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Hydrogen Adsorption and Parahydrogen Conversion over Chromia Supported on α-Alumina*

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This work was a continuation of that previously reported on the catalytic and adsorptive properties of ruby, a dilute solid solution of Cr_2O_3 in α-Al_2O_3. Samples of chromia supported on α-Al_2O_3 were prepared by impregnation, and of chromia concentration approximately equal to or greater than the surface concentration of chromium ions in ruby. Parahydrogen conversion rates over these samples proved to be almost entirely magnetic in mechanism. The rate of poisoning by hydrogen and the volumetric adsorption of hydrogen were measured on all samples under a variety of conditions. From these data calculations were made of the relative fractions of chromia in clusters and in the form of isolated ions. However, no sample produced appreciable hydrogen–deuterium equilibration. The conclusion from this is that chromia subsequent to being heated at 500° in hydrogen may chemisorb hydrogen readily, but neither in the form of single isolated ions, nor as clusters in a wide range of particle sizes, is it able to catalyze the equilibration reaction, provided that reduction with hydrogen has been complete.

INTRODUCTION

The purpose of this work was to define more precisely the active sites in transition metal oxide catalysts, with particular reference to the activation of hydrogen as in the hydrogen–deuterium equilibration reaction. Chromia was chosen for investigation because it lends itself readily to a variety of approaches, and because of the wealth of information already available about it (*1*). The guiding principle throughout was to minimize the number of variables in each system studied. Substantial reliance was placed on the parahydrogen conversion rate as an indicator of surface structure and reactivity.

Previous work from this laboratory (*2, 3*) has shown that ruby (a dilute solid solution of chromia in α-alumina) has, after treatment with hydrogen at 500°C, almost no equilibration activity below 450°, but that it has a large magnetic conversion activity. The chromium ions on the surface of ruby are accessible to molecular hydrogen, but they are subject to poisoning by hydrogen at moderately elevated temperatures. Rate studies of this effect, together with volumetric hydrogen adsorption measurements, have shown that the poisoning of chromium ions on the surface of ruby occurs through a primary rate-determining adsorption of hydrogen on α-alumina, followed by migration to, and capture by, the chromium. The failure of ruby to catalyze the hydrogen–deuterium equilibration reaction under the conditions described was thus shown to be due, not to any failure to chemisorb hydrogen, but possibly to the lack of chromium–chromium ions pairs in appreciable concentration in the ruby. It is this possibility that was further investigated in the present work.

EXPERIMENTAL SECTION

Extension of the studies previously reported required that the surface chromia

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be present in a form that would lend itself to epr measurements, and also that surface clusters be prepared and examined under controlled conditions. Neither objective can be achieved with ruby. Consequently it was necessary to proceed to supported chromia. For this purpose single-crystal sapphire (α-Al_2O_3) was crushed and powdered in a pure α-Al_2O_3 mortar and pestle to a specific surface of 2.0 m^2. The choice of sapphire was dictated by two considerations. First, the sapphire differs from the ruby previously studied only in that the chromia concentration ($\sim$ 1%) in solid solution has been lowered to zero; and second, that the dissociative catalytic activity always found over alumina, strongly heated in hydrogen, decays rapidly in sapphire. The reason for this rapid decay as contrasted with that in, say, γ-alumina is doubtless the much higher lattice energy in the near-perfect crystal as compared with that in the near-amorphous, more conventional, high-area support.

The powdered sapphire was impregnated with a volume of dilute aqueous chromic nitrate solution just sufficient for complete adsorption. The sample was then dried and heated in hydrogen for 1 hr at 500°C. Three supported samples of differing chromia concentration were prepared in this way, with the expectation that a certain fraction of the chromia would be present in clusters in each sample, and that the fraction so clustered would be larger with larger overall chromia concentration. The total concentration of chromia was then known accurately, and the fraction of the chromia accessible to molecular hydrogen was found as described below by a combination of parahydrogen conversion rate studies and volumetric adsorption. It was hoped that the most dilute supported sample would have an accessible concentration of chromia about equal to that in ruby. Unfortunately, the surface concentration of chromia in ruby cannot be estimated very accurately, but for a 1 atom % ruby there are in the neighborhood of 3.6×10^{16} Cr^{3+} ions per square meter of surface. The supported samples contained, respectively, 0.0028, 0.012, and 0.045% by weight of Cr_2O_3. The lowest concentration was probably the same as the surface concentration in the ruby within a factor of 3 or 4. The highest is moderately lower than the surface concentration in a typical chromia-alumina dehydrogenation catalyst.

Parahydrogen conversion rates were measured as previously described (*2*) at hydrogen flow rates of 50 ml/min at 1 atm over samples weighing 0.500 g. Conversions were, for the most part, up to about 70% of the maximum $1:1 \rightarrow 3:1$ o-p-H_2 ratio. Hydrogen–deuterium equilibration rates were measured under similar conditions with either chromatographic or mass spectrometer analysis as was the more convenient. [Further experimental details and evidence of freedom from accidental contamination in the flow reactor are given in refs. (*2*) and (*3*).]

The adsorption of hydrogen at various temperatures from 25° to 250° was done on 1.00-g samples, all at 1 atm. The adsorbed volumes were measured by desorption at 500° directly into a McLeod gauge. Procedure as described (*3*) was, in general, to adsorb at a given temperature for a given time, then to evacuate at 100° for 60 min to remove all physically adsorbed hydrogen and all weakly chemisorbed hydrogen. All adsorptions were monitored by parahydrogen conversion poisoning rate measurements performed on separate samples. The necessity for this procedure arose from the expectation that clustered chromia would exhibit a decay rate pattern different from that observed for isolated chromium ions, as in ruby. This expectation was realized.

EXPERIMENTAL RESULTS

Parahydrogen conversion decay rates. It is possible to make these measurements in either of two ways. After the sample has been heated in hydrogen for about 30 min at 500° it may be evacuated, and cooled in vacuum, to the desired temperature. Hydrogen is then admitted for the start of measurements. Alternatively, the sample may be quenched from 500° in the presence of 1 atm hydrogen. If the rate of cooling over the sensitive range (400° to 150°) is not less than about 25° per min, then the chemisorption of hydrogen leading to poisoning is negligible. Both methods of cooling yield the same conversion results but quenching in hydrogen is the more convenient. This method was used for most of the studies reported.

Figure 1 shows the initial parahydrogen conversion activity and the decay rate at 25° for the supported sample, $Cr_2O_3/\alpha\text{-}Al_2O_3$, containing 0.0028% Cr_2O_3. Figure 1 also gives the same information for the sample containing 0.045% Cr_2O_3. The decay curve at 25° for the 0.012% Cr_2O_3, which is more complicated, is shown in Fig. 2.

Figure 3 shows the decay curve for the 0.012% Cr_2O_3 at 90°. This figure also shows the curve for the same sample at 155°.

Hydrogen–deuterium equilibration. The equilibration rates for all samples were small. The rates increased moderately with temperature and with increasing chromia content, reaching 20% for the 0.045% Cr_2O_3 sample at 250°. This is about three times greater than the rates previously reported (*2*) for sapphire and for ruby under similar conditions.

Hydrogen adsorption. As described in the Introduction conditions for the adsorption of hydrogen on the samples were determined from the time and temperature necessary for complete poisoning. Thus for the 0.0028% Cr_2O_3 sample the hydrogen exposure time was selected as 190 min at 25° and 1 atm, followed by evacuation at 100° for 60 min, and desorption at 500°. Results for all samples are given in Table 1.

Remarks on results. For the 0.0028% Cr_2O_3 sample the conversion decay curve, with an induction period followed by a straight line, is almost identical with that

TABLE 1

CHEMISORPTION OF HYDROGEN ON $Cr_2O_3/\alpha\text{-}Al_2O_3$

Sample, Cr_2O_3%	Total exposure, latm	μliter (STP) H_2/g sample
0.0028	190 min 25°C	1.37
0.012	90 min 25°	2.52
0.012	60 min 150°	4.20
0.045	190 min 25°	0.97

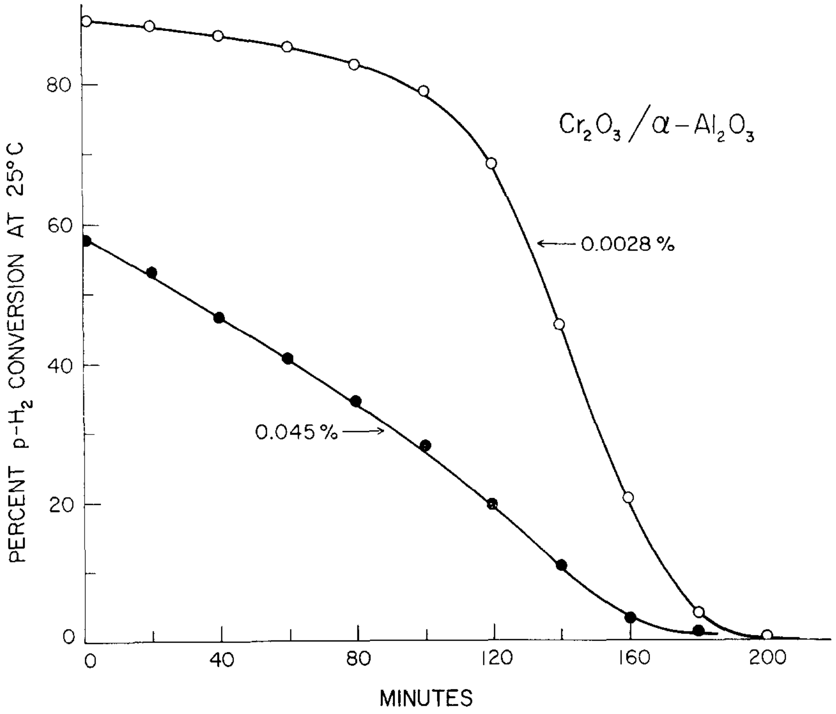

FIG. 1. Magnetic parahydrogen decay rates at 25°C for 0.0028% and 0.045% Cr_2O_3 supported on $\alpha\text{-}Al_2O_3$.

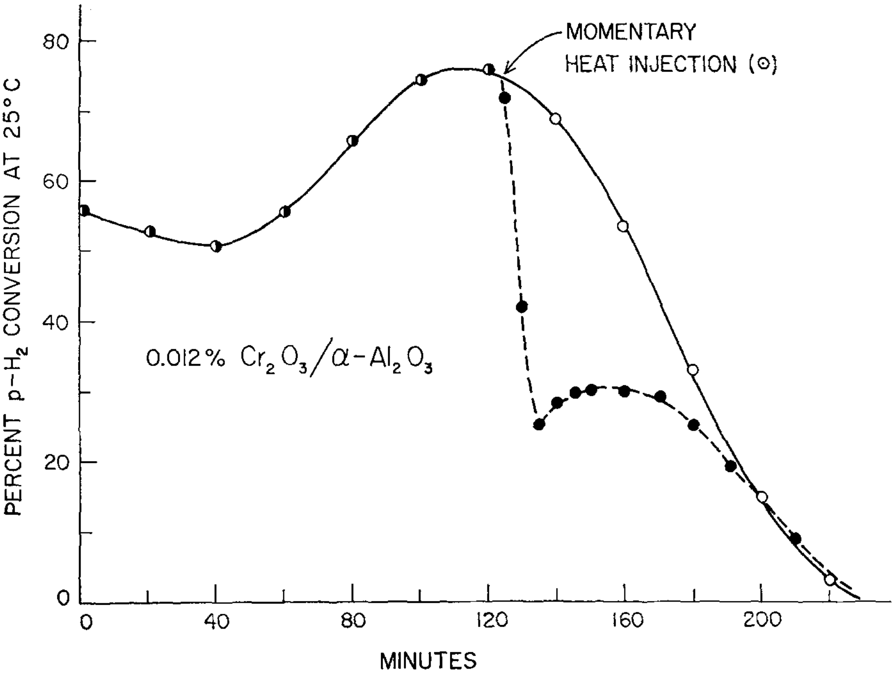

FIG. 2. Parahydrogen decay rate for 0.012% Cr_2O_3 supported on α-Al_2O_3 at 25°, and showing the rate increase, and effect of momentary heat injection.

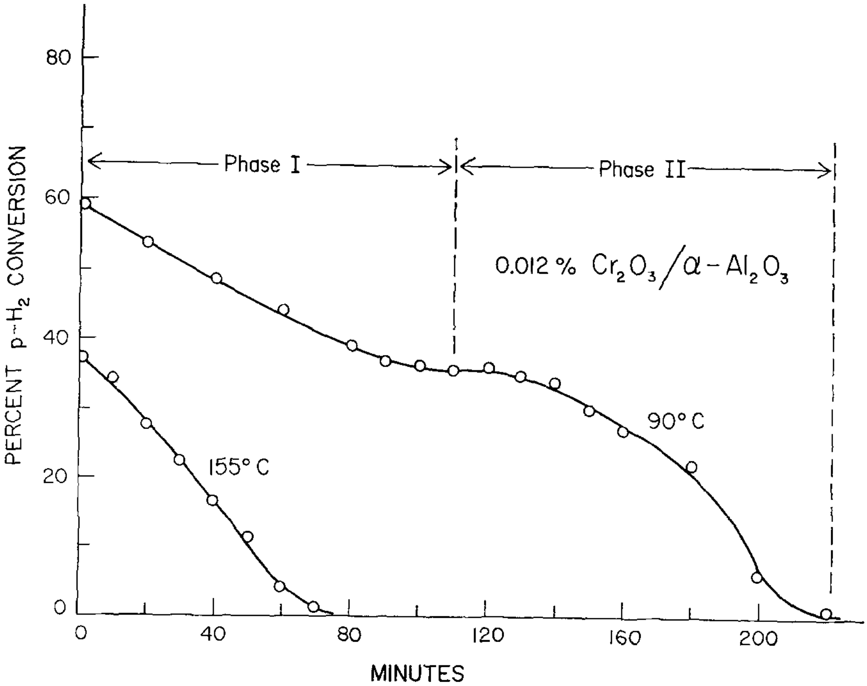

FIG. 3. Parahydrogen decay rates for 0.012% Cr_2O_3 supported on α-Al_2O_3 at 155°C and at 90°; the latter showing two steps.

previously reported (*3*) for ruby, except that the time necessary for complete decay is less. Inasmuch as the induction period is related to direct chemisorption of hydrogen on sites exclusive of chromia in the sample (*3*), it was suspected that the impregnation step, during preparation, somehow increased the concentration of such sites in the supported samples. To test this hypothesis a sample of ruby previously studied was moistened with very dilute nitric acid solution, then dried and heated to 500°. This treated ruby then showed the same shorter induction period as observed for the supported sample, although the initial activity was not changed. It may, therefore, be concluded that, at least in this case, the preparation of a sample by the familiar impregnation process may alter the concentration of primary adsorption sites in the support itself. The short induction periods for both supported catalyst and ruby were found to be lengthened by holding the samples at 500° for several hours.

The conversion decay rate for the 0.0028% Cr_2O_3, shown in Fig. 1, gives no indication that chromia clusters, if present in appreciable concentration, adsorb hydrogen in any manner different from that on ruby. It is, however, readily shown that the method used is not very sensitive to the concentration of clusters. The magnetic conversion rate is approximately proportional to $cp\mu^2/d^6$ where c is the total chromium ion surface concentration, p is the fraction of these ions accessible to molecular hydrogen, μ is the magnetic moment, and d is the distance of nearest approach. For isolated Cr^{3+} ions $p = 1$ and $\mu = 3.87$ Bohr magnetons. On the other hand, for a cluster consisting of, say, five oxide ion layers p is only 0.1 and, for antiferromagnetic α-Cr_2O_3, the moment effective in parahydrogen conversion is about 1.9. Hence for a supported sample in which half of the chromia is in clusters the conversion rate contribution of the clusters would be only 2.3% of the total. This is barely measurable.

The 0.012% Cr_2O_3 sample shows at 25°, in contrast to the 0.0028% sample, a complicated conversion decay rate. As shown in Fig. 2 the decay starts in a more or less normal manner but then it changes sign and the activity slowly rises to a level considerably higher than the initial activity. From that point the decay pattern depends on how the sample is treated. If left at 25° the sample slowly loses activity, becoming inactive after an hour or more. But if at the highest point of activity the temperature is abruptly raised quite moderately (say to 70°) the activity almost instantly falls to somewhat less than half the initial activity, and then decays slowly to zero in the normal manner as for ruby.

The rather strange effects described in the preceding paragraph do not directly concern the main purpose of the work, but speculation about them may be helpful because it may aid in the interpretation to be given in the following section. It is not difficult to imagine mechanisms by which, under certain conditions, the activity during poisoning of a catalyst should rise above the initial activity, provided that an appreciable fraction of the observed activity is due to chromia in clusters. As the clustered phase becomes poisoned by hydrogen a fall of activity can only reflect denial of access, and there is considerable evidence (*2*) that this denial must be caused by a hydride ion. As the space charge builds up it is probable that positive ions will migrate toward the surface. If this should occur for isolated Cr^{3+} ions there will be no change of effective magnetic moment, but only a change of accessibility. But in an antiferromagnetic cluster, any migration from the lattice will permit the effective moment to become larger. This will be illustrated for two cases of two atoms each. In one case the Cr^{3+} ions are isolated and of moment 3.87, while in the other the ions are clustered and of effective moment 1.9. The poisoned atom in each case is shown thus ( ), and the conversion activity enters as μ^2.

Case 1: $\mu^2 = 3.87^2 + 3.87^2 = 30.0$ initially, and becomes $(3.87)^2 + 3.87^2 = 15.0$ half-poisoned, that is to say, the poisoned system always has a lower activity.

Case 2: $\mu^2 = 1.9^2 + 1.9^2 = 7.2$ initially, and becomes $(1.9^2) + 3.87^2 = 15.0$ half-poisoned, for a gain of 108% in activity. (We have, therefore, the anomaly that a half-poisoned catalyst may be more active than a clean one.) Attention should be directed to the remarkable fragility of the partially poisoned phase as shown by the abrupt loss of activity when the sample is gently heated.

For the 0.012% Cr_2O_3 sample at 90° there are clearly defined plateaus of activity decay, as shown in Fig. 3. These plateaus appear to be due to the effect expected, namely a difference in pattern of hydrogen chemisorption by chromia in clusters as contrasted with isolated chromium ions. The plateaus will be discussed in detail in the following section. At 155° the decay rate is obviously too rapid to show the effect observed at 90°.

The 0.045% Cr_2O_3 decay rate as shown in Fig. 1, has little indication of the induction period characteristic of the 0.0028% sample, and of ruby. This, of course, suggests that most of the activity in this sample is due to chromia clusters.

From the low hydrogen–deuterium equilibration data it may be concluded that certainly below 100° all activities observed are essentially magnetic in origin. This view is supported by the negative temperature coefficients of initial activity.

The hydrogen adsorption data are subject to rather large experimental errors due, for the most part, to the small volumes involved. The only important systematic error of which the author is aware is the very small volume that migrates and is captured by indigenous alumina sites as previously described (*3*). With one possible exception, noted below, the adsorption data appear to be adequate for their purpose.

DISCUSSION OF RESULTS

If the conversion decay pattern shown for the 0.012% Cr_2O_3 sample at 90° in Fig. 3 is correctly related to differences in mechanisms and rates of hydrogen chemisorption on chromia clusters as compared with isolated chromium ions, then we may proceed to identify phases I and II (Fig. 3). First, the initial straight-line decay (Phase I) becomes more important as the total chromia concentration is increased. Thus Phase I is absent in the 0.0028% Cr_2O_3 sample, but strong in the 0.045% sample. Second, Phase II, characterized by an induction period as for ruby, is strong in the 0.0028% sample, but virtually absent in the 0.045% sample. The conclusion is, therefore, as would be predicted from the method of preparation, namely that Phase I is related to chromia clusters, Phase II to isolated ions. Further evidence that this identification is correct will be given below.

Now we consider the relative contributions of Phase I and II to the initial (time zero) parahydrogen conversion rate. As mentioned in the previous section the rate of conversion $R = kcp\mu^2/d^6$, and we assume that the number of chromium ions accessible to molecular hydrogen, cp, is equal to h/a, where h is the number of hydrogen atoms necessary to poison all the chromium, and a is the H/Cr ratio at each poisoned site. Further, it is assumed that k and d are the same for Phases I and II, hence dividing the initial rates, R_1 and R_2, attributable to Phases I and II respectively, we have

$$\mu_1 = \mu_2 \left(\frac{R_1 h_2 a_1}{R_2 h_1 a_2}\right)^{1/2}$$

It is not known *a priori* if $a_1 = a_2$. Calculations will, therefore, be made for each of the more probable cases, namely $a_1/a_2 = 2$, 1, or ½. The moment of an isolated Cr^{3+} ion is 3.87 Bohr magnetons, that of Cr^{2+} is 4.90; from Fig. 3 (90°) $R_1/R_2 = 0.68$; and from Table 1, $h_2/h_1 = 0.67$. The results of this calculation are shown in Table 2. All calculations wherein the identification of Phases I and II are reversed lead to impossibly high magnetic moments for the unidentified species, and are therefore omitted. All values of μ_1 enclosed in parentheses ( ) are too high to receive consideration for an antiferromagnetic clustered phase and consequently the value of $a_1/a_2 = 2$ may be eliminated. (It

TABLE 2
Estimation of Magnetic Moments in Phase I Chromia

Assumed Phase II identification	μ_2	a_1/a_2	μ_1
Isolated Cr^{3+}	3.87	2	(3.7)
		1	2.6
		$\frac{1}{2}$	1.8
Isolated Cr^{2+}	4.90	2	(4.7)
		1	(3.3)
		$\frac{1}{2}$	2.3

is true that this calculation is based on data obtained at 90° and that the Néel temperature of α-Cr_2O_3 is about 34°. However, the magnetization–temperature curve is a flat one, and the moment effective in p-H_2 conversion does not change much in this region.) Our conclusions from Table 2 are, therefore, that the identification of Phases I and II is correct, that the oxidation state of the isolated chromium ions is probably 3+ or possibly 2+, that the H/Cr ratio for clusters is either equal to, or half, that for isolated ions. It is difficult to see how the H/Cr ratio for poisoned isolated ions could be less than 1. Hence the ratio for accessible ions in clusters could be 1, if $a_2 = 1$, or 1 if $a_2 = 2$.

From the data presented for the 0.012% Cr_2O_3 sample it is possible to estimate the fraction of the chromium in isolated sites *versus* clusters, and also the approximate size of the clusters. Phase II (Fig. 3, and Table 1) was found to adsorb 0.150 μmole H per gram of sample and, if $a_2 = 2$, as possible, then Phase II contains 0.075 μmole Cr per gram which is 4.7% of the total Cr, namely 1.58 μmole/g. This leaves 1.50 μmole Cr per gram in Phase I which adsorbs 0.225 μmole of H per gram of sample. If $a_1 = 1$ then 0.225/1.50 = 15% of the Cr in Phase I is on the surface of the clusters, which must then be between three and four atom (oxide ion) layers thick.

For the 0.0028% Cr_2O_3 sample all the measurable activity is due to Phase II. It is possible to make a rough estimate of particle distribution by considering the total hydrogen adsorption necessary to poison the sample and, in addition, the initial activity before any poisoning has occurred. The initial 0.0028% sample activity stands to the initial 0.012% sample Phase II activity as 89/35 and, in the 0.012% sample this was shown above to be caused by 0.075 μmole Cr per gram. Hence the 0.0028% sample has about (89/35) × 0.075 = 0.19 μmole Cr per gram in its Phase II. The total chromia in this sample is 0.37 μmole/g, so that even at this dilution there is about 48% of the chromia in clusters. The 52% of the chromia in isolated sites should, if H/Cr = 2, adsorb 0.38 μmole H, but this is more than the total hydrogen taken up. If H/Cr = 1 for this Phase, then about 17% of the chromia in clusters is on the surface of the clusters. The data are obviously not accurate enough for further estimates, but it may almost certainly be stated that even in the 0.0028% sample a portion of the chromia is aggregated, although the fraction in clusters is, as expected, less than in the 0.012% sample.

Similarly for the 0.045% sample, all the measurable activity of which is due to clusters, we have an adsorption of 0.082 μmole H on 5.92 μmole Cr, showing that about 1.4% of the total chromia is accessible to hydrogen. These results are summarized in Table 3.

Summary

It has already been shown that, subsequent to heating in hydrogen at 500° and

TABLE 3
Summary of Conversion Activity and Hydrogen Adsorption for Ruby and for Cr_2O_3/α-Al_2O_3

Weight percent Cr_2O_3	~2 (ruby)	0.0028	0.012	0.045
μgram Cr_2O_3 m^{-2} surface	5 ?	14	60	225
Activity g^{-1} surface Cr_2O_3	100 (arb)	78	11	3
H/Cr for complete poisoning	0.8 ?	0.3	0.24	0.014

cooling either in vacuum or in hydrogen, isolated chromium ions, as on the surface of ruby, do not measurably accelerate the hydrogen–deuterium equilibration reaction, although the accessibility of such ions to molecular hydrogen and their ability to chemisorb hydrogen at room temperature and higher have been firmly established (*1*). The oxidation state, insofar as the term has a definite meaning for a surface atom, for such ions is probably 3+, or possibly 2+.

The present paper shows that exactly the same may be said of clusters of similarly treated supported chromium ions as on α-Al_2O_3, due to consideration being given to the transitory equilibration activity always shown by alumina itself under these conditions.

These studies having been extended over the range from single isolated chromium ions to, and including, massive single-crystal α-Cr_2O_3, it may be said that chromia, treated as described, still lacks some essential feature (such as some unique structural arrangement or some combination of oxidation states) necessary for the very great equilibration activity shown by a typical chromia/alumina dehydrogenation catalyst treated in exactly the same way. The fact that isolated chromium ions, as in ruby, are able to catalyze the hydrogenation of ethylene at room temperature (*4*) shows, merely, that this is a less demanding reaction.

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