JOURNAL OF CATALYSIS 43, 252–259 (1976)

Magnetic Effects on the *ortho–para*Hydrogen Conversion over α-Cr_2O_3, CoO, and MnO

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Received July 7, 1975; revised March 5, 1976

Catalyzed ortho–parahydrogen conversion rates were measured on two antiferromagnetic oxides, α-Cr_2O_3 and CoO over a range of temperature and both with and without an extrinsic magnetic field. A few measurements were made on MnO. The conversion mechanism was, in all cases, nondissociative. Results for the three catalysts, while qualitatively similar, differed in detail. A correlation between the zero field conversion rate and the extrinsic field rate suggests a relation to the paramagnetic–antiferromagnetic phase transition in catalysts of high surface site density. A positive extrinsic field effect was observed only at temperatures above the Néel point (T_N). Negative effects were found, in some cases, both above and below T_N. The latter results were characterized by a maximum rate decrease just below T_N and by a rate saturation effect that was a function of applied field strength. The several effects observed suggest that, on high site density surfaces, two or more mechanisms are operative in an extrinsic field. These, and other related results, show that the current state of conversion theory over magnetic surfaces is still incomplete.

INTRODUCTION

The nondissociative ortho–parahydrogen conversion has been studied for many years but the mechanism for this reaction remains uncertain. An attempt was made by Leffler (*1*) to apply modern theoretical methods to this problem. Subsequently it was found that the mechanism proposed was unable to explain various experimental results. Ilisca and Legrand (*2*) criticized Leffler's treatment on the ground that nuclear and rotational states are coupled according to the Pauli principle and that, owing to this coupling, the conversion involves energy much higher than that merely related to nuclear spin flips but that the energy could be supplied by magnon absorption or emission. Petzinger and Scalapino (*3, 4*) using an approach similar to that of Ilisca and Legrand, and considering energy transfer supplied by other types of molecular motion, developed conversion rates for magnetically dilute and concentrated catalyst surfaces.

The experimental properties of this system on surfaces of high site density were extended by Misono and Selwood (*5*) who found that the conversion rate could be increased if the catalyst is placed in a magnetic field in the 10 kOe range (1 Oe = 79.6 A m^{-1}). They also found an indication that on α-Cr_2O_3 the effect of the extrinsic field is related to the magnetic phase transition at the Néel point and that in zero field

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the conversion rate suffers a change at T_N. Subsequently, Arias and Selwood (*6*) made use of these effects to gain structural information on chromia preparations of high specific surface such as are used in catalytic hydrogenations and dehydrogenations. The same authors (*7*) also found that the ferromagnetic oxide, EuO, shows no change of zero field activity at the Curie point (T_c) region although a positive extrinsic field effect was observed above T_c. There appear to be no measurements of this kind on ferromagnetics having T_c in a more convenient region. The oxide CrO_2 is too reactive chemically to be exposed to hydrogen at T_c.

The purpose of the work presented in this paper was to extend the conversion rate measurements on α-Cr_2O_3 and to add two other oxides, CoO and MnO, to those already studied. Results are given for extrinsic fields up to about 18 kOe. It is felt that this information may aid in the development of a complete theoretical treatment. It is also clear that no theory of the conversion is likely to succeed unless it can explain both the intrinsic field effect (that produced by the atomic magnetic moments on the surface of the catalyst) and also the extrinsic field effect.

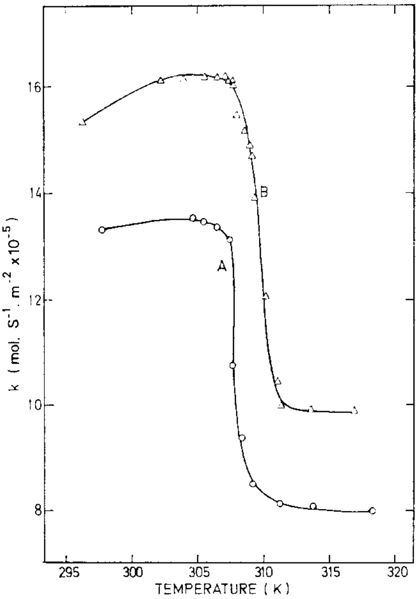

FIG. 1. Zero field p-oH_2 conversion rates over α-Cr_2O_3. (A and B) Obtained over different experimental arrangements.

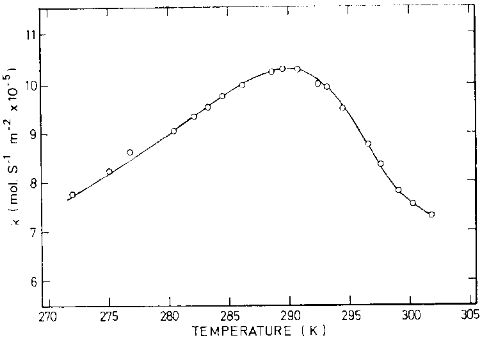

FIG. 2. Zero field p-oH_2 conversion rates over CoO.

EXPERIMENTAL METHODS

α-*Chromia*

Samples were prepared by ignition in air at 1073 K of $Cr(OH)_3$ obtained by room temperature precipitation from aqueous solutions of the reagent grade nitrate plus

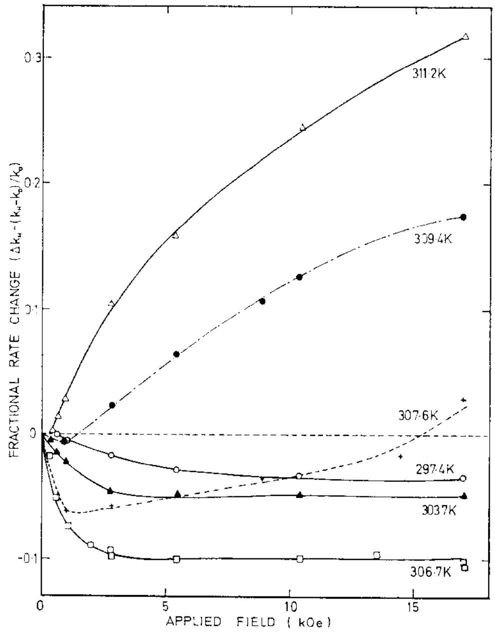

FIG. 3. Δk_H (fractional rate change) vs applied field for p-oH_2 conversion over Cr_2O_3 at various temperatures. (○), (▲), (□) Based on one set of data; (+), (●), (△) on another.

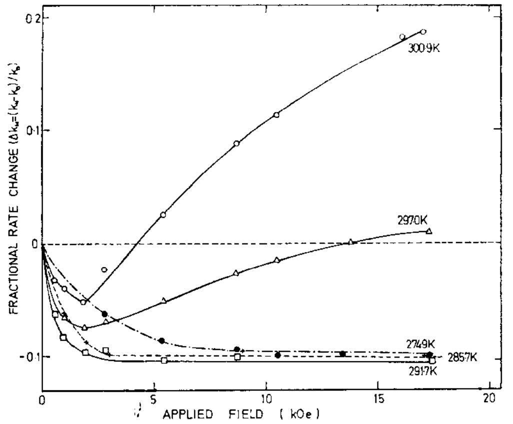

FIG. 4. Δk_H vs applied field for p–$o$$H_2$ conversion over CoO at various temperatures.

ammonia. The product gave the expected ESR signal and X-ray diffraction pattern. The surface area (BET, N_2) was 6 $m^2\ g^{-1}$. The bright green sample was heated in the reactor at a temperature of 823 K in flowing hydrogen for 1.5 hr, or more, then rapidly cooled to room temperature before conversion rate measurements were started. Rapid cooling in this manner was found in earlier experiments to minimize poisoning of the surface by hydrogen. Some Cr^{2+} may have been generated by the activation process.

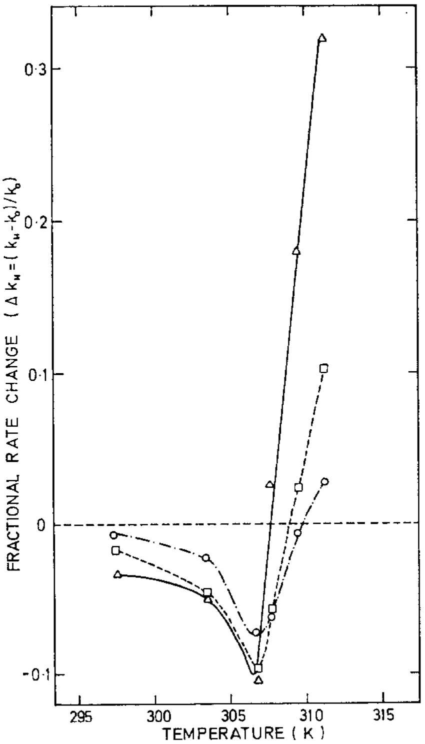

FIG. 5. Δk_H vs temperature for p–$o$$H_2$ conversion over α-Cr_2O_3 at several applied fields (kOe): (○) 0.99, (□) 2.8, (△) 17.

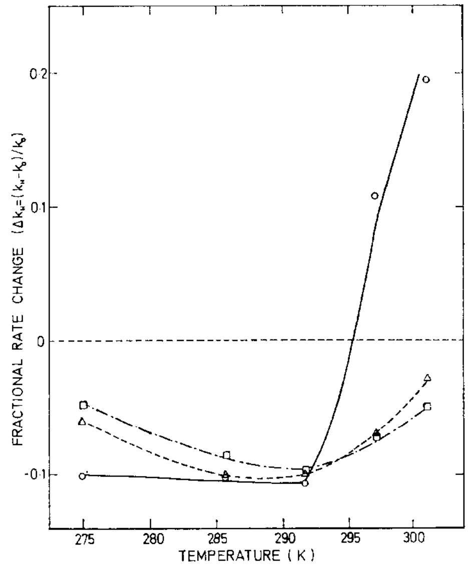

FIG. 6. Δk_H vs temperature for p–$o$$H_2$ conversion over CoO at several applied fields (kOe): (□) 1.8, (△) 2.8, (○) 17.3.

Cobalt Monoxide

The sample was prepared by thermal decomposition of the carbonate obtained by precipitation from reagent grade nitrate solution with sodium carbonate as described by Brauer (*8*). The black powder gave the X-ray diffraction pattern for CoO both before and after the rate measurements, no lines characteristic of higher oxides being present. The surface area was 5.8 $m^2\ g^{-1}$. Activation by hydrogen being precluded for obvious reasons, the sample was heated in purified flowing helium at 823 K for 2 hr, then cooled to room temperature.

Manganese Monoxide

The starting material for this reactive oxide was reagent grade $Mn(NO_3)_2 \cdot 6\ H_2O$.

TABLE 1

Summary of Properties and Results for α-Cr$_2$O$_3$, CoO, and MnO

	α-Cr$_2$O$_3$	Temp (K)	CoO	Temp (K)	MnO	Temp (K)
Surface (m^2 g^{-1})	6.0		5.8		5	
T_N(K)	307		291		(122)	
$k_0{}^a$($\times 10^5$ mol s^{-1} m^{-2})	16.0^b	307	10.1	291	—	
k_0($\times 10^5$ mol s^{-1} m^{-2})	9.8^b	313	7.4	301	0.6	296
$\Delta k_{17} = (k_{17} - k_0)/k_0$	+0.32	313	+0.19	301	2.0	296
k_0($\times 10^5$ mol s^{-1} m^{-2})	5.1	77	2.2	77	0.83	77
Δk_{17}	−0.07	77	0		—	

[a] k_0 is the specific conversion rate in zero extrinsic field, k_{17} the rate in 17 kOe.

[b] Based on curve B, Fig. 1.

This was heated to dryness, yielding MnO$_2$ which was characterized by its X-ray diffraction pattern. The MnO$_2$ was transferred to the reactor and heated *in situ* in flowing H$_2$ at 823 K for 12 hr. The product was light green. Owing to its high sensitivity to air no attempt was made at further characterization of the MnO.

Conversion Rate Measurements

All conversion results were obtained with apparatus previously described (*5*), at atmospheric pressure, with minor modifications. Temperatures were maintained within a few tenths of a degree. For experiments on the extrinsic field effect the reactor was placed between the pole tips of a 12 in. magnet with fields reproducible to about 0.1%. The minimum field in which any change of rate could be measured was a few hundred oersteds. The change of rate was, so far as could be determined, instantaneous on application of the field.

RESULTS

Zero Field Conversion Near T_N

The specific rates calculated for a flow reactor are presented, as a function of temperature, for α-Cr$_2$O$_3$ and for CoO in Figs. 1 and 2, respectively. Those for α-Cr$_2$O$_3$ are qualitatively similar to those of Arias and Selwood (*6*) except that the rates are somewhat lower. It is clear that a rate maximum exists for both antiferromagnetics near T_N, but there are differences in detail. For CoO the rate curve is symmetrical around T_N, with a broad maximum. For α-Cr$_2$O$_3$ the curve is asymmetric and characterized by a rapid rise on the approach to T_N from the high temperature side and a slow fall below T_N. It will be noted that, for both oxides, the maximum rate occurs very near T_N, namely 307 K for α-Cr$_2$O$_3$ as compared with the accepted value of 308 K, and 291 K for CoO, accepted 291 K, as given by Schieber (*9*).

Extrinsic Field Effect Near T_N

It was found that an extrinsic field caused a change of conversion rate and that the change was a function of temperature and of field strength. The effect was found to be especially sensitive to field strength at temperatures near T_N. In Figs. 3 and 4 the fractional rate changes $\Delta k_H = (k_H - k_0)/k_0$ are plotted against field strength (k_0 is the specific rate at zero applied field and k_H that at a field H). In Figs. 5 and 6 Δk_H values are plotted against temperature for some values of H. The data of Figs. 3 and 5 are based on two runs for α-Cr$_2$O$_3$ while five runs were used for CoO shown in Figs. 4 and 6. It was observed that some catalyst poisoning occurred during runs over a long period of time.

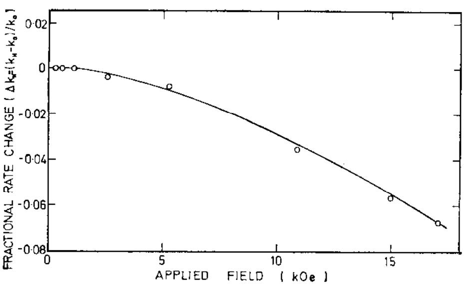

FIG. 7. Δk_H vs applied field for p–oH$_2$ conversion over α-Cr$_2$O$_3$ at 77 K.

From Figs. 3–6 it will be seen that these antiferromagnetic oxides have qualitative similarities near T_N. The following features will be mentioned:

1. While the extrinsic field effect is negative below T_N, the maximum negative effect for a given field occurs very near T_N.
2. Figures 5 and 6 show that for α-Cr$_2$O$_3$ there is an abrupt change in the plot of Δk_H vs T, but for CoO there is a broad, shallow trough. This difference parallels that shown in Figs. 1 and 2.
3. From Figs. 3 and 4 it may be seen that a positive field effect occurs just above T_N provided that the field strength is high. For α-Cr$_2$O$_3$, Δk_H becomes positive at ~4 K above T_N for fields of 17 kOe and down to 0.4 kOe. But for CoO Δk_H remains negative at ~9.5 K above T_N for a field of 4.1 kOe.
4. Figures 3 and 4 show that when the temperature is just above T_N there appears to be a field strength at which the negative field effect reaches a maximum. For CoO this occurs at ~2 kOe. For α-Cr$_2$O$_3$ the maximum is less well defined but is between 1 and 2 kOe.
5. Below T_N, for both oxides, there is a field strength above which little further change in Δk_H takes place. In other words there is a field "saturation" effect and this field increases as $T_N - T$ increases. But Δk_H is smaller as $T_N - T$ is larger.

Field Effects far Below T_N

Conversion rate measurements were also made below T_N at 77 K for α-Cr$_2$O$_3$, CoO, and MnO, the direction of conversion being from *ortho* to *para* at this temperature. The results are summarized in Table 1. For α-Cr$_2$O$_3$ the zero field specific rate is about $\frac{1}{3}$ of the maximum near T_N, while for CoO the rate is about $\frac{1}{5}$. The α-Cr$_2$O$_3$ showed a small but definite negative field effect at 77 K as shown in Fig. 7. No field effect was observed for CoO at 77 K.

Field Effects Far above T_N.

Because of the low T_N it is possible to make conversion rate measurements over MnO at temperatures far above T_N without encountering dissociative activity or chemical interaction. Table 1 summarizes the limited data available on MnO, and Fig. 8 shows a typical plot of Δk_H vs H at room temperature. The specific rate was approximately 0.6×10^{-5} mol s^{-1} m^{-2} at 296 K and this rose by 200% at an extrinsic field of 17 kOe.

DISCUSSION

The Zero Field Conversion Near T_N

As shown in Figs. 1 and 2, both α-Cr$_2$O$_3$ and CoO have an anomaly in conversion rate near their respective Néel points. The CoO plot has a broad peak centering at 291 K, while for α-Cr$_2$O$_3$ the peak is less

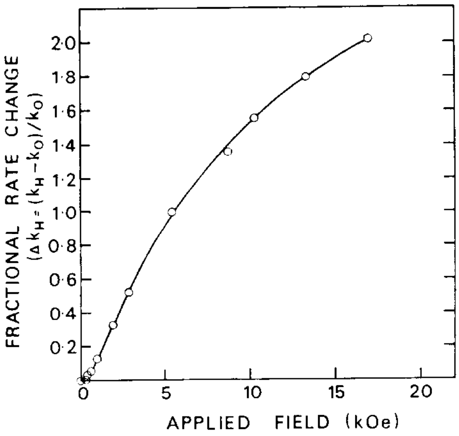

FIG. 8. Δk_H vs applied field for p–oH$_2$ conversion over MnO at room temperature.

well defined. The theoretical treatment of Petzinger and Scalapino (*3, 4*) led to the conclusion that, for a surface of high site density, the $o \rightleftarrows p$ conversion can be assisted by either magnon absorption (or emission) or, alternatively, be determined by the translational motion of H_2 molecules. (For convenience in connection with the following discussion some of the more significant data obtained are summarized in Table 1). For the former case the conversion rate was shown to be dependent on the magnon density with energy close to the energy of separation, $W_{11'}$, between the two lowest o and p states (2.4×10^{-21} J K^{-1}) and should, therefore, exhibit a more or less monotonous temperature dependence [Eq. (83) of Ref. (3)]. But for the latter case, when energy for the conversion is supplied by molecular hydrogen translational motion, the rate should increase as the temperature is lowered through the magnetic phase transition from paramagnetic to antiferromagnetic [Eqs. (89) and (90) of Ref. (*3*)]. Furthermore, the rate should continue to increase gradually as the temperature is lowered until it is about twice that just above T_N. This is because the term for spatial correlation of neighboring spins $\langle \mathbf{S}_0 \cdot \mathbf{S}_1 \rangle$ is zero above T_N. Below T_N it becomes negative and eventually approaches -1 at 0 K when the spins are completely antiferromagnetically ordered.

The results reported here for α-Cr_2O_3 and CoO do indeed show an abrupt increase of conversion rate as the temperature is lowered through T_N. The magnitude of the change is about that predicted. Earlier work on α-Cr_2O_3 (*6*) showed a somwehat larger change but such experimental differences obtained on different preparations are not unexpected. (The specific rates under identical conditions differed by one order.)

But as the temperature continues to be lowered below T_N there are effects that cannot be explained by the magnon assisted process. The conversion rates actually decrease for both α-Cr_2O_3 and CoO, and there is an unexplained broad maximum in the CoO curve which has no explanation even if some surface inhomogeneity is allowed for. The possibility that a spin wave correlation at a magnetic phase change may not be significant for the conversion at low temperatures has already been pointed out by Arias and Selwood (*7*) who found no measurable conversion rate change over EuO near the Curie point (~70 K).

Zero Field Conversion Far below T_N

The conversion rates in zero field at 77 K were found to be lower, over both α-Cr_2O_3 and CoO, than at only moderately below T_N. It is possible that the larger decrease, to $\frac{1}{3}$, for CoO as compared with α-Cr_2O_3 ($\frac{1}{2}$) might be caused by variation in geometrical structure on the surfaces of the two catalysts. Decreases of this kind are not infrequently found. They probably are related to diffusion control.

Extrinsic Field Effects

The only theoretical considerations of extrinsic field effects appear to be those of Ilisca and Legrand (*2*) and Ilisca and Gallais (*10*) and of Golovin and Buyanov (*11*). The former proposed that the applied field might cause an orientation effect on the surface magnetization of a ferromagnetic catalyst. The treatment was not extended to a surface without magnetic ordering and there is no evidence that extrinsic field effects may occur on ferromagnetic surfaces (*7*). The latter (*11*) proposed that the observed effects are related to a mechanism not involving nuclear spin decoupling. Such a mechanism is based on the waiving of Pauli's requirements of coupling the rotational state and nuclear spin state as a result of H_2 adsorption on the surface. The operating philosophy of the two groups of authors are obviously quite different.

In view of the complexity of the experimental results it is doubtful if a single mechanism is involved. A few remarks will be made in phenomenological and speculative terms. Examination of Figs. 3 and 5 suggests that there must be at least two mechanisms for the extrinsic field effects, one responsible for the negative effect and another for the positive. The shapes of the rate vs temperature and of the field induced change vs temperature curves show a strong correlation for both α-Cr_2O_3 and CoO (Figs. 1, 5 and 2, 6). This suggests that the field effects are related to the zero field mechanisms. Furthermore, the presence of a maximum negative field effects near the Néel point (Figs. 5, 6), the persistence of the effect some little distance above T_N, and the occurrence of a "saturation" field strength which is apparently dependent on $T_N - T$ (Figs. 3, 4) all suggest that a negative field effect in systems of this kind is characteristic of a magnetically dense surface. The positive field effect appears to be due to a mechanism operative only at $T > T_N$ and for which the temperature dependence is greater for a stronger field while field dependence is greater for a higher temperature. It is significant that Misono and Selwood (*5*) found that for a magnetically dilute catalyst (a dilute solid solution of α-Cr_2O_3 in α-Al_2O_3) the positive field effect was observed down to 173 K. The present results are consistent with a "positive" field effect mechanism requiring magnetic centers without ordering. This implies that the occurrence of a "negative" field effect (at relatively high fields) may indicate some surface ordering even though the sample is nominally dilute.

Further evidence that more than one mechanism must be operative is found in Selwood's observations (*12*) that self-supported Pr_2O_3, Nd_2O_3, Sm_2O_3, and Yb_2O_3 show a moderate negative effect in a field of 40 Oe, or even less, and then a larger positive effect at fields in the kilooersted region. The high field results have been confirmed by Ng (*13*) on Nd_2O_3, Sm_2O_3, and Yb_2O_3, and also for Nd_2O_3 by Eley *et al.* (*14*). But at very low surface spin density on activated Y_2O_3 and Lu_2O_3 Baron and Selwood (*15*) showed that the "negative" rate change was the only one observed at fields from ~3 Oe to 18 kOe. It may be noted that over the two antiferromagnetics α-Cr_2O_3 and CoO the "positive" effect and the "negative" effect have distinctly different field dependence characteristics. All of these results tend to show that more than one field effect can occur. However, it is not implied that the negative "weak field" effect observed over activated Lu_2O_3 and Y_2O_3 (*15*) necessarily bears any relationship to the negative effects observed over α-Cr_2O_3 and CoO in the antiferromagnetic phase. In this connection attention is drawn to the remarkably large fractional field effect found over MnO in the paramagnetic phase. Such a large effect is obviously difficult to be accommodated solely by the mechanism proposed by Golovin and Buyanov (*11*), on the basis of the time average projection of magnetic moment on the direction of an applied field (*2*). It may be noted also that the failure to observe a field effect for the o–pH_2 conversion at 77 K should not be accepted yet as proof that an effect is absent under these conditions. The result obtained may well lie in the pretreatment method of the samples. Further experimental data are required to confirm this point.

In conclusion it can only be said that there is still no complete understanding of the zero field, nondissociative *ortho–para*-hydrogen conversion either in the paramagnetic or in the ordered catalyst phases. It is obvious that a comprehensive theory of this reaction must be capable of explain- both the zero field and the extrinsic field conversion rates.

ACKNOWLEDGMENT

This work was supported in Santa Barbara by the U. S. Army Research Office. The University of Hong Kong is thanked by C.F.N. for the award of a research grant.

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