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Parahydrogen Conversion Over Chromiagel Near the Néel Point

J. A. ARIAS AND P. W. SELWOOD[1]

Department of Chemistry, University of California, Santa Barbara, California 93106

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Parahydrogen conversion rate measurements have been made over amorphous chromiagel, microcrystalline chromiagel, and macrocrystalline α-Cr_2O_3. The decrease in conversion rate that occurs over α-Cr_2O_3 as the temperature is raised through the Néel point is also observed over the microcrystalline gel, but not over the amorphous gel. Antiferromagnetic ordering has been shown to be associated with a large increase of conversion rate and this is independent of the increase in rate due to improved accessibility, as crystallinity develops. Magnetic ordering, when it occurs, is present in those catalyst ions accessible to molecular hydrogen and thus, of necessity, on the catalyst surface.

INTRODUCTION

In recent papers Dyne, Butt, and Haller (*1*) have described preparative conditions for obtaining reproducible properties in chromiagel, and they have added new relationships between structure and catalyst specificity. They have, in brief, confirmed and extended earlier observations by Burwell *et al.* (*2*) that a gel obtained by hydrolysis and then heated in helium at 400°C remains amorphous, although it shows a well-defined X-ray diffraction radial distribution curve; and they have shown that a similar gel heated in hydrogen at 400°C yields, in part, a microcrystalline structure of the same kind as present in macrocrystalline α-Cr_2O_3.

An observation reported from this laboratory (*3*) has made it possible to take a further step in the direction of estimating local ordering, of the kind found in α-Cr_2O_3, and to do this for those chromium ions actually accessible to reactant gas molecules. This observation is the change in rate of the catalyzed parahydrogen conversion that occurs at the magnetic phase transition (the Néel point) of antiferromagnetic solids. The purpose of the present paper is to describe parahydrogen conversion rate measurements over chromiagel prepared in both amorphous and microcrystalline forms, to compare the results with those over macrocrystalline α-Cr_2O_3, and to interpret the data in terms of local ordering of the chromium ions near enough to the surface of the catalyst to influence the rates.

EXPERIMENTAL

The chromiagel samples were prepared as described by Dyne *et al.* (*1*), as follows: the gel obtained by urea hydrolysis of dilute aqueous chromic nitrate solution at near 100°C was dried at 110°C, then heated at one degree per minute to 300°C in flowing hydrogen. For part of the sample, heating was continued at the same rate in hydrogen to 400°C, where it was held for 12 hr. For the remainder of the sample, heating above 300°C was conducted in helium at the same rate to 400°C where it was held for 12 hr. The sample heated in helium is referred to as "amorphous," that heated in hydrogen as "microcrystalline." A sample of gel heated in air at 1100°C for 18 hr, and thus consisting of pure α-Cr_2O_3, is referred to as "macrocrystalline." Specific

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[1] To whom enquiries should be addressed.

surfaces (BET, N_2) of these samples were: amorphous, 228 m^2g^{-1}; microcrystalline, 104 m^2g^{-1}; and macrocrystalline, 3.0 m^2g^{-1}.

Hydrogen was passed through an Englehard Palladium Purifier. Helium, freed from hydrogen over hot copper oxide, was passed over Linde Molecular Sieve 5× at −196°C.

Parahydrogen conversion rates, from the 1:1 toward the 3:1 o-p H_2 mixtures, were measured in a Vycor flow reactor at atmospheric pressure as previously described (*4*) with the addition of an inlet for purified helium, and with omission of the solenoid used for study of the extrinsic field effect. Temperature control was improved to permit holding the reactor to within ±0.05°C in the range 0–60°C. During rate measurements the hydrogen flow rate was 50 cm^3 (SC) min^{-1}. A limited number of measurements was also made in the field of a 12-in. electromagnet as described elsewhere (*5*).

Throughout all the rate measurements the mechanism of conversion was, over the 0–60°C temperature range investigated, solely magnetic. Any dissociative mechanism, as determined by hydrogen–deuterium equilibration and by the absence of a positive temperature coefficient, contributed less than 1% to the reported rates.

RESULTS

Specific formation rates, k, for orthohydrogen from 0 to 60°C, in mol m^{-2} s^{-1}, are shown in Fig. 1. These were calculated in the usual manner from the relation $k = (F/S)\ln[(C_{eq} - C_0)/(C_{eq} - C_x)]$, where F is the hydrogen flow rate, S the total catalyst surface, C_{eq} the equilibrium fractional concentration of o-H_2, C_0 the initial concentration, and C_x the emerging concentration. These rates are referred to below as activities. The reproducibility of activities for a given sample was about ±2%, that for different samples about ±20%. All changes in activity were reversible with temperature within the limits shown. Dissociative activity for the two gel samples became about 10% of the total at 135°C.

After having been allowed to stand in flowing hydrogen at room temperature for several days the activity pattern of the amorphous gel changed somewhat in the direction of becoming like that of the microcrystalline sample, but no further change occurred over several weeks. During the whole series of measurements on the gels there was no indication of the poisoning caused by hydrogen chemisorption that is observed over α-Cr_2O_3, powdered ruby, and some forms of supported chromia on alumina (*5*). Over α-Cr_2O_3 the sample was cooled rapidly from 500°C to room temperature where hydrogen poisoning is not a serious problem. It is to be noted that the rate of change of activity with respect to temperature over macrocrystalline α-Cr_2O_3 is almost immeasurably rapid close to 34°C.

In addition to the results given above it was found that the microcrystalline gel showed a positive extrinsic field effect in 18 kOe at 50°C and a small negative effect at 0°C.

DISCUSSION

Were it not for its effectiveness and versatility as a catalyst the self-supported high-area form of partially hydrated chromia known as chromiagel would be of minor interest. It also lends itself to a variety of experimental methods that have as their chief purpose a bettering of our understanding of catalyst surface structure, although this understanding remains far from complete. A present view is that the gel consists of a chain polymer (*6*) which may be represented as $Cr_2O_3 \cdot nH_2O$. Progressive dehydration and condensation lead to structures, as described by Burwell *et al.* (*2*), in which there are various stages of coordination unsaturation with respect to both Cr^{3+} and O^{2-} ions on the surface. The final stage of dehydration is α-Cr_2O_3 to which the gel structure bears increasingly close resemblance as dehydration proceeds. The appearance of X-ray diffraction lines characteristic of α-Cr_2O_3 is accelerated by carrying out the dehydration in hydrogen rather than in an inert gas. Dehydration approaching completion may be achieved, with care, without the catastrophic loss of surface area that normally occurs when the gel is ignited.

Dyne, Butt, and Haller (*1*) report that a

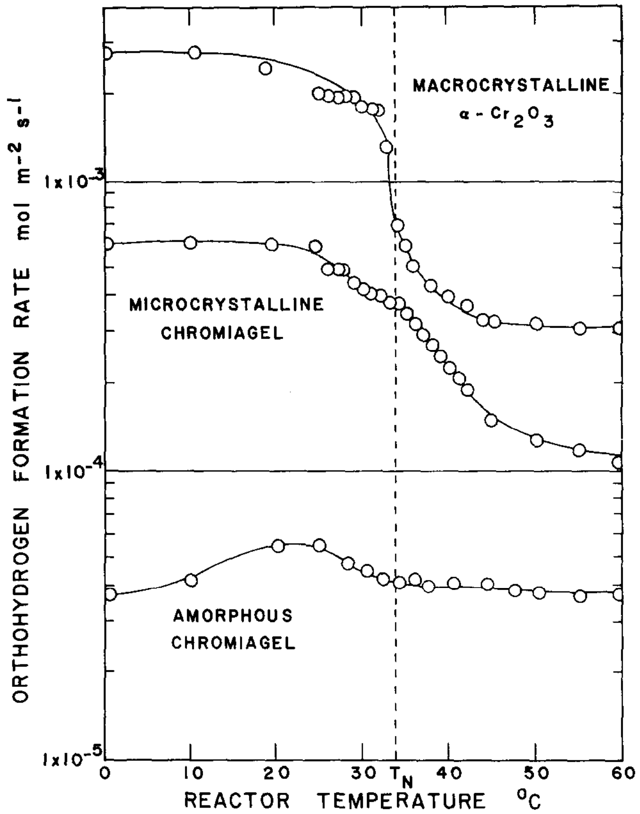

Fig. 1. Orthohydrogen formation rates over three preparations of chromia in the neighborhood of the magnetic phase transition, T_N, at 34°C.

gel dehydrated for 12 hr at 400°C in flowing helium gives a radial distribution curve indicating local crystallographic ordering over a 10 Å distance. This ordering is of the kind present in α-Cr_2O_3 although the interatomic distances are slightly larger. The unit thought to be present is Cr_8O_{12}. But dehydration in flowing hydrogen under otherwise identical conditions yields a crystalline phase of dimension 110–200 Å. The percentage of this present is believed to be in the range 5–30%. The microcrystalline phase is considered to be "supported" on amorphous gel.

Macrocrystalline chromia, like many solids of interest in catalysis, exhibits a magnetic phase transition. As the temperature is raised through the Néel point the solid changes from antiferromagnetic to to paramagnetic. For α-Cr_2O_3, this point is at 34°C. Catalytic activities have often been observed to change at phase transitions. For the parahydrogen conversion occurring by the magnetic mechanism over α-Cr_2O_3 the rate of reaction falls by about one order of magnitude as the temperature is raised through 34°C (*3*). Antiferromagnetic solids are characterized by antiparallel ordering of the neighboring atomic moments. Magnetic ordering is thus quite different from the geometric ordering revealed by X-ray diffraction. Nevertheless, a sharply defined Néel point is indicative of geometric ordering on, at least, a local scale. Furthermore, molecular hydrogen cannot be appreciably influenced by chromium ions much below the surface. The existence of a catalytic rate change at, or near, 34°C over chromiagel is, therefore, evidence not only of magnetic ordering on the part of those chromium ions actually accessible to molecular hydrogen but also of geometric ordering like that found for α-Cr_2O_3, albeit on a micro-scale. This, then, offers an opportunity to overlap and to extend somewhat the structural surface conclusions reached by Dyne, Butt, and Haller (*1*).

It will be convenient to list the activities of each sample at 0°C and at 60°C and as relative to the activity of the amorphous gel at 0°C. This is done in Table 1.

Table 1 shows that in the paramagnetic region (60°C) increasing crystallinity is associated with a substantial rise of activity. Even if the magnetic moment of the chromium on the surface rises (because the oxidation state has fallen to 2+, as is not unlikely) this would have little effect on the conversion rate (*7*). It must, therefore, be concluded that these differences in activity are due to changes in the accessibility of molecular hydrogen to the region of the paramagnetic ions. (By accessibility is meant the product of the number of surface chromium ions, and the distance of nearest approach raised to a high power.) This conclusion is consistent with previously expressed views concerning the comparative surface structures (*2, 7*).

It is also shown in Table 1 that, in the antiferromagnetic region (0°C), increasing crystallinity is associated with a greater rise in activity, namely, ratios of 1:16:74 as compared with 1:5.5:8.8 for the paramagnetic region. It is difficult to understand how the accessibility could suffer a large reversible change when the temperature is changed by a few degrees through a second-order phase transition. The observed relative activities in the antiferromagnetic region show that, other significant parameters being substantially the same, a surface in which antiferromagnetic ordering is present is more active for the magnetic parahydrogen conversion than is one in which ordering is not present.

TABLE 1
RELATIVE ACTIVITIES OF CHROMIA PREPARATIONS

Sample	at 0°C	at 60°C	k_0/k_{60}
amorphous gel	1	1	1
microcrystalline gel	16	2.9	5.5
macrocrystalline α	74	8.4	8.8

In summary, it may be said that heating the amorphous gel in hydrogen at 400°C increases the accessibility by a factor of 2.9 (as measured at 60°C) and that the magnetic ordering simultaneously produced on the surface is associated with an increase of activity by a factor of 5.5, yielding a total increase (as measured at 0°C) of 16-fold. Similarly, formation of the macrocrystalline α-Cr_2O_3 increases the accessibility by a factor of 8.4 (as compared with the amorphous gel) and magnetic ordering is associated with a further increase by a factor of 8.8, yielding a total increase of 74-fold.

It will be noticed that magnetic ordering in the α-Cr_2O_3 is associated with a larger increase of activity than is the case for the microcrystalline gel. This is reasonable because it can hardly be expected that all the activity in the microcrystalline gel is related to an ordered surface.

Dyne, Butt, and Haller (*1*) expressed the view that geometric ordering in the microcrystalline gel was on the surface. This view was reached, in part, because there appeared to be no other explanation for the catalytic specificity shown by this sample. We can state that the magnetic ordering present in this sample is also associated with sites accessible to molecular hydrogen and thus on, or very near, the surface. It is true that antiferromagnetism may be observed in truly amorphous solids as, for instance, is the case because of cobalt ion interactions in an alumina-silica glass (*8*). But in such cases the Néel point is at a far lower temperature than in pure CoO. In the microcrystalline chromiagel the Néel point transition effect is only moderately less abrupt than it is in the macrocrystalline α-Cr_2O_3. Our conclusion is, therefore, that the observed change in catalytic specificity in the microcrystalline gel, as compared with the amorphous, is definitely associated with magnetic ordering of the kind present in microcrystalline α-Cr_2O_3. But whether there is a cause-and-effect relationship between catalyst specificity and ordering of either kind (or both kinds) remains to be shown. Magnetic ordering is not present at the temperature generally used for dehydrogenation and related reactions.

The plot of activity vs temperature for the microcrystalline gel (Fig. 1) shows a less abrupt change at the Néel point than does the macrocrystalline α-Cr_2O_3. A spreading out of phase transitions in slightly inhomogeneous matter is of frequent occurrence and there is no reason why the gel should behave otherwise. But this behavior could also be produced by random association of the small particles and, possibly, by the influence of surface hydroxide ions on the dipole–dipole interaction (*9*). It must be emphasized that although no surface phase transition for the amorphous gel was observed in the 0–60°C region, it is possible that a transition could occur at a lower temperature. But the existence of a normal paramagnetic susceptibility at $-196°C$ (*6*) shows that any possible antiferromagnetic interaction in the amorphous gel would be at still lower temperature and probably very difficult to observe by a surface reaction. There have, of course, been extensive studies on metal–metal ion-exchange interactions involving no more than two ions, in a great variety of compounds (*10*). These studies include spectroscopic and other evidence for interaction between Cr^{3+} ions in ruby (a dilute solution of Cr_2O_3 in Al_2O_3). But no indication of any anomaly in the catalyzed parahydrogen conversion rate is found over ruby in a wide range of temperature, and the extrinsic field effect is positive throughout (*3, 5, 7*). The theory of the change in catalytic activity near the Néel point is dealt with by Petzinger and Scalapino (*11*) who show that in a high concentration of ordered spins the conversion rate may, as proposed by Ilisca and Legrand (*12*), be determined by emission and absorption of spin waves. Near the magnetic phase transition the change of conversion rate with respect to temperature is predicted to be negative because the exchange integral, which is negative for antiferromagnetics, appears in the rate equation. This is what is found to be the case for macrocrystalline, and to a degree in microcrystalline, chromia.

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