALS

Sample A1

Standard chromium oxide gel was prepared by slow precipitation of chromic nitrate with dilute ammonium hydroxide solution. The product was washed free of ammonium and nitrate ions, filtered, and dried overnight at 110° C.²

¹ Turkevich, Fehrer, and Taylor, *J. Am. Chem. Soc.* **63**, 1129 (1941).

² V. Kohlschutter, *Zeits. f. anorg. u. allgem. Chemie* **220**, 370 (1934).

Sample A2

The product A1 was reduced by purified hydrogen at 475°C until no more water was formed. The sample was then pumped off by a mercury diffusion pump at 475°C for three days to remove the adsorbed hydrogen. It was then cooled to room temperature and purified nitrogen was introduced.

Sample A3

The product A1 was reduced by a stream of hydrogen at 475°C until no more water was formed and, to insure chemisorption of hydrogen, cooled to room temperature in the course of twenty-four hours in hydrogen.

Sample A4

The product A1 was reduced *in situ* in a catalytic reaction vessel and used for the dehydrogenation of *n*-heptane to toluene until the catalyst was thoroughly poisoned. The catalyst was then treated for twelve hours with nitrogen containing about 2 percent oxygen to burn off the carbon deposited on the surface. The catalyst was cooled in nitrogen.

Sample B1

This sample was chromium oxide prepared by the interaction of one molar solution of ammonium hydroxide and chromic nitrate at 100°C, repeated washings, filtration, drying, and reduction with hydrogen slowly raising the temperature to 450°C. It should be noted that during the careful reduction with hydrogen, the oxide

underwent a glow phenomenon at about 150°C and that the resultant product was an inactive "crystalline" form of chromium oxide.

PROCEDURE

The magnetic susceptibilities were determined by the Gouy method using the apparatus described by Turkevich and Selwood.³ Temperatures above room temperature were obtained by appropriate vapor baths.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the magnetic measurements are given in Table I. None of the samples studied was ferromagnetic in the temperature range studied.

Comparison of the results obtained on active sample A3 and inactive sample B1 shows that within the error of the magnetic measurement, there is no difference in the magnetic susceptibility between the active and inactive forms. These two forms show, however, marked differences in catalytic activity¹ and in hydrogen adsorption characteristics.⁴

Comparison of measurements obtained with samples A2 and A3 shows that activated adsorption has little effect on the susceptibility of chromium oxide in the temperature range studied.

The values obtained on samples A2, A3, and B1 agree well both in absolute value and temperature dependence with the results reported in the literature for Cr₂O₃.⁵

Measurements on samples A1 and A4, samples obtained before hydrogen reduction and after treatment with oxygen, respectively, reveal a marked difference in magnetic characteristics from the samples previously examined. The values of the magnetic susceptibility are higher and markedly temperature dependent, suggesting the identification of these samples with oxides intermediate in oxygen content to Cr₂O₃ and

CrO₃. There has been considerable confusion concerning such oxides, but recent investigation of Bhatnagar, Cameron *et al.*⁵ reports the existence of a dioxide and two non-stoichiometric oxide ranges CrO_{2.6-2.2} and CrO_{1.9-1.7}, the values of magnetic susceptibility for the different samples lying between 42.2 and 26.9 × 10⁻⁶. Their magnetic measurements on the effect of oxygen and hydrogen were less conclusive than those obtained in this investigation because they measured this effect at one temperature and also because the chromium oxide they used was of inferior catalytic activity than the gel standard form.

On the basis of the results of this investigation the following mechanism for the formation of the active chromium oxide catalyst is suggested: The precipitation, washing, filtration, and drying at 110°C of the product of interaction of chromic

TABLE I. Specific susceptibilities × 10⁶ of chromium oxides.

| | 90 | 184 | 273 | 373 | 457 | 575 | 707°K |
|----|----|-----|-----|-----|-----|-----|-------|
| A1 | — | 54 | 41 | 37 | — | — | — |
| A2 | 21 | 19 | 21 | — | — | — | — |
| A3 | 20 | 19 | 21 | 22 | 21 | 19 | 18 |
| A4 | — | 40 | 35 | — | — | — | — |
| B1 | 21 | 20 | 21 | 22 | 21 | 19 | 18 |

nitrate and ammonia result not in the formation of a hydrate of chromium sesquioxide but of a hydrate of an oxide higher in oxygen content than that demanded by the formula Cr₂O₃. This oxygen is removed from the solid by hydrogen reduction. The process of catalyst revivification⁶ results not only in the removal of carbon from the surface but also in a reoxidation of the catalyst to this higher oxide. Since it has been established that the catalytic activity is not impaired by the revivification process, the active catalyst must have sufficient open structure to accommodate this oxygen. This view has been substantiated by the preparation of a very active catalyst by the reduction of chromic acid to an "intermediate" oxide by alcohol, drying, and final reduction with hydrogen.¹

³ J. Turkevich and P. C. Selwood, J. Am. Chem. Soc. **63**, 1077 (1941).

⁴ R. L. Burwell and H. S. Taylor, J. Am. Chem. Soc. **58**, 1753 (1936).

⁵ S. S. Bhatnagar, A. Cameron, E. H. Harbard, P. L. Kapur, A. King, and B. Prakash, J. Chem. Soc., p. 1437 (1939).

⁶ D. J. Salley, H. Fehrer, and H. S. Taylor, J. Am. Chem. Soc. **63**, 1131 (1941).