Extrinsic Field Acceleration of the Magnetic Parahydrogen Conversion

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Abstract: The magnetic mechanism parahydrogen conversion, catalyzed by chromia, has been found to be accelerated by an extrinsic magnetic field. The effect may be observed over ruby (a dilute solid solution of chromia in α-alumina), over various surface concentrations of chromia supported on α-alumina, and over pure α-chromia. If the paramagnetic species is dilute (as in ruby) the acceleration becomes larger below room temperature. If the paramagnetic species is sufficiently concentrated to show appreciable exchange interaction, then the acceleration becomes a complicated function of the surface magnetic phases present. The acceleration tends toward saturation at magnetic fields approaching 10,000 Oe.

This paper is a more nearly complete description of the effect reported earlier,[1] namely a change of reaction velocity of the parahydrogen conversion on application of an extrinsic magnetic field.

There have been many investigations, and more than a few reports, of chemical reaction acceleration in the presence of a magnetic field. Some of these reports dealing with the influence of intrinsic fields produced by paramagnetic species such as cupric ion or DPPH appear to be substantiated. But in the area of heterogeneous catalytic reactions subject to an extrinsic field, that is to say, a field coming from the outside, the results are controversial. Justi and Vieth[2] have reported that the parahydrogen conversion over metallic nickel at elevated temperatures (and thus almost certainly the dissociative mechanism) is accelerated by an extrinsic field. But Schwab and Kaiser[3] have failed to confirm that observation. In a recent review[4] Figueras Roca states that proof of the existence of a magnetocatalytic effect in a heterogeneous system still remains to be made. It is to be noted that the effect described below is observed for a reaction that, almost certainly, is magnetic in origin and therefore probably does not involve the breaking of any chemical bonds.

Experimental Section

Catalyst Samples. The intrinsic magnetic field was supplied by chromium ions in several preparations differing chiefly in magnetic surface concentration. The highest concentration was in single-crystal α-Cr_2O_3 obtained from Union Carbide Corp., Linde Division, and powdered in a pure alumina mortar and pestle to a specific surface of 14.6 m^2 as previously described.[3] Chromia supported on powdered single-crystal α-Al_2O_3 (sapphire) of specific surface 2.0 m^2 was made by impregnation, ignition, and reduction in hydrogen. Dilute solid solutions of chromia in α-Al_2O_3 in the form of ruby (also obtained from Linde) were powdered to 2 $m^2\ g^{-1}$. All preparations were heated in hydrogen for 3 hr at 500° and then quenched to room temperature unless otherwise described. The purpose of quenching was to prevent appreciable chemisorption of hydrogen.[3,4] The concentration of chromia in each sample is given below under Results.

Conversion Measurements. Most of the parahydrogen conversion rates were measured as previously described[5,6] except that the reactor was in the form of a small slender silica trap arranged to fit in the cavity of a Varian V-4502 X-band epr spectrometer with a 9-in. magnet. This arrangement made it possible to monitor magnetic phase transitions in the catalyst simultaneously with the measurement of parahydrogen conversion rates, and as the extrinsic field was changed from 0 to ~8000 Oe. The samples ranged from 50 to 200 mg, and the hydrogen flow rate was 35 ml min^{-1}. The temperatures covered were from −150 to 150°. A few measurements were made exactly as previously described[4] except that the reactor was in the gap of a 12-in. electromagnet producing fields up to 17,300 Oe. Catalyst sample masses and hydrogen flows were chosen so as to give rates easily measurable, but in no case more than a moderate fraction of conversion to equilibrium.

Results

The magnetic parahydrogen conversion often exhibits a negative temperature coefficient, but this is by no means general. Farkas and Sandler[7] have, for instance, shown that the coefficient over neodymium oxalate changes sign in the neighborhood of 0°. Furthermore, it was found in the present work that the acceleration caused by an extrinsic field approached, in several samples, a saturation at about 8000 Oe, above which little further acceleration occurred, at least not up to 17,300 Oe. In view of the above two complications, it was thought most appropriate to present the results for each sample in the form of graphs giving the zero field conversion in micromoles of orthohydrogen formed per minute as a function of temperature, and also to give in the same figure the fractional acceleration of conversion on application of a near-saturating field, at each temperature.

Figure 1 shows the conversion at zero field and the fractional acceleration, both as a function of temperature, for pure α-Cr_2O_3. The acceleration was measured at 7500 Oe. The observed change in epr signal intensity in this temperature region is shown in Figure 2 and is similar to that reported by Maxwell and McGuire.[8] Figure 3 shows fractional acceleration for the same sample as a function of field at several temperatures. It will be noted that, for this sample and for a certain temperature region, saturation was not achieved at

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[1] M. Misono and P. W. Selwood, *J. Am. Chem. Soc.*, **90**, 2977 (1968).

[2] E. Justi and G. Vieth, *Z. Naturforsch.*, **8a**, 538 (1953).

[3] G.-M. Schwab and A. Kaiser, *Z. Physik. Chem.* (Frankfurt), **22**, 220 (1959).

[4] F. Figueras Roca, *Ann. Chim.*, **2**, 255 (1967).

[5] P. W. Selwood, *J. Am. Chem. Soc.*, **88**, 2676 (1966).

[6] P. W. Selwood, 4th International Congress in Catalysis, Moscow, 1968, paper 66.

[7] L. Farkas and L. Sandler, *J. Chem. Phys.*, **8**, 248 (1940).

[8] L. R. Maxwell and T. R. McGuire, *Rev. Mod. Phys.*, **25**, 279, (1953).

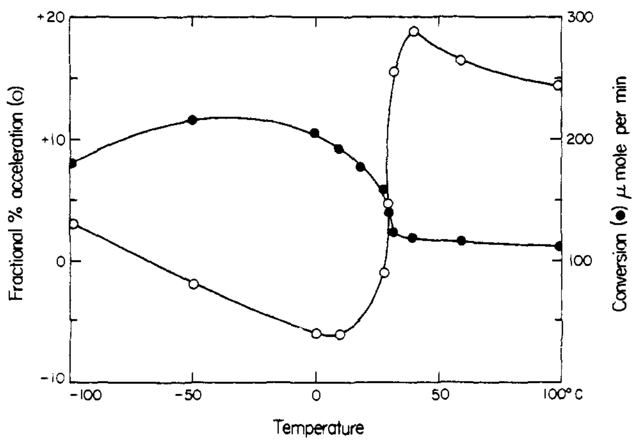

Figure 1. Parahydrogen conversion in zero field, and acceleration in a field of 7500 Oe, over 58 mg of powdered α-Cr_2O_3.

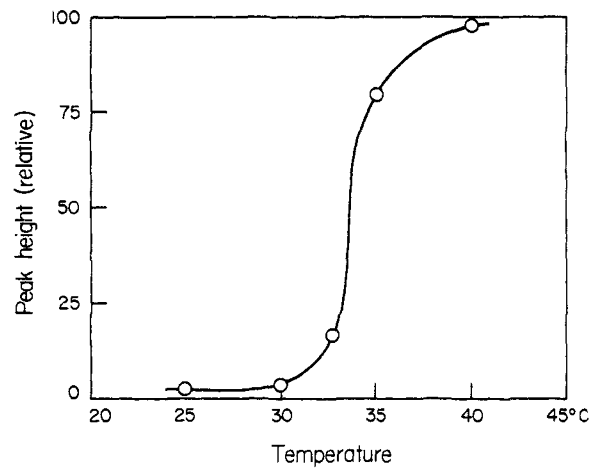

Figure 2. Epr resonance absorption near $g = 1.97$ for α-Cr_2O_3 (obtained simultaneously with Figure 1).

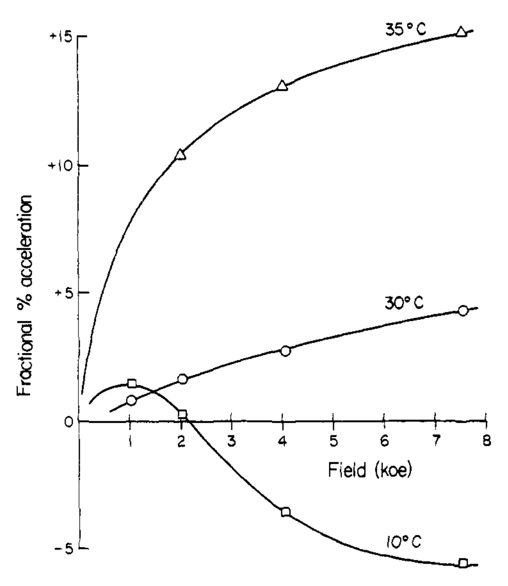

Figure 3. Acceleration as a function of extrinsic field over α-Cr_2O_3 as in Figures 1 and 2.

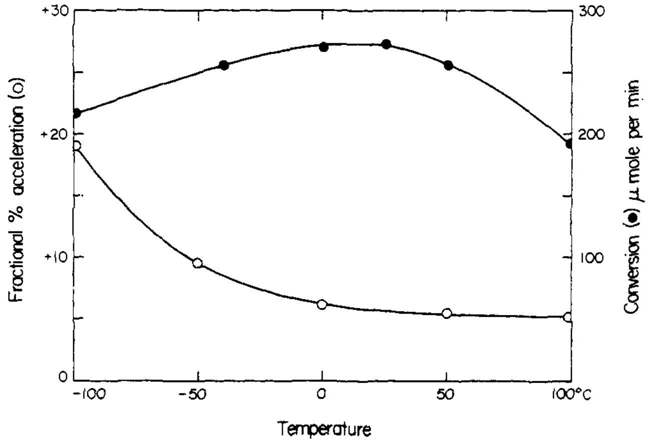

Figure 4. Conversion in zero field, and acceleration in a field of 7500 Oe, over 154 mg of 1 atom % powdered ruby.

8000 Oe. At still lower temperatures the acceleration for α-Cr_2O_3 became positive again over most of the field dependence, as indicated for 7500 Oe in Figure 1 near −100°.

Figure 4 shows conversion and acceleration as a function of temperature over 1.0 atom % ruby. The difference between these results and those over α-Cr_2O_3 shown in Figure 1 will be clear. In previous papers[5,6] attention has been drawn to the conversion poisoning of ruby and related systems caused by the chemisorption of hydrogen at room temperature and higher. It was found that while the conversion rate was diminishing, owing to this poisoning, the *fractional* acceleration caused by fields of 7500 Oe and up to 17,300 Oe did not change. This was found to be true both for ruby and for a 0.012% supported chromia on α-Al_2O_3. Figure 5 shows the fractional acceleration over 1.0% ruby as a function of field with, again, a marked contrast to the results on α-Cr_2O_3 shown in Figure 3.

Further measurements of this kind were done on a more dilute ruby containing only 0.1% chromia. The results were quite similar to those shown in Figure 4 except, of course, that the conversion rate was considerably smaller, owing to the smaller surface concentration of paramagnetic ions. But there was no important qualitative difference between the behavior of 0.1 and 1.0% ruby.

Figures 6–8 show acceleration data on the supported chromia on α-Al_2O_3. The chromia surface concentrations range from far below, to about equal to, that in a typical chromia–alumina dehydrogenation catalyst. Figure 6 shows conversion and acceleration as a function of temperature for a 0.0028% chromia sample; Figure 7 gives the same information for a 0.17% chromia sample; Figure 8 shows acceleration as a function of field for a 0.17% sample. The acceleration as a function of field for the 0.0028% sample closely resembled that for ruby as in Figure 5. A 0.045% sample gave results intermediate between the 0.0028 and the 0.17%.

It will be noted that the conversion activities of these samples differ considerably per unit mass of catalyst, and to a much larger extent if calculated per chromium ion accessible to molecular hydrogen. The masses of catalysts were chosen, as mentioned above, to give a conveniently measurable over-all conversion. A detailed

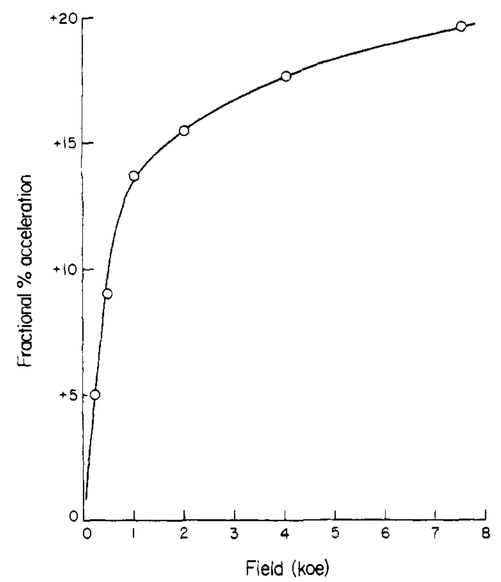

Figure 5. Acceleration as a function of extrinsic field over ruby as in Figure 4, at −100°.

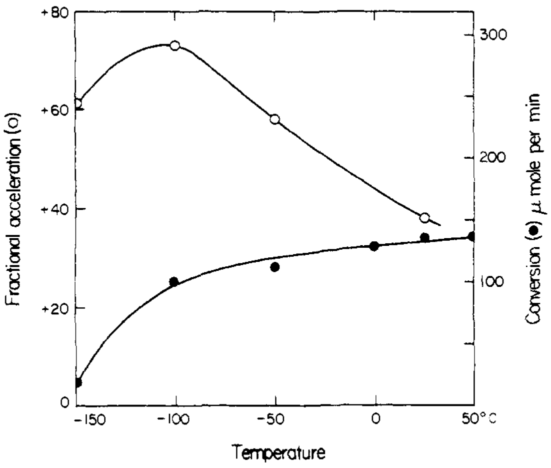

Figure 6. Conversion in zero field, and acceleration in a field of 7500 Oe, over 156 mg of 0.0028% Cr_2O_3 supported on α-Al_2O_3 after 2 hr in H_2 at 535°.

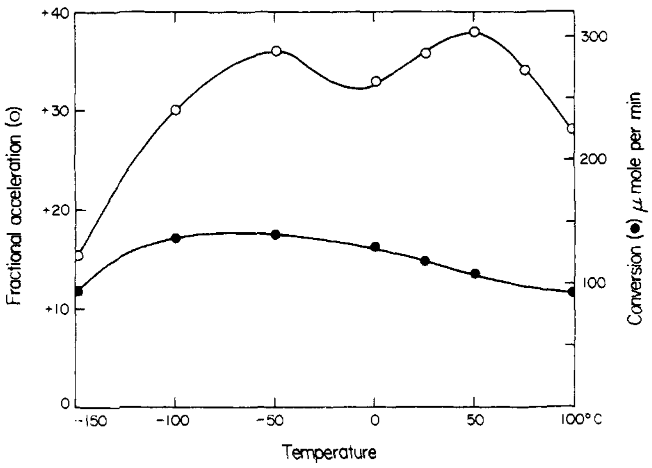

Figure 7. Conversion in zero field, and acceleration in a field of 7500 Oe, over 154 mg of 0.17% Cr_2O_3 supported on α-Al_2O_3.

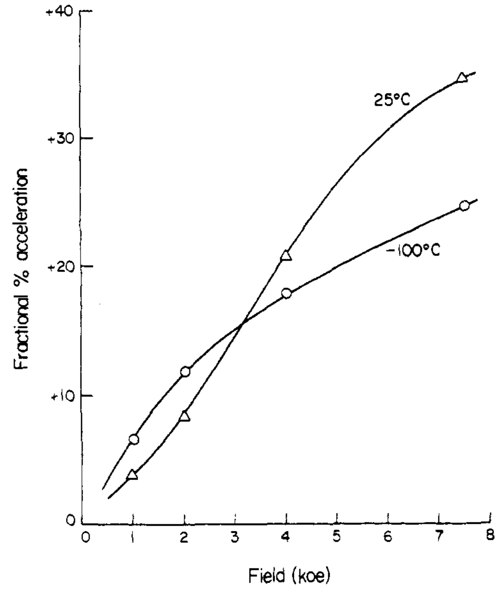

Figure 8. Acceleration as a function of extrinsic field over 206 mg of 0.17% Cr_2O_3 supported on α-Al_2O_3.

analysis of magnetic conversion activity and hydrogen adsorption over these samples is given elsewhere.[7]

Several further points will be mentioned. Like nearly all catalyst surfaces, the ones described here proved to be sensitive to pretreatment. Thus a 0.0028% supported sample after 2.5 hr in H_2 at 490° gave at −100° an acceleration in 7500 Oe of 25%. The identical sample after treatment for 2 hr in H_2 at 535° gave a moderately *smaller* zero field conversion, but an acceleration in 7500 Oe of 74%. Similar acceleration changes as a function of pretreatment were also observed for ruby and for α-Cr_2O_3. In all cases the acceleration decayed with time, even for conditions under which no progressive conversion poisoning had been observed. Another point concerns the remote possibility that the acceleration could be caused by a field-induced dissociative activity. But this possibility was eliminated by passing a 1:1 hydrogen–deuterium mixture over the catalyst and analyzing for HD with a mass spectrometer. No increase of HD concentration could be observed in fields up to 17,300 Oe. It was also found that all accelerations observed were completely reversible on application or removal of the extrinsic field. The rate changes appeared to take place instantaneously and were recorded as soon as the flowing hydrogen reached the thermal conductivity cell (about 2 min after adjustment of the field). In the absence of the catalyst, the conversion in an extrinsic field to 17,300 Oe remained zero.

Discussion

In previous papers[5,6,9] it has been shown that none of the catalyst samples studied shows measurable hydrogen–deuterium equilibration activity after the pretreatment and over the temperature range involved in the present work. The presumption is, therefore, strong that the

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[9] P. W. Selwood, *J. Catalysis*, in press.

conversion reaction reported here is exclusively magnetic in origin. The following statements may be made concerning the conversion acceleration observed on application of an extrinsic magnetic field.

1. The velocity of conversion may be changed reversibly and apparently instantaneously.
2. The acceleration may be negative or positive on a magnetically concentrated catalyst such as α-Cr_2O_3, and apparently only positive on a magnetically dilute system such as ruby.
3. The fractional acceleration is larger at lower temperatures, provided that no complicating factors such as a magnetic phase change occur in the catalyst, as is the case for α-Cr_2O_3 near room temperature.
4. The effect tends toward saturation at moderately elevated field.
5. While the zero field conversion rate is, as expected, sensitive to magnetic and other surface changes, it was found that the acceleration is even more sensitive.

It is well known that the heterogeneous magnetic parahydrogen conversion rate is influenced by the surface concentration and the square of the magnetic moment of the intrinsic field source, by a high power of the distance of nearest approach of the hydrogen molecule to the paramagnetic species, and by other factors such as the surface concentration of molecular hydrogen. It is not immediately obvious that any of these parameters are normally changed by a homogeneous magnetic field coming from the outside. Several possible explanations for the acceleration effect will be discussed briefly.

The effect could be produced by a moderate change of effective surface moment in the species, such as Cr^{3+}, giving the intrinsic field. The acceleration change observed (Figure 1) as the catalyst temperature rises through the Néel point (34°) strongly suggests that the acceleration may be related to a magnetic surface phase transition.[10] This explanation is almost certainly correct, but it cannot possibly be the sole explanation. A 1% ruby, in which Cr–Cr exchange interaction is far less than in α-Cr_2O_3, shows an even greater acceleration effect, although this becomes large only at lower temperatures, as shown in Figure 4. Proof that the acceleration effect may be influenced by, but cannot be completely dependent on, a magnetic phase transition is shown by the results on 0.1% ruby in which exchange interaction is still further reduced, yet the fractional acceleration at $-100°$ is even greater than it is on the 1% ruby.

A second possible explanation for the acceleration effect might be thought to be found in the magnetoelectric polarization induced in α-Cr_2O_3 by a magnetic field.[11] The magnetic field strength dependence of the electric polarization[12] in powdered α-Cr_2O_3 shows a resemblance to the saturation of the acceleration effect (Figures 5 and 8). However, observation of the acceleration effect in dilute ruby would appear to make this resemblance coincidental.

Still another possible explanation of the effect is possibly to be found in the theoretical treatment of Nagaev[13] for a field-induced increase of moment in a two-dimensional layer of adsorbed paramagnetic atoms exhibiting exchange interaction. But here also the results on ruby appear to exclude any such explanation.

The explanation that seems most promising in the light of the results reported in this paper is some kind of dynamic polarization,[14] or conceivably some field-induced change of rotation state transition energies, with the attendant effect on the collision efficiency of the conversion.

Whatever may be the explanation for the acceleration effect, it is clear that the effect is remarkably sensitive to surface magnetic phase changes. A comparison of Figures 6 and 7 shows how the increased fraction of chromia in clusters as opposed to isolated ions, in the more concentrated sample, produces a definite anomaly in the room-temperature region (near the Néel point). It is particularly noteworthy that this anomaly is readily identified for the acceleration effect but that it cannot be detected from the normal (zero field) conversion. This illustrates a possible application of the effect, namely in the characterization of surface states of transition metal oxides. It is to be noted also that at the present, limited, state of our understanding of the acceleration effect we cannot exclude the possibility that the extrinsic field modifies the surface magnetic state of the catalyst. So long as this possibility exists it complicates the interpretation of magnetic susceptibility, epr, and nmr data on solids of interest in heterogeneous catalysis.

Acknowledgment. This work was supported in part under grant from the Army Research Office (Durham).

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[12] T. J. Martin and J. C. Anderson, *ibid.*, **11**, 109 (1964).

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