Hydrogen–Deuterium Equilibration and Parahydrogen Conversion over Ruby, Chromia, and Chromia on Alumina

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Abstract: Supported chromia on alumina catalyst has great activity for the hydrogen–deuterium equilibration reaction above about 200°. This is caused by a disperse phase of chromia quite different from massive (crystalline) chromia which has virtually no activity. The active disperse phase is characterized by its low, but not negligible, antiferromagnetic exchange interaction. Ruby (a dilute solid solution of chromia in alumina) has almost no equilibration activity, but it possesses a very large parahydrogen magnetic conversion activity. The chromium ions on the surface of ruby are accessible to hydrogen, but they are subject to rapid poisoning by hydrogen at moderately elevated temperatures. The failure of ruby to show appreciable equilibration activity is due not to the failure to chemisorb hydrogen, but either to the lack of chromium–chromium ion pairs, or possibly to the stabilization of the 3+ oxidation state, or to both. All rate data were over equal numbers of accessible chromium ions under conditions to ensure freedom from contamination.

This work is part of an attempt to identify more precisely those structural attributes responsible for catalytic activity in transition metal oxides. The present paper is an amplification and extension of results previously reported on chromium sesquioxide systems.[1] Chromium sesquioxide was chosen for this study because of the wealth of information already available on it as a catalyst and adsorbent, and because of its importance in catalytic dehydrogenation. It is, for instance, known that chromia/alumina catalysts and self-supported chromia gels exhibit a substantially diminished, though not negligible, antiferromagnetic exchange interaction as compared with massive (crystalline) chromia, and this effect has been used to show that the chromia in chromia/alumina is aggregated into very small particles on the surface of the alumina, rather than forming a true two-dimensional solid solution.[2] This conclusion has been confirmed by O'Reilly,[3] and others, who have also shown by epr studies that some of the chromium ions in chromia/alumina are at a low magnetic concentration and must be considered to be isolated from other chromiums. But the results of attempted oxidation show that these isolated ions are probably not accessible to reactant gases.[4] It has also been proposed by several groups[5–7] that chromium in the dipositive state may be present under certain conditions, and it is generally accepted that some possible change of oxidation state is helpful, if not essential, for catalysis of the hydrogen–deuterium equilibration.

A difficulty in the search for structural sources of catalytic activity is that many different atomic environments are to be found at the surface of any practical solid catalyst. It was thought that ruby (a dilute solid solution of chromia in alumina) would present certain simplifications, namely, that the number of different atomic environments present at the surface is less and that exchange interaction is minimized. In ruby, at the chromia concentration used, the concentration of chromium–chromium ion pairs is roughly ascertainable from the law of mass action and, for the purposes of this work, is believed to be negligible.[8]

The work described in this paper consisted of hydrogen–deuterium equilibration[9] and parahydrogen conversion over powdered ruby, over powdered chromia derived from a single crystal, and over a typical supported chromia/alumina dehydrogenation catalyst. An attempt was made to adjust the space velocity (by altering the catalyst mass) so that each catalyst system offered the same total number of chromium ions accessible to molecular hydrogen. Measurements were also made on pure powdered sapphire (α-alumina).

Experimental Section

Catalyst Preparation. Large broken pieces of synthetic ruby were obtained from Union Carbide Corporation, Linde Division. It was necessary to powder the ruby and, in view of its hardness, the grinding was done with a pure alundum mortar and pestle in a motor-driven assembly. This procedure resulted in substantial contamination with alumina, the final concentration of chromia being 1.1 atom % as determined by analysis. Contamination with α-alumina presented no objectionable feature, but the possibility of concomitant contamination with any catalytically active metal, or other species, could not be tolerated. X-Ray fluorescence analysis revealed no intolerable contamination. However, confidence in the catalytic purity of the powdered ruby was established by treating colorless synthetic sapphire (crystalline α-alumina), also from Linde, in exactly the same way. All activity data found over the powdered ruby were compared with those over the powdered sapphire, the latter being found to be only slightly more active than the empty reactor. It is well known that ruby turns dark when it is heated to 500°, but this is reversible. A tendency for both ruby and sapphire to remain very slightly gray after being heated in hydrogen at 500°, in the reactor, was possibly due to a trace of carbonaceous matter in the gases used in their manufacture, or subsequently adsorbed. Cycling in oxygen and then in

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[1] P. W. Selwood, *J. Am. Chem. Soc.*, **87**, 1804 (1965).

[2] R. P. Eischens and P. W. Selwood, *ibid.*, **69**, 1590 (1947).

[3] D. E. O'Reilly, *Advan. Catalysis*, **12**, 31 (1960).

[4] L. L. Van Reijen, W. M. H. Sachtler, P. Cossee, and D. M. Brouwer, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, 829 (1965).

[5] J. Givaudon, E. Nagelstein, and L. Leygonie, *J. Chim. Phys.*, **47**, 304 (1950).

[6] S. W. Weller and S. E. Voltz, *J. Am. Chem. Soc.*, **76**, 4695, 4701 (1954).

[7] R. L. Burwell, A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *ibid.*, **82**, 6272 (1960).

[8] A. L. Schawlow, private communication.

[9] Following current practice [J. J. F. Scholten and J. A. Konvalinka, *J. Catalysis*, **5**, 1 (1966)] *equilibration* is used to mean the heterogeneously catalyzed reaction between gas-phase hydrogen isotopes. *Conversion* means the catalytic change of parahydrogen to an equilibrium ortho–parahydrogen mixture. However, the word *exchange* is not used here for a catalytic reaction but is rather reserved for the Heisenberg exchange interaction between adjacent chromium ions. No attempt is made in this paper to distinguish between equilibration, defined as above, and the reaction of a gas-phase molecule with an adsorbed molecule.

hydrogen at 500° removed this grayness, but the oxygen treatment had a negligible effect on the catalytic activity of either sapphire or ruby. The specific surface of the powdered ruby was 2.0 m^2 (BET, N_2). Examination of the conversion data given below shows that it is probably correct to assign most of this area to the ruby rather than to the alumina inadvertently added.

Single crystal chromium sesquioxide was also obtained from Linde. It was easily powdered to a specific surface of 14.6 m^2. Except in one experiment, as described below, the crystalline oxide was heated merely in hydrogen, in the reactor, at 500° prior to use.

Chromia/alumina was prepared in the usual way by impregnation of "gamma" alumina with chromic acid solution, followed by drying, ignition, and reduction in hydrogen at 500°. The chromia concentration was 5.0 atom %, and the specific surface 200 m^2. This surface is, of course, that of the whole catalyst and not merely that of the chromia. A Harshaw chromia/alumina dehydrogenation catalyst containing the same chromia concentration gave almost identical results. Both were heated in hydrogen to 500°, in the reactor, prior to use.

Estimation of Accessible Chromium. The purpose of the work was to compare catalytic activity per chromium ion accessible to hydrogen in each of the preparations. There are experimental methods based on reaction kinetics for determining the surface concentration of active sites, but they do not seem appropriate for systems in which the activity, and specificity, was expected to be, and was found to be, greatly different from sample to sample. An attempt was therefore made to determine the probable chromium ion concentration by consideration of the geometry for each sample. While this method is crude, it must be pointed out that the results are in reasonable agreement with the conversion data and, furthermore, that an error by a factor of 100 does not invalidate the final conclusions reached concerning the active catalyst species for equilibration.

We consider first the ruby and the concentration of Cr^{3+} ions on the surface of a close-packed layer of O^{2-} ions. The O^{2-} ion surface packing efficiency is 90.7%, and the radius 1.4 A. Hence, a 1-g sample of surface 2.0 m^2, all attributable to close-packed O^{2-}, would contain

$$\frac{2.0 \times 10^4 \text{ cm}^2 \text{ g}^{-1} \times 0.907}{\pi (1.4 \times 10^{-8})^2 \text{ cm}^2} = 2.95 \times 10^{19} \text{ O}^{2-} \text{ ions g}^{-1}$$

Resting on this plane, prior to fracture of the crystal, the number of metal ions (Al^{3+} or Cr^{3+}) will be two-thirds the number of O^{2-}, each of these being in an octahedral hole. Subsequent to fracture between the close-packed planes the number of metal ions exposed on each face will be one-third the number of O^{2-}, this being necessary to maintain local electrical neutrality. Each of the surface metal ions exposed in this way

 equivalent to

$$\begin{matrix} & O^{2-} \\ O^{2-}\text{-}Cr^{3+} & \\ & O^{2-} \end{matrix}$$

should be able to accept either one or three adsorbate ligands to form a tetrahedral or an octahedral complex, respectively. However, the close-packed face is not the only one to be exposed. It will be arbitrarily assumed that metal ion exposure on other faces is slightly less, and that a correction factor of $^2/_3$ is not unreasonable. This yields $(2.95 \times 10^{-19})(^1/_3)(^2/_3) = 6.56 \times 10^{18}$ metal ions g^{-1}, and, of these, an average 1.1% is chromium. This gives 7.2×10^{16} Cr^{3+} ions on the surface per gram of ruby.[10]

The method for obtaining Cr^{3+} ion accessibility in the crushed single crystal of Cr_2O_3, and which had a specific surface of 14.6 m^2, is the same as for the ruby except that here all the metal present is Cr^{3+}. The result is 4.8×10^{19} Cr^{3+} ions on the surface per gram of sample.

The supported Cr_2O_3/Al_2O_3 catalyst offers more difficulty. It is known that a fairly large fraction of the Cr^{3+} ions must be on the surface, but exactly what this fraction is cannot readily be determined. From the total known concentration of chromium as Cr_2O_3, namely 5.0 atom %, it is clear that 1 g of catalyst contains 8.0×10^{20} Cr^{3+} ions. Knowing that most of this chromia is aggregated, but that the aggregates are so small as to exhibit much diminished exchange interaction, we shall arbitrarily assume that $^1/_{20}$ of the Cr^{3+} ions is exposed. (It is difficult to see how this estimate could be in error by a factor larger than 10.) Consequently 1 g of supported catalyst has 4.0×10^{19} Cr^{3+} ions on the surface.

In all the work described below, with one exception duly noted, the weights of samples used were as follows: ruby, 1.00 g; crystal, 1.5 mg; Cr_2O_3/Al_2O_3, 1.8 mg.

By using this method of adjusting the space velocity at constant hydrogen, or deuterium, flow rate it was hoped to have the accessibility of chromium to hydrogen the same in all cases. But the fraction of the chromium present as chromium–chromium ion pairs; that is to say, the fraction of chromium present in the normal relationship as in massive sesquioxide was only 0.25% for the ruby, while it was 100% for the crystal. It is impossible to say what the fraction was for supported chromia, but the magnetic susceptibility data[2] and the epr results[3] show that it is certainly larger than for ruby and less than for crystal.

Reagents. The hydrogen (electrolytic) used was purified by passage through an Engelhardt palladium diffusion process purifier. The deuterium had its own purifier. Helium, used in the chromatographic analysis of hydrogen-deuterium mixtures, was purified by passage over copper oxide at 600°, then through silica gel (Tel-Tale) desiccant at −196°.

Reactor. A flow system was used, the reactor being of Vycor with the catalyst placed on a medium porosity fritted Vycor disk 20 mm in diameter. For a 1-g sample of powdered ruby this gave a bed thickness of about 1 mm. The gas flow was in a downward direction at 50 ml (STP) min^{-1}, as monitored on a calibrated Matheson 610 flowmeter. The pressure was 1 atm. Owing to the essentially nonporous nature of the catalysts used (except possibly for the chromia/alumina), it was not considered necessary to work at lower pressures to avoid diffusion effects.

The reactor was enclosed in a large Hevi-Duty furnace which, with appropriate programming controls, held the temperature within ±2° from 25 to 500°, and ±5° from 500 to 800°. Alternatively, the temperature could be raised or lowered at any rate up to 50 deg min^{-1}. The sensing thermocouple was in a Vycor well which actually touched the catalyst. Prior to use the reactor was washed with boiling nitric acid, then repeatedly with distilled water. It was then heated to 600° with oxygen flowing through the system and then with hydrogen after introduction of the catalyst sample.

Parahydrogen Analysis. Hydrogen from the diffusion purifier was passed over two wires of the four-wire Gow-Mac TRIII A, W2, thermal conductivity cell assembly, which was operated at 60°. Sensitivity was more than sufficient even at this elevated temperature, and no conversion as a result of contact with the tungsten wires could be detected under the conditions used. The hydrogen gas stream was then led through a converter at −196°. This was filled with commercial chromia/alumina catalyst pellets which possessed more than enough conversion activity for the purposes of this work. The converter was carefully packed with Pyrex wool to prevent any passage of catalyst dust out of the liquid nitrogen bath, which was kept filled by an automatic regulator. Subsequently, the approximately 1:1 para-orthohydrogen mixture was passed through an empty cold trap, then into the reactor. Emerging from the reactor the hydrogen stream was passed through another empty cold trap and then over the second pair of wires in the thermal conductivity cell. Finally the hydrogen reached exit through the flowmeter. The output from the Gow-Mac 405 C 1 power and control unit was monitored on a Leeds and Northrup W 1-mv recorder. Sensitivity was about ±1.0% of full-scale deflection which was adjusted to represent complete 1:1 to 1:3 para to ortho conversion.

Hydrogen–Deuterium Analysis. Hydrogen and deuterium from separate diffusion purifiers were mixed in a 1:1 volume ratio, then led as above, bypassing the converter but through an automatic sampling valve operating, generally, every 20 min. The main gas stream then went on to flowmeter and exit. The 1-ml gas sample extracted was analyzed chromatographically, essentially as described by Moore and Ward.[11] The sample was carried in a purified helium stream moving at 70 ml (STP) min^{-1} through 18 ft of $^1/_8$ in. o.d. stainless steel tubing filled with 150–200 mesh acti-

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(10) D. A. Dowden (Coloquio sobre Quimica Fisica de Procesos en Superficies Solidas (Madrid 1964), 1965, p 177) regards this problem of surface exposure in metal oxides rather differently, considering the loss of only one O^{2-} ligand from the octahedral complex. Whatever may be the relative merits of the two approaches, there is no important difference in our final conclusions.

(11) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, 80, 2909 (1958).

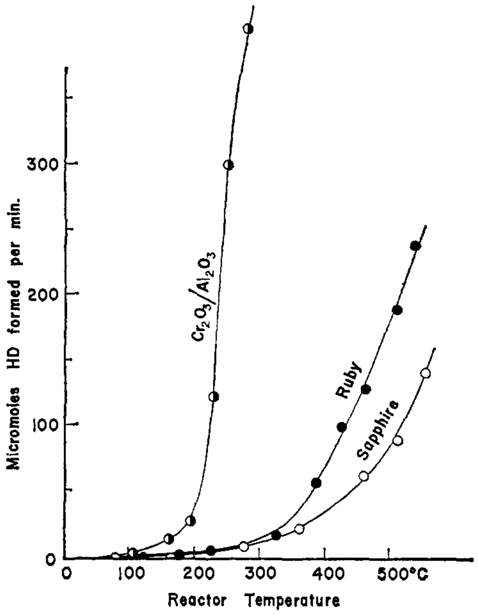


Figure 1. Hydrogen-deuterium equilibration activity over sapphire, ruby, and alumina-supported chromia.

vated alumina promoted with iron oxide. The gas stream was then passed over copper oxide at 600°, over two wires of a Gow-Mac W 1 thermal conductivity cell held at 125° by a thermistor placed deep in the cell block. The gas stream, still carrying its H_2O, HOD, and D_2O, was then passed through a silica gel, Tel-Tale trap at room temperature and, thus dehydrated, back over the other two wires of the cell, to flowmeter, and exit. Sensitivity was such that about 2 parts of HD per 1000 of total sample gas could be detected.

Results

All results are reported in micromoles of o-H_2, or of HD, formed per minute, as a function of reactor temperature. Reaction maxima reported are about 50% of equilibrium for o-H_2 and 40% for HD. No attempt was made to calculate rate constants and activation energies because, as mentioned before, the catalyst systems themselves were found to change in both activity and specificity in manners not previously reported.

Figure 1 shows the equilibration activity over sapphire, ruby, and Cr_2O_3/Al_2O_3. All runs were made with the temperature rising at 1°/min on samples which had been slowly cooled in hydrogen from 500°. The activity of the empty reactor was about half that of sapphire. In these and all other data reported below no correction has been made for the empty reactor activity nor, in the case of ruby, for the underlying sapphire activity. The results were the same for the cooling cycle.

Figure 2 shows conversion activity over powdered single crystal Cr_2O_3, powdered ruby previously slowly cooled in hydrogen from 500°, and powdered single crystal Cr_2O_3 first heated in oxygen, then in hydrogen at 500°. All runs were made with the temperature rising at 1°/min.

In addition to the results reported in Figures 1 and 2, the following information was obtained.

The empty reactor and the powdered sapphire both gave conversion activities virtually the same as the equilibration activities.

Conversion activity over ruby was found to depend on previous treatment in a complicated way, as follows. A ruby sample heated in hydrogen at 500° and cooled *in vacuo* (10^{-6} mm) from 500° to room temperature was found to exhibit a conversion activity of about 400 μmoles/min. Approximately the same result was found for ruby "quenched" in hydrogen from 500° to room temperature at a rate not less than 40°/min in the critical range of about 350 to 150°. This high room-temperature activity was not duplicated for the equilibration reaction, which was immeasurably slow under these conditions. The high room-temperature conversion activity was found to be slowly lost over a period of days. At 100° the activity was half-lost in about 2 hr, and at 175° in 15 min. The high conversion activity exhibited at room temperature after cooling *in vacuo* from 500° was found to be independent of rate of cooling.

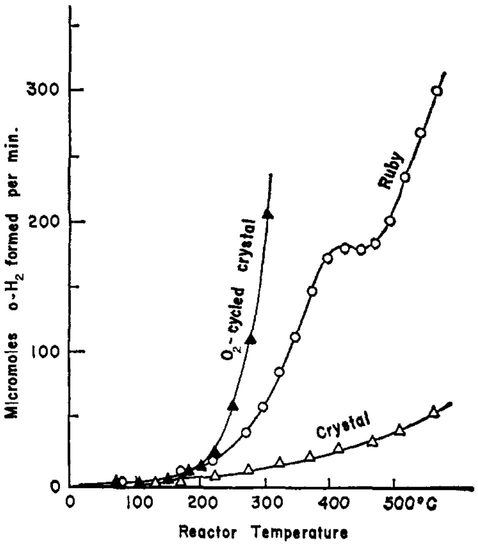


Figure 2. Parahydrogen conversion activity over crystalline chromia, ruby, and oxygen-cycled crystalline chromia.

The Cr_2O_3/Al_2O_3 gave conversion activity almost the same as that reported for the equilibration activity in Figure 1. Rapid cooling to room temperature in hydrogen from 500° yielded somewhat irregular conversion activities averaging 40 μmoles/min, and no measurable equilibration.

In view of the surprisingly low conversion activity over the powdered single crystal of Cr_2O_3, the experiment was repeated with a 100-fold increase of catalyst mass (to 150 mg), but the results were almost exactly the same.

Discussion

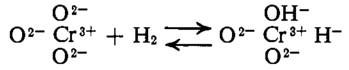
All results, except in one instance to which explicit reference is made, were obtained on systems in which the number of chromium ions accessible to hydrogen was the same, or approximately so. But the fraction of chromium–chromium ion pairs varied from nearly 0 to 100%. Chromium oxidation states higher than 3+ were unlikely and are not considered. In what follows, each of the three catalyst systems will be discussed separately, starting with the powdered ruby.

The powdered ruby showed no measurable hydrogen–deuterium equilibration activity below 300°, and above that temperature the activity was only moderately greater than that of the empty reactor. Virtual elimination of exchange interaction appears, therefore, to parallel elimination of equilibration activity. To express this in another way, it may be said that a single chromium ion, relatively far from other chromium ions, is unable to activate the hydrogen molecule. This confirms a view often expressed.[12] There is, however, a question as to what degree the chromium ions are actually accessible to hydrogen molecules. An attempt was therefore made to measure the parahydrogen conversion activity, and this attempt led to a series of results which help to illuminate the whole problem.

Ruby, heated to 500° in hydrogen and then slowly cooled to room temperature in hydrogen, shows no conversion activity below about 250°. Above 250° the activity rises at a moderate rate with increasing temperature, reaches a plateau near 400°, and then rises again above 475°. The sapphire gave the same rate of equilibration as of conversion, thus showing that the rates are correctly assumed to be equal at moderately elevated temperatures where zero-point differences have a negligible influence, and where the magnetic conversion process is unimportant. Subtraction of the equilibration activity from the conversion activity may, therefore, be used to give an estimate, at the temperatures employed, of the pure magnetic conversion activity. This is shown in Figure 3, where it can be seen that chromium ions on the surface of ruby are indeed accessible to hydrogen molecules at moderately elevated temperatures. But the peculiar form of Figure 3 shows that a more complete investigation of the conversion process over ruby is merited, and this was done.

The conversion activity was remeasured, but with the following change, namely that the initial cooling of the sample from 500° was done *in vacuo* rather than in hydrogen. Under these conditions the ruby showed an astonishingly high activity at room temperature, and the absence of any equilibration activity on the identical sample under the same conditions showed that the conversion activity was entirely magnetic in origin.[13] This high magnetic conversion activity could only arise from a large increase in the number of active sites, or from a large increase in the effective magnetic moment of the active sites, or from a decrease in the distance of nearest approach of the hydrogen molecule to the active site. It is difficult to see how the number of chromiums, or any other paramagnetic species, could be greatly altered by the evacuation process. Reduction of Cr^{3+} to Cr^{2+} would cause a moderate increase of magnetic moment (from about 3.8 to 4.9 μ_B), but the effect of this increase would be opposed by the increase of ionic radius (in the approximate proportion 0.69 to 0.84 A), and, as the radius affects the magnetic activity to a high negative power, it is doubtful if reduction of chromium could produce the change in rate observed. This leaves only the final suggested explanation, namely that the high activity observed, after evacuation from elevated temperatures, is related to remarkably close approach of the hydrogen molecule to the paramagnetic Cr^{3+} (or possibly Cr^{2+}) ion.

If now the active ruby was heated to about 100° it began to lose its activity as a function of time. At 100° the activity diminished to one-half in several hours, at 175° in 15 min. It has been known for a long time that hydrogen is chemisorbed by chromia in this temperature range.[14–16] The implication is that adsorbed hydrogen blocks access to the active sites. This could occur by the formation of a polarized adsorbate molecule, $H^{\delta+}$–$H^{\delta-}$ or by heterolytic adsorption and blocking by the hydride ion,[17] in the following manner


$$\begin{array}{c}O^{2-}\\ O^{2-}\ Cr^{3+}\\ O^{2-}\end{array} + H_2 \rightleftarrows \begin{array}{c}OH^-\\ O^{2-}\ Cr^{3+}\ H^-\\ O^{2-}\end{array}$$

although this does not mean that the possibility of Cr^{2+} is eliminated. The large radius of the hydride ion is more than sufficient to account for the complete loss of magnetic conversion activity, and the mechanism suggested above is consistent with the observation that when the ruby has been poisoned it remains poisoned even at low temperatures. The poisoning of ruby by hydrogen in the 100–200° range suggests that activation energies for the adsorption of hydrogen by ruby could readily be obtained by measuring the conversion rate as a function of temperature. This work is now in progress.

When the poisoned ruby was heated above 250°, it began slowly, and then more rapidly, to regain its conversion activity. This was almost entirely magnetic in origin below 300°, then slowly became more dissociative above 350°. The plateau in the 400–450° region seems clearly to represent complete desorption of hydrogen, just below the temperature at which a dissociative mechanism and a rising equilibration activity become dominant. These results show that the heat of reversible adsorption of hydrogen on ruby in the 300–450° range could be obtained by measuring the changing conversion rate with temperature. This work also is in progress. It is to be noted that the method will give essentially the heat at zero coverage—this being true because of the widely separated active sites involved.

The adsorption of hydrogen on chromia, at least in the 200° region, requires an appreciable activation energy.[15] It was, therefore, thought that quenching a sample in hydrogen from 500° to room temperature would have the same effect as evacuation. This proved to be the case. When the ruby was cooled through the critical region (350 to 150°) at not less than 40°/min, then it retained its high room-temperature conversion activity. That the poisoning attributed to hydrogen during slow cooling was not due to some phase change in the ruby, unrelated to hydrogen,

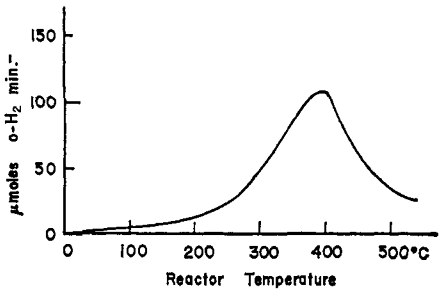


Figure 3. Net magnetic conversion activity over ruby.

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[12] See, for instance, D. D. Eley in ref 10, p 159.

[13] S. W. Weller and S. E. Voltz (*J. Am. Chem. Soc.*, **75**, 5227 (1953)) reported equilibration activity at subzero temperatures over chromia gel previously evacuated from 500°. The experiments are probably not comparable.

[14] J. Howard and H. S. Taylor, *ibid.*, **56**, 2259 (1934).

[15] R. L. Burwell, Jr., and H. S. Taylor, *ibid.*, **58**, 697 (1936).

[16] J. F. Garcia de la Banda, ref 10, p 260.

[17] D. A. Dowden and D. Wells, *Actes Congr. Intern. Catalyse, 2e, Paris, 1960*, **2**, 1489 (1961).

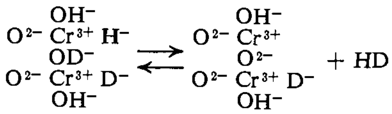
was shown by cooling the ruby slowly *in vacuo* from 500° to room temperature; on admission then of hydrogen, the high magnetic conversion activity was observed.

A crushed single crystal of chromia catalyzes the conversion reaction at a rate scarcely any greater than the sapphire. The equilibration activity must, therefore, also be negligible. This result was not changed when the catalyst mass was increased 100-fold. Failure of the crystal to exhibit much magnetic conversion activity is understandable because the *effective* magnetic moment as defined by Van Vleck,[18] is diminished in this substance at room temperature to about half its value for magnetically dilute Cr^{3+} ions. But this would result in a magnetic conversion activity loss to about one-fourth that of the dilute ion. The complete loss of activity implies a degree of antiferromagnetic spin alignment greater on the surface than in the bulk.[19]

One of the most familiar processes in heterogeneous catalysis is the cyclic heating in oxygen and hydrogen thought to be necessary to "activate," or to "stabilize," or to "clean" the surface. After the crushed crystal had been heated to 500° in oxygen and then in hydrogen, it exhibited a strong equilibration (and conversion) activity above 200°. This "activation" of the catalyst might be attributed merely to an increase of surface, but it has already been shown that increasing the catalyst mass (and surface) by 100-fold produced no measurable activity. It may also be surmised that the oxygen cleaned the surface. But the pretreatment of the single crystal was identical with that of the ruby which did not require any treatment with oxygen before it would exhibit a strong conversion activity. Rather, the high activity shown by the crystal chromia, after oxygen treatment followed by reduction of the surface, may be attributed to formation of a disperse layer of chromia in which the number of oxide ions coordinated to a chromium ion is further diminished, the normal chromium–oxygen distance may be increased, and the average number, and distance apart, of chromium–chromium nearest neighbors is also diminished.[20]

We turn finally to the typical supported chromia/alumina catalyst of the kind widely used in dehydrogenation. Here the pattern is that of a truly disperse chromia. The room-temperature conversion activity was actually somewhat less than that of the ruby even though both had been "quenched" as described above. This result is not unexpected, because the effective magnetic moment of the chromium is less than that in a magnetically dilute environment.[2] In other words, the exchange interaction is diminished but not negligible in the supported system. At, however, about 125° the equilibration (and conversion) activity begins to rise; at 225° it is increasing more than twofold for every 5° temperature rise. At 250° the supported chromia has the same activity as the ruby does at 565°. At 250° the activity of the supported chromia is not less than 500 times greater than that of the ruby at the same temperature. On a weight of catalyst basis the supported system is not less than 3×10^5 times more active than the ruby, or than the single crystal prior to oxygen–hydrogen cycling of the crystal at 500°, and this activity is all dissociative. The activity was such that once the chromia/alumina had been admitted to the reactor it became quite difficult to return the reactor to its virgin state.

It is difficult to believe that the activity shown by the supported system at 200–250° is mechanistically the same as that shown by ruby at 500°. A possible alternate is the free-radical chain reaction initiated by reduction of the chromium with generation of atomic hydrogen. It seems more probable that a familiar phenomenon, namely the decreasing heat of adsorption with increasing surface coverage, is also to be expected in disperse chromia. In ruby, with the chromiums relatively far apart, virtually no adjacent active sites are available, and with no adjacent sites no decrease of the heat of adsorption with increasing coverage is possible. Thus ruby has, under appropriate conditions, excellent parahydrogen conversion activity but little hydrogen–deuterium equilibration activity. Disperse chromia, produced in any way, has great activity for both reactions, the mechanism being possibly a familiar one[4]



$$\begin{array}{cccccccc} & \mathrm{OH^-} & & & & \mathrm{OH^-} & & \\ \mathrm{O^{2-}} & \mathrm{Cr^{3+}} & \mathrm{H^-} & & \mathrm{O^{2-}} & \mathrm{Cr^{3+}} & & \\ & \mathrm{OD^-} & & \rightleftarrows & & \mathrm{O^{2-}} & & +\ HD \\ \mathrm{O^{2-}} & \mathrm{Cr^{3+}} & \mathrm{D^-} & & \mathrm{O^{2-}} & \mathrm{Cr^{3+}} & \mathrm{D^-} & \\ & \mathrm{OH^-} & & & & \mathrm{OH^-} & & \end{array}$$

The extraordinary activity of the disperse form of chromia for the activation of hydrogen is such that 0.01% of this form accidentally present in truly crystalline chromia would give the mass a fairly large equilibration and conversion activity. Yet the presence of this form as a trace impurity would scarcely be detectable by any measurement other than the catalytic. Certainly it would raise the specific surface by no more than a factor of 2 in a region difficult of precise measurement, it would show no X-ray diffraction pattern, and, except at very low temperatures, it would not influence the magnetic susceptibility. The effect is reminiscent of the "terme inconnue" reported by Weiss and Forrer[21] in their determination of the saturation magnetization of crystalline nickel, and which was shown by Stoner[22] to be due to very finely divided interstitial nickel metal in single domain particles. In view of this it would seem that experimental studies on matter of high crystallinity, or theoretical studies related to structural properties present in crystals but not necessarily present in the catalytically active phases, can contribute indirectly to an understanding of heterogeneous catalysis. The method of using ruby to gain, indirectly, information concerning the mode of catalytic action of chromia, is applicable to other transition metal oxide systems.

Acknowledgment. This work was performed under contract with the Army Research Office (Durham).

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(18) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Clarendon Press, Oxford, 1932, p 242.

(19) D. A. Dowden, ref 10, p 194(a).

(20) Many authors state that chromia is active for conversion even after it has been ignited. Taylor, however [H. S. Taylor, *Nature*, **128**, 636 (1931)], claimed that a sample of chromia gel which had been heated through the glow temperature was inactive. It is entirely possible that the glow phenomenon could have produced local heating high enough to sinter the chromia so that it had properties as prepared from the melt, as for the single crystal. The loss of surface does, of course, contribute to the loss of activity, but the change of every trace of the disperse form to the massive form of chromia is the qualitative change that destroys the activity.

(21) P. Weiss and R. Forrer, *Ann. Phys.*, **5**, 153 (1926).

(22) E. C. Stoner, *Phil. Trans. Roy. Soc. London*, **A235**, 165 (1936).