

## The Low-Temperature Orthohydrogen Conversion over Supported Oxides and Metals

NORIAKI WAKAO, J. M. SMITH, AND P. W. SELWOOD

*From the Departments of Chemistry and Chemical Engineering,  
Northwestern University, Evanston, Illinois*

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Rate data corrected for diffusion effects have been obtained for the ortho-hydrogen  $\rightarrow$  parahydrogen conversion at  $-196^{\circ}\text{C}$  and up to 23.2 atm over alumina-supported oxides of copper, nickel, manganese, and terbium. Other catalysts used were alumina-supported copper, nickel, and palladium metals, and zirconia-supported terbium oxide.

The supported nickel metal catalysts showed the highest activity; a sample prepared by multiple impregnation, and hence containing highly dispersed nickel, was 90 times more active than commercial 19% chromia-alumina used for comparison.

In relation to atomic radius and magnetic moment, the supported nickel metal was over  $10^3$  times more active than the oxides. Possible reasons for this effect are explored. Evidence is presented to show that the low-temperature conversion on nickel metal probably does not involve dissociated hydrogen.

### INTRODUCTION

Several studies have been made on the low-temperature, heterogeneous ortho  $\rightarrow$  parahydrogen conversion, and the reaction mechanism is reasonably well understood. Recent technological interest in liquid hydrogen has led to some need for more knowledge concerning the various parameters which contribute to over-all catalyst efficiency. The purpose of the present investigation was to determine more precisely the contribution of the magnetic moment of the active catalyst under conditions of controlled accessibility, of diffusion effects, and of ferromagnetism and collective paramagnetism (superparamagnetism).

The heterogeneous ortho  $\rightarrow$  parahydrogen conversion over paramagnetic oxides was observed by Taylor and Diamond (1) under conditions which precluded dissociative adsorption of the hydrogen. The theory of the magnetic conversion was

given by Wigner (2) for the homogeneous reaction, and later successfully applied by Harrison and McDowell (3) to the case of physically adsorbed hydrogen on a paramagnetic surface. Even earlier, Taylor and Sherman (4) had observed that the reaction was catalyzed by reduced nickel-kieselguhr at  $-190^{\circ}\text{C}$ , and had noted that a nickel catalyst sample cooled in hydrogen had a lower activity than one cooled in vacuum or in helium. This latter observation was extended by Harkness and Emmett (5) to other metals. Interpretation of the results on reduced metals was hampered by uncertainty concerning dissociative adsorption and possible "activated" adsorption.

In later years the low-temperature conversion over supported chromia on alumina, and also supported iron oxide on alumina, has been studied by Johnston (6, 7) who showed that, in agreement with the Wigner theory, the activities of these

catalyst systems were approximately proportional to the square of the magnetic moment of the paramagnetic ion. This conclusion involves some assumptions concerning the distribution of the active ions on the surface. Still later studies by Chapin (8) and others have emphasized the poisoning effect of water and other possible contaminants on these catalysts.

Our chief concern is with the report of Weitzel *et al.* (9) dealing with work done at the National Bureau of Standards Cryogenic Laboratory. Weitzel *et al.* list space velocities required to convert 25% orthohydrogen to 90% parahydrogen at 20°K and 15 psig. Commercial Harshaw 20% chromia-alumina was used as a standard catalyst and is said to have unit activity. Of the fifteen catalysts studied gadolinium oxide was the poorest with a relative activity of 0.2, and hydrous ferric oxide was the best with relative activity of 6.6.

For our purposes the most interesting results were the following three:

1. The rare earth oxides performed quite poorly in spite of the high magnetic moments present in some of them. It is easy to dismiss this poor showing as probably resulting from a low specific surface, but in the absence of surface area data this conclusion is perhaps not justified. Our question is, then: Is there some unique feature about rare earth ions which makes them less effective as orthohydrogen catalysts?

2. The 0.5% nickel-alumina studied by Weitzel *et al.* showed surprisingly high activity. On a weight (of paramagnetic oxide) basis it was by far the most active catalyst. It is probable that in this catalyst the nickel was present, at least in part, as oxide. The question is: What caused this enhanced activity?

3. Weitzel *et al.* report that some samples of hydrous ferric oxide exhibiting ferromagnetism were more active catalysts than those in which ferromagnetism was absent. The only reasonable source of ferromagnetism in hydrous ferric oxide is  $\gamma$ -ferric oxide or, possibly, magnetite. In either case the saturation magnetic moment of the iron is even less than that in hydrous ferric oxide which, owing to ex-

change interaction between adjacent iron ions, has a moment per atom of about 4.0 Bohr magnetons as compared with 6.0 in many ferric salts (10). Our question is, then: Is there any reason why the presence of ferromagnetism should be associated with catalytic activity?

The plan of the present work was to obtain activity data on several supported oxides under conditions which would permit direct comparison of one catalyst system with another. A series of oxides was selected showing a wide range of magnetic moments. These oxides were prepared in supported form at a concentration of 0.5% on  $\gamma$ -alumina from a single batch. The oxides selected were CuO, Mn<sub>2</sub>O<sub>3</sub>, NiO, and Tb<sub>2</sub>O<sub>3</sub>. Supported copper and nickel were also studied in the reduced, metallic state, as was supported palladium. Additional studies were made on 0.5% terbium oxide supported on high-area zirconia, and on 5.0% reduced nickel metal on alumina, in two preparative procedures.

The catalytic reaction kinetics were studied at elevated pressures under conditions believed to yield the true surface activity of each sample, at -196°C, and the magnetic moments of most samples were determined by direct magnetic susceptibility measurements. A matter which calls for comment is the distribution of the magnetic ions on the support surface. All samples except palladium were prepared by impregnation of  $\gamma$ -alumina with an appropriate volume of nitrate solution at such concentration as to yield ~0.5% supported oxide in the finished catalyst. It may then be wondered if the paramagnetic ions were distributed at infinite magnetic dilution on the surface or if they aggregated into microcrystals in which the accessibility of some ions to molecular hydrogen would obviously be diminished? That such ions are effectively dispersed at such low concentrations has been established for most of the systems investigated by magnetic susceptibility measurements (11,12), and, at least for chromia, by electron-spin resonance studies (13). The question as to whether all of the paramagnetic ions are on the surface in such

supported systems is more difficult. Cunningham and Johnston (7) showed that their data are consistent with the view that the magnetic ions are on the surface. This is to be expected if the preparation procedure involves exchange of surface aluminum or hydrogen ions (or possibly residual alkali ions) but not if small aggregates of the oxides are formed. It seems probable in the various samples studied that, at least, a reasonably definite proportion of the paramagnetic ions was situated on the surface. It will be noted that in no case were any of the samples heated sufficiently to cause solid solution formation.

The question of atomic distribution in reduced supported metal catalysts is quite different and will be discussed after the results have been presented.

#### EXPERIMENTAL METHOD

##### *Preparation of Samples*

For each of the catalyst samples used there are given: first, the designation; second, the preparative procedure; and third, some remarks concerning the structure and composition.

19%  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ . This was used as a standard of reference in the catalytic studies. This was Harshaw chromia-alumina No. Cr-1403T containing 19% chromia. It was used as obtained in the form of  $\frac{1}{8}$ -in. pellets. Before use the catalyst was heated in the reactor in  $\text{H}_2$  at  $400^\circ\text{C}$  for 5 hr, then cooled in  $\text{H}_2$  to  $-196^\circ\text{C}$  for the ortho-parahydrogen run.

$\gamma\text{-Al}_2\text{O}_3$ . This was used as a catalyst support; it was prepared in the usual manner by dissolving pure aluminum metal in sodium hydroxide solution, partially neutralizing with nitric acid, then completing precipitation with carbon dioxide. The precipitate was washed, filtered, and dried at  $400^\circ\text{C}$ . The ability of the  $\gamma\text{-Al}_2\text{O}_3$  to sorb water was then determined, and portions were impregnated with nitrate solutions of the several paramagnetic ions made up of such concentration as to yield 0.5% (as oxide) of each of the supported systems described in the following. After the im-

pregnation step each sample was dried in air at  $450^\circ\text{C}$ . The samples were pelleted into  $\frac{1}{8}$ -in. tablets, with the aid of 5% stearic acid which was later removed by heating the pellets in air at  $500^\circ\text{C}$  for 4 hr. The pellets were then packed into the reactor. There was no significant formation of dust from the catalyst pellets.

0.5%  $\text{CuO}/\text{Al}_2\text{O}_3$ . The sample was heated in air at  $400^\circ\text{C}$  for 2 hr, and cooled in air to room temperature. The air was displaced by purified helium, the sample was cooled to  $-196^\circ\text{C}$ , and hydrogen was admitted for the catalytic run. There is some uncertainty concerning the oxidation state of the copper.

0.5%  $\text{NiO}/\text{Al}_2\text{O}_3$ . Treatment was identical with that already described for 0.5%  $\text{CuO}/\text{Al}_2\text{O}_3$ . It is probable that the average oxidation state of the nickel was greater than +2. This matter is discussed later.

0.5%  $\text{Cu}/\text{Al}_2\text{O}_3$ . The 0.5%  $\text{CuO}/\text{Al}_2\text{O}_3$  described was heated in hydrogen at  $400^\circ\text{C}$  for 4 hr and then cooled in hydrogen to  $-196^\circ\text{C}$  for the run. The actual concentration of copper as metal was, of course, about 0.4%.

0.5%  $\text{Ni(A)}/\text{Al}_2\text{O}_3$ . Treatment of 0.5%  $\text{Ni}/\text{Al}_2\text{O}_3$  was same as for the 0.5%  $\text{Cu}/\text{Al}_2\text{O}_3$  except that the reduction step was continued for 12 hr.

0.5%  $\text{Ni(B)}/\text{Al}_2\text{O}_3$ . Treatment was the same as for 0.5%  $\text{Ni(A)}/\text{Al}_2\text{O}_3$  except that it was cooled from  $400^\circ\text{C}$  in flowing purified helium to remove chemisorbed hydrogen.

0.5%  $\text{Mn}_2\text{O}_3/\text{Al}_2\text{O}_3$ . Treatment was the same as for 0.5%  $\text{Cu}/\text{Al}_2\text{O}_3$ . It is probable that the average oxidation state of the manganese was a little lower than +3.

0.5%  $\text{Tb}_2\text{O}_3/\text{Al}_2\text{O}_3$ . Treatment was the same as for 0.5%  $\text{Cu}/\text{Al}_2\text{O}_3$ . The oxidation state was almost certainly +3.

The following additional systems were also prepared:

0.5%  $\text{Pd}/\text{Al}_2\text{O}_3$ . The  $\gamma\text{-Al}_2\text{O}_3$  was impregnated with palladous chloride solution. The mixture was then heated in flowing hydrogen until no further hydrogen chloride was evolved. The pelleted sample was heated in the reactor in hydrogen at  $400^\circ\text{C}$  for 4 hr and then cooled in hydrogen to

−196°C. This treatment insured complete hydrogenation of the palladium metal.

5.0% Ni(I)/Al<sub>2</sub>O<sub>3</sub>. This was prepared as described for 0.5% Ni(A)/Al<sub>2</sub>O<sub>3</sub> except that the solution used for impregnation was sufficiently concentrated to yield 5.0% Ni (as oxide) in the finished catalyst.

5.0% Ni(X)/Al<sub>2</sub>O<sub>3</sub>. The impregnation step was carried out in ten successive stages (14) in order to obtain a more effective dispersion of the nickel. Apart from this difference the preparation was as described for 5.0% Ni(I)/Al<sub>2</sub>O<sub>3</sub>.

0.5% TbO<sub>2</sub>/ZrO<sub>2</sub>. This was prepared by impregnation of zirconia with terbium nitrate solution, followed by heating in air at 400°C for 2 hr. The sample was cooled in

air to room temperature, flushed with helium, cooled to −196°C, then treated with hydrogen for the catalytic run. The zirconia was obtained from the Norton Company and stated to have a surface area of 250 m<sup>2</sup>/g as supplied after heating at 300°C. The surface area was stated to be 65 m<sup>2</sup>/g after heat treatment at 550°C for 3 hr. The finished catalyst sample was tan in color and the oxidation state of the terbium was almost certainly close to +4.

#### Reactor and Analyzer

Figure 1 shows the apparatus used for the kinetic experiments. Electrolytic grade hydrogen was passed through a Deoxo unit to remove oxygen and through three

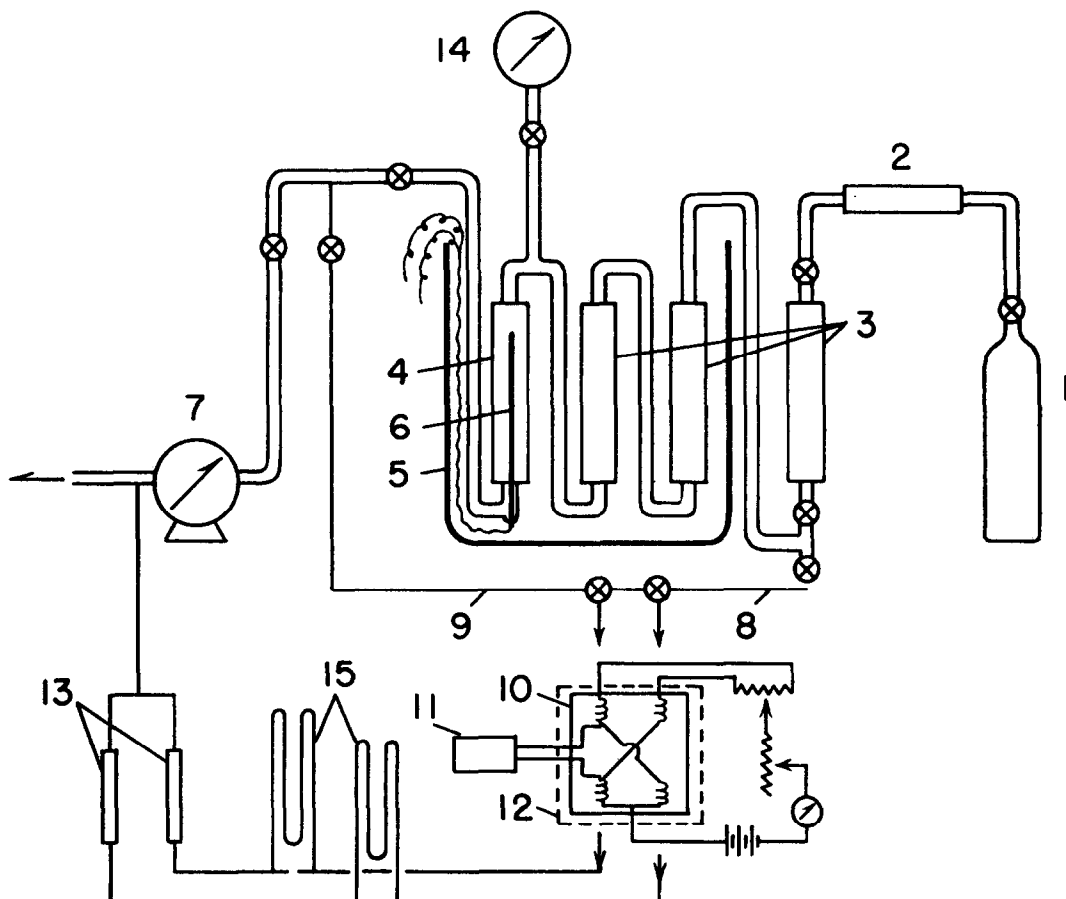


FIG. 1. Schematic drawing of apparatus. 1, Electrolytic hydrogen cylinder; 2, Deoxo unit; 3, silica gel tube; 4, catalyst chamber; 5, liquid nitrogen bath; 6, thermocouple probe; 7, wet gas meter; 8, reference gas; 9, sample gas; 10, thermal conductivity cell; 11, potentiometer; 12, constant temperature bath; 13, soap film meter; 14, pressure gauge; 15, manometer and orifice meter.

tubes filled with silica gel to remove water. The final two silica gel tubes and the reactor were immersed in a constant temperature bath containing liquid nitrogen at atmospheric pressure. The reactor was of stainless-steel tubing,  $\frac{1}{2}$  in. i.d. and 10 in. long. The catalyst was supported by 1 cm of glass wool contained on a stainless steel screen. A 1-cm layer of glass wool was also placed directly above the catalyst.

The composition of the hydrogen leaving the reactor was measured with a thermal conductivity cell (Gow-Mac Company, 30-S geometry) as described by Weitzel and White (15). The reference gas was normal hydrogen containing the equilibrium amount (at room temperature) of the para form, 25%. Both reference and sample streams were passed through the cell at rates of 10 cc/sec. The cell was operated as a constant current device at 140 ma and was maintained at 28.3°C with a constant temperature bath.

Calibration was effected by using the reactor and an active catalyst at very low flow rates to obtain gas of the equilibrium composition. Operation at successively lower flow rates until the composition showed no further change was assumed to give the equilibrium composition. Synthetic gas mixtures of known parahydrogen content were obtained by mixing known flow rates of normal hydrogen and the effluent from the reactor at liquid nitrogen temperature. The relationship between the parahydrogen concentration and its emf was linear (0.0475 mv/% parahydrogen).

The temperature within the reactor was measured with a copper-constantan thermocouple inserted in a  $\frac{1}{8}$ -in. o.d. probe contained in the reactor (see Fig. 1). The temperature in the reactor was not measurably different from that in the nitrogen bath which was also measured with a copper-constantan thermocouple.

Preliminary experiments with an empty reactor, and one containing the carrier  $\text{Al}_2\text{O}_3$ , showed no activity.

Rate measurements were made with the apparatus for each catalyst over a range of gas flow rates and at pressures from 4.4

to 28.2 atm all at  $-196^\circ\text{C}$  (liquid nitrogen boiling point at atmospheric pressure).

#### *Magnetic Susceptibilities*

Susceptibilities were measured by the Gouy method. The low concentrations of the paramagnetic ions, the effect of hydration on the susceptibility of alumina, and the effect of traces of ferromagnetic impurities, especially in the zirconia-supported sample, made precision poor. Magnetic measurements were made on the oxidized phases only. With the exception of terbium, all had previously been studied exhaustively in this laboratory (10).

#### *Surface Areas*

These were determined as required by the Brunauer-Emmett-Teller (nitrogen) standard procedure.

#### *Hydrogen-Deuterium Exchange*

A 1:1 mixture of  $\text{H}_2$  and  $\text{D}_2$  at 1 atm pressure was passed over catalyst samples, as indicated in the following at  $-196^\circ\text{C}$ , under conditions of space velocity as nearly as possible the same as those used in the orthohydrogen activity tests. The gases were analyzed on a mass spectrometer.

#### *Adsorption of Hydrogen*

The sorption of hydrogen at room temperature on reduced nickel samples, as indicated in the following, was measured volumetrically by standard techniques. Purified helium was used to determine the dead space.

#### *Calculation of Conversion Rates*

A rate equation which satisfactorily correlated the kinetic measurements is of the form

$$r = k(1 + 1/K)(Y_{\text{eq}} - Y) \quad (1)$$

where

$$k = k_c P / (1 + K_{\text{ads}} P) \quad (2)$$

These expressions result when it is postulated that the reaction occurs (a) by adsorption of orthohydrogen on a single active site of the catalyst surface, (b) by conversion to parahydrogen on the surface,

and (c) by desorption of parahydrogen into the gas phase.

When external diffusion resistances are significant, the mole fraction  $Y$  in Eq. (1) must be the value at the catalyst surface and not the composition in the gas stream. This situation existed for the 5% Ni(X)/Al<sub>2</sub>O<sub>3</sub> and the 0.5% Ni(B)/Al<sub>2</sub>O<sub>3</sub> catalysts because the rates of reaction were relatively high. For these two catalysts corrections were made for external diffusion by the method described in detail in another paper (16).

To evaluate  $k$  values and hence activities for the various catalysts, it was necessary to write the equation for reaction in a steady-state flow system, i.e.,

$$\bar{r}dW = FDy \quad (3)$$

The average rate  $\bar{r}$  for a porous catalyst must take into consideration the diffusion resistance within the catalyst pores. The relation between  $\bar{r}$ ,  $r$ , and the effectiveness factor  $E$  is

$$\bar{r} = rE = k(1 + 1/K)(Y_{eq} - Y)E \quad (4)$$

Combining Eqs. (3) and (4) and integrating between the feed ( $Y_1$ ) and outlet ( $Y_2$ ) compositions of the reactor, yields

$$\frac{W/F}{\ln [(Y_{eq} - Y_1)/(Y_{eq} - Y_2)]} = \frac{1}{k(1 + 1/K)E} \quad (5)$$

Equation (5) and the experimental data were used to calculate values of  $k$  for each catalyst. The equilibrium constant at  $-196^\circ\text{C}$  is 1.01 (17, 18). Effectiveness factors  $E$  were estimated by a trial and error procedure using Buckingham's (19) relationship between the effective diffusivity and the void fraction. The void fraction was calculated from the measured density of the catalyst pellet and the chemical density of the solid material in the pellet (3.2 for Al<sub>2</sub>O<sub>3</sub> and 5.68 for zirconia). The effectiveness factor was determined from the effective diffusivity by employing the Wheeler (20) procedure.

#### NOTATION\*

$E$	Effectiveness factor of the catalyst particle
$F$	Flow rate through reactor, moles/sec
$k$	Rate parameter, defined by Eq. (2), moles/(g of catalyst) (sec)
$k_c$	Specific reaction rate, moles/(g of catalyst) (sec) (atm)
$K$	Thermodynamic equilibrium constant
$K_{ads}$	Adsorption equilibrium constant, 1/atm
$P$	Total pressure, atm
$r$	Rate of reaction, moles/(g of catalyst) (sec)
$\bar{r}$	The average value for the catalyst particle
$W$	Mass of catalyst in reactor, g
$Y$	Mole fraction parahydrogen
$Y_{eq}$	The equilibrium value at $-196^\circ\text{C}$ , i.e., 0.503

#### RESULTS

Table 1 summarizes the results and includes, in addition to  $k$  values, catalyst pellet densities and effectiveness factors. The last column presents relative activities of the various catalysts at 28.2 atm based upon the 19% Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.

Magnetic susceptibilities and derived moments are given in Table 2. The moments are "effective" moments calculated in the usual manner (10) but on the assumption that exchange interaction at these concentrations is negligible. This assumption has been justified in earlier work (11). Table 2 also gives moments reported elsewhere. It is well known that supported paramagnetic oxides may exhibit magnetic properties quite different from those of pure massive oxides, and that very small particles of reduced metals may also show unique magnetic properties. Some comment on the data is, therefore, called for.

The 0.5% CuO/Al<sub>2</sub>O<sub>3</sub> was found to have a rather high effective moment. Owing to the poor precision there is some doubt concerning this value, but possible explanations are developed in the following.

The moment given for 0.5% Ni(A)/

\* Subscripts 1 and 2 refer to conditions of the feed and effluent of the reactor.

TABLE I  
 ACTIVITIES OF THE CATALYSTS

Catalyst sample	Density (g/cm <sup>3</sup> )	Weight (g)	Pressure (atm)	<i>E</i>	<i>k</i>	Relative activity
19% Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	1.34	9.30	28.2	0.99	0.099 × 10 <sup>-4</sup>	1.0
			7.8	0.99	0.076 × 10 <sup>-4</sup>	
			4.4	0.99	0.060 × 10 <sup>-4</sup>	
0.5% CuO/Al <sub>2</sub> O <sub>3</sub>	1.26	3.86	28.2	0.97	0.33 × 10 <sup>-4</sup>	3.3
			7.8	0.98	0.27 × 10 <sup>-4</sup>	
0.5% NiO/Al <sub>2</sub> O <sub>3</sub>	1.43	3.66	28.2	0.95	0.51 × 10 <sup>-4</sup>	5.2
			7.8	0.96	0.34 × 10 <sup>-4</sup>	
0.5% Cu/Al <sub>2</sub> O <sub>3</sub>	1.26	3.86	28.2	—	0	0
			7.8	—	0	
0.5% Ni(A)/Al <sub>2</sub> O <sub>3</sub>	1.43	3.66	28.2	0.77	3.0 × 10 <sup>-4</sup>	30
			7.8	0.81	2.2 × 10 <sup>-4</sup>	
			4.4	0.85	1.7 × 10 <sup>-4</sup>	
0.5% Ni(B)/Al <sub>2</sub> O <sub>3</sub>	1.33	3.21	28.4	0.70	5.2 × 10 <sup>-4</sup>	53
			4.4	0.81	2.7 × 10 <sup>-4</sup>	
0.5% Mn <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	1.28	3.38	28.2	0.94	0.76 × 10 <sup>-4</sup>	7.7
			7.8	0.95	0.63 × 10 <sup>-4</sup>	
0.5% Tb <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	1.69	4.70	28.2	0.93	0.41 × 10 <sup>-4</sup>	4.1
			7.8	0.94	0.32 × 10 <sup>-4</sup>	
0.5% Pd/Al <sub>2</sub> O <sub>3</sub>	1.41	4.11	28.2	—	0	0
			7.8	—	0	
5.0% Ni(I)/Al <sub>2</sub> O <sub>3</sub>	1.84	3.84	28.2	0.85	0.84 × 10 <sup>-4</sup>	8.5
			7.8	0.86	0.69 × 10 <sup>-4</sup>	
5.0% Ni(X)/Al <sub>2</sub> O <sub>3</sub>	1.91	2.55	28.2	0.42	8.9 × 10 <sup>-4</sup>	90
			7.8	0.45	5.7 × 10 <sup>-4</sup>	
0.5% TbO <sub>2</sub> /ZrO <sub>2</sub>	2.63	6.58	28.2	0.96	0.20 × 10 <sup>-4</sup>	2.0
			7.8	0.97	0.17 × 10 <sup>-4</sup>	
			4.4	0.98	0.11 × 10 <sup>-4</sup>	

Al<sub>2</sub>O<sub>3</sub> is the saturation moment per atom estimated on the basis of studies on fine nickel particles at considerably higher concentration. The normal saturation moment is lowered somewhat by the presence of chemisorbed hydrogen. These remarks apply to the several reduced nickel samples except, probably, 0.5% Ni(B)/Al<sub>2</sub>O<sub>3</sub> for which an effort was made to prevent hydrogen reaching the surface until the temperature was lowered to -196°C.

The 0.5% Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was measured

on a sample before the heat treatment in hydrogen. This doubtless accounts for the low moment which, for Mn<sup>3+</sup> in dispersed form, should be about 4.9 Bohr magnetons.

The 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> is diamagnetic, as expected, in the presence of hydrogen. Pd is normally paramagnetic with a moment of about 0.6 in massive form but which may change in dispersed form (25).

The 0.5% TbO<sub>2</sub>/ZrO<sub>2</sub> has apparently not previously been studied. A trace of ferromagnetic impurity in the ZrO<sub>2</sub> pre-

TABLE 2  
MAGNETIC SUSCEPTIBILITIES  $\chi$ , AND MOMENTS  $\mu$ , AT ROOM TEMPERATURE

Sample	$\chi \times 10^6$ (cc g <sup>-1</sup> )	$\mu_{\text{eff}}$ (Obs.) (Bohr magnetons)	$\mu$ (Ref.) (Bohr magnetons)
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-0.43	0	0
ZrO <sub>2</sub>	0.01?	0	0
19% Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	—	—	3.2 (21)
0.5% CuO/Al <sub>2</sub> O <sub>3</sub>	-0.17	2.7	2.0 (22)
0.5% NiO/Al <sub>2</sub> O <sub>3</sub>	-0.06	3.3	3.3 (14)
0.5% Cu/Al <sub>2</sub> O <sub>3</sub>	—	—	0 (22)
0.5% Ni(A)/Al <sub>2</sub> O <sub>3</sub>	—	—	0.6 (23)
0.5% Ni(B)/Al <sub>2</sub> O <sub>3</sub>	—	—	0.6 (23)
0.5% Mn <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.14	3.9	3.8 (24)
0.5% Tb <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	1.01	10.6	9.6 (10)
0.5% Pd/Al <sub>2</sub> O <sub>3</sub>	—	—	0 (10)
5.0% Ni(I)/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	—	—	0.6 (23)
5.0% Ni(X)/Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	—	—	0.6 (23)
0.5% TbO <sub>2</sub> /ZrO <sub>2</sub>	—	—	8.0 (10)

<sup>a</sup> The susceptibilities of these two samples were measured in the oxidized phase. The moments were 3.3 magnetons in both cases.

vented accurate determination. The moment of the Tb<sup>4+</sup> was, therefore, assumed to be about the same as that of the iso-electronic Gd<sup>3+</sup> ion. Owing to the low catalytic activity of this preparation, the matter was not further pursued.

The following additional information was obtained as an aid in the interpretation of the activity data.

The rate of hydrogen-deuterium exchange at -196°C was obtained on samples 0.5% NiO/Al<sub>2</sub>O<sub>3</sub> and 0.5% Ni(A)/Al<sub>2</sub>O<sub>3</sub>. There was a trace of exchange on the former, virtually none on the latter. Schuit *et al.* (26) reported similar results on silica-supported nickel at -196°C.

The sorption of hydrogen at 27°C was measured on a sample of 5.0% Ni(X)/Al<sub>2</sub>O<sub>3</sub>. The total sorption was about 8 cc/g nickel. A small fraction of this may have been the result of physical adsorption on the support.

The specific surface of 5.0% Ni(X)/Al<sub>2</sub>O<sub>3</sub> was found to be 155 m<sup>2</sup>. Most of this surface was, of course, contributed by the alumina.

#### DISCUSSION

While the Wigner theory (2) of low-temperature orthohydrogen conversion is an approximation, it is instructive to compare catalyst activities in terms of the

parameter  $\mu^2/r^6$ . This is done in Table 3 for all the catalysts which may be considered comparable in terms of per cent active component, support, and method of preparation. Most of this discussion will be devoted to the performance of the reduced nickel catalysts, but some remarks will first be made on the oxides.

TABLE 3  
COMPARISON OF ACTIVITIES IN RELATION TO  
MAGNETIC MOMENT AND ATOMIC  
(OR IONIC) RADIUS<sup>a</sup>

Sample	$r$ (Å)	$kr^4/\mu^2$
0.5% CuO/Al <sub>2</sub> O <sub>3</sub>	0.72 (?)	$6.3 \times 10^{-7}$
0.5% NiO/Al <sub>2</sub> O <sub>3</sub>	0.73	$7.1 \times 10^{-7}$
0.5% Ni(A)/Al <sub>2</sub> O <sub>3</sub>	1.154	$1.2 \times 10^{-3}$
0.5% Ni(B)/Al <sub>2</sub> O <sub>3</sub>	1.154	$3.3 \times 10^{-3}$
0.5% Mn <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.66	$4.8 \times 10^{-7}$
0.5% Tb <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	1.02	$5.0 \times 10^{-7}$

<sup>a</sup> The radii given are approximate only. There is uncertainty concerning the oxidation state, the magnetic moment, and the radius of each paramagnetic ion present.

The four oxides supported on alumina, namely, 0.5% CuO/Al<sub>2</sub>O<sub>3</sub>, 0.5% NiO/Al<sub>2</sub>O<sub>3</sub>, 0.5% Mn<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and 0.5% Tb<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, show relative activities about as expected. It will be shown that there is uncertainty concerning the oxidation state (and hence of the magnetic moment and



radius) for several of the paramagnetic ions. In view of this uncertainty, a constancy of the rate constant multiplied by  $r^6/\mu^2$ , that is,  $kr^6/\mu^2$ , within considerably less than one order of magnitude is quite satisfactory. The showing of terbium is a little disappointing in view of the very high magnetic moment of the  $Tb^{3+}$  ion. The high moment appears to be counterbalanced by the large radius. It is well known that in the rare earth series the 4f electrons which are responsible for the paramagnetism are shielded from the fields of adjacent ions and dipoles. A possible reason for the relatively poor activity of the terbium is that this shielding influence may also be operative as far as the magnetic ortho  $\rightarrow$  parahydrogen conversion is concerned, but the results on  $Ni^{2+}$  and  $Mn^{3+}$  do not support this view. In any event, the high magnetic moments of some rare earth ions do not make them very good catalysts for this reaction.

The high activity reported by Weitzel *et al.* for 0.5% nickel-alumina has been confirmed in the present work,<sup>†</sup> and has been shown to be related to the presence of reduced nickel. Metallic nickel has a saturation magnetic moment of only about one-fifth that of  $Ni^{2+}$  ions in dispersed oxides or other magnetically dilute environments, and the radius of the atom in the metal is substantially larger than that of the  $Ni^{2+}$  in NiO. Together with the enhanced activity found, these several factors yield a parameter  $kr^6/\mu^2$  some  $10^3$  times larger than for the supported nickel in the form of the oxide.

There are several possible explanations for the effect described. The first explanation which comes to mind is that the reaction on the nickel metal is the familiar dissociative mechanism which, as is well known, is operative at room temperature and higher. According to this view the hydrogen molecules would be dissociatively adsorbed to form Ni—H bonds. Recom-

<sup>†</sup> The 0.5% nickel-alumina used by Weitzel *et al.* was not so active as hydrous ferric oxide, but this is obviously because of the much larger fraction of catalyst present in the latter.

bination leads to the equilibrium ortho-para concentration at  $-196^\circ C$ .

The dissociative mechanism is known to occur on some catalysts at low temperatures and it cannot be excluded completely on nickel, but there is evidence against it. First, studies of adsorption mechanisms (27, 28) show that, if dissociative adsorption occurs at  $-196^\circ C$ , the volume of gas so adsorbed is small and the hydrogen atoms are very tightly bound to the nickel. Second, the rate of  $H_2$ - $D_2$  exchange on this catalyst at  $-196^\circ C$  is negligibly small. It may possibly be true, as pointed out by Eley (29), that a small difference in zero-point energy could make the  $H_2$ - $D_2$  exchange reaction several orders slower than the dissociative ortho  $\rightarrow$  para conversion. But we find that hydrogenized palladium shows no ortho-para activity at  $-196^\circ C$  although palladium, like nickel, is a powerful dissociating catalyst at higher temperatures. In view of these considerations we shall examine other possible reasons for the activity of the reduced nickel.

The next possibility is related to the unique magnetic properties of small ferromagnetic particles. There is certainly no obvious reason why ferromagnetism per se should lead to high catalytic activity, but the Stoner-Néel theory (30-32) shows that small particles of ferromagnetic substances, of which nickel is one, may show the field strength dependence and temperature dependence of magnetization characteristic of paramagnetic, rather than of ferromagnetic, matter. The principal difference is that the magnetic moment per particle is given by the product of the atomic moment times the number of atoms in the particle. For nickel particles less than  $100\text{\AA}$ , in radius, and containing about  $10^4$  atoms, the effective magnetic moment would be about  $6 \times 10^3$  Bohr magnetons. If the number of atoms in a particle is  $n$ , then the catalytic activity should be proportional to  $(\mu n)^2$  rather than to  $\mu^2 n$  for a similar total number of mutually isolated atoms.

The difficulty with the idea expressed

above is twofold. First, the radius of the particle will also increase at a rate proportional to  $n^{1/3}$ , so that little or nothing is gained if the quantity  $\mu^2/r^6$  is reasonably useful in predicting activity. Furthermore, it is now well established that chemisorbed hydrogen destroys the magnetic moment of the nickel to the extent of about 0.7 Bohr magneton per hydrogen atom adsorbed (23). There is, therefore, no apparent reason why the unique magnetic properties of very small particles should be particularly effective in promoting the ortho  $\rightarrow$  para conversion. In this connection the difference in activity of samples 0.5% Ni(A)/Al<sub>2</sub>O<sub>3</sub> and 0.5% Ni(B)/Al<sub>2</sub>O<sub>3</sub> is instructive. The former presumably had a monolayer of chemisorbed hydrogen which destroyed about 0.7 Bohr magneton for each hydrogen atom so adsorbed (23). The latter did not have this chemisorbed hydrogen, or at least did not have so much of it. Consequently the activity of the (B) sample would be expected to be somewhat higher. It is also possible that the combined hydrogen in the (A) sample makes the catalyst surface somewhat less accessible in the sense of increasing the effective radius.

Our third approach to the problem of high activity in the reduced nickel samples is rather to look for sources of *low* activity in the several supported oxide systems. The method of preparation by impregnation from quite dilute solutions leads, as pointed out in the Introduction, to a very high degree of dispersion in the finished catalyst, and probably to a substantial fraction of the paramagnetic ions in effective isolation from each other. We may consider that such an ion could exist on the surface of a close-packed oxide ion lattice which is part of the alumina. The paramagnetic ion could reach such a position by exchange of an aluminum ion or, possibly, by incorporation into an extension of the oxide ion lattice. To simplify the discussion we shall confine it to the supported nickel oxide system, and will represent the several possible sites as shown in Fig. 2.

It has been shown (14) that nickel oxide supported on high area alumina requires for reduction, in the low concentration range, somewhat in excess of two atoms of hydrogen for every nickel atom present. This was attributed to nickel in an average oxidation state higher than 2+. The presence of an active oxidizing agent on the

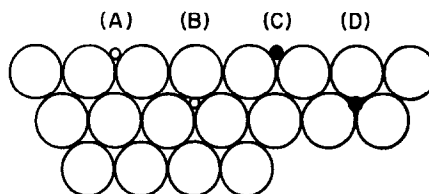


FIG. 2. Possible sites for supported nickel oxide system. (A) Al<sup>3+</sup> on the surface and hence lacking one O<sup>2-</sup> for normal coordination; (B) Al<sup>3+</sup> in normal coordination below the surface; (C) Ni<sup>2+</sup> replacing Al<sup>3+</sup> on the surface (three Ni<sup>2+</sup> required for every two Al<sup>3+</sup>); and (D) Ni<sup>2+</sup> below the surface. KEY: (○) oxide ion, O<sup>2-</sup>; (○) aluminum ion, Al<sup>3+</sup>; (●) nickel ion, Ni<sup>2+</sup>.

surface of nickel oxide under these conditions has recently been confirmed by Gossel (33) on the basis of oxygen adsorption isotherms and iodimetric titrations. In the supported systems one might, of course, regard the nickel oxide as essentially all on the surface. Extrapolation of Gossel's data to such a large specific surface yields results in agreement with those of Hill and Selwood (14).

The active oxidizing agent present on the surface of these preparations is often referred to as "chemisorbed oxygen." A current view is that a surface Ni<sup>2+</sup> ion as in site (C) is capable of undergoing oxidation to Ni<sup>3+</sup> and that this oxidation may be accomplished readily by molecular oxygen, an atom of which then completes the tetrahedral coordination around the Ni<sup>3+</sup>, as shown in Fig. 3.

The effect of this oxidation of the nickel is that, for our present purposes, molecular hydrogen at  $-196^{\circ}\text{C}$  can no longer approach the paramagnetic ion closer than (at best) the radius of an O<sup>2-</sup> ion. In view of the large radius of the oxide ion, we then have a mechanism by which the rate

of the ortho  $\rightarrow$  parahydrogen conversion (dependent on  $r^{-6}$ ) may be diminished by several orders of magnitude, and the supposedly abnormal activity of reduced nickel is actually, probably, *subnormal* activity on the part of the supported oxides.

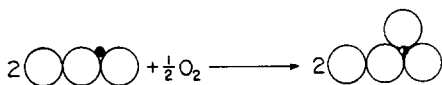


FIG. 3. Possible mechanism by which  $\text{Ni}^{2+}$  on the surface becomes oxidized to  $\text{Ni}^{3+}$  by chemisorbed oxygen, with simultaneous completion of the normal coordination. KEY: ( $\circ$ ) oxide ion,  $\text{O}^{2-}$ ; ( $\bullet$ ) nickel ion,  $\text{Ni}^{2+}$ ; ( $\odot$ ) nickel ion,  $\text{Ni}^{3+}$ .

Before leaving this topic we may refer to two papers which seem to deny the possibility that surface nickel atoms in the oxide may have an oxidation state higher than +2, in spite of the established fact that electronic transitions may occur to vacancy sites created when nickel oxide is annealed in oxygen (34). The first paper is that of Holm *et al.* (35) who reported no abnormal oxidation state in 1.7% nickel oxide supported on silica-alumina. The presence of silica complicates matters because the mechanism of nickel nitrate sorption by silica is rather more an occlusion of solution instead of exchange of ions. The silica content of the support was 90%. Dr. Bailey informs us (private communication) that on an alumina support the nickel was found, by the same technique, to have an average oxidation state higher than 2.

In the other paper, Rymer *et al.* (12) concluded, on the basis of magnetic susceptibility data, that the isolated nickel ions in alumina-supported nickel oxide had an oxidation state of +2 in the low concentration range. The magnetic moments reported ( $\sim 3.3$  Bohr magnetons) are the same as those previously (14) reported from this laboratory and also found in the present investigation as shown in Table 2. It is true that  $\text{Ni}^{2+}$  in tetrahedral coordination may have a moment considerably higher than the moment of 2.8 magnetons corresponding to the "spin-only" value for two unpaired electrons. The difficulty here

is that nickel ions supported on the *surface* of alumina must lack the fourth oxide-ion neighbor and, consequently, cannot have tetrahedral coordination. If the fourth oxide ion is brought in, then the nickel oxidation state rises to +3, which should have a spin-only magnetic moment of about 3.8 magnetons.

A few words of comment are called for on the remaining catalysts for which data are given in Table 1. The poor showing of the 19%  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ , in spite of the high concentration of paramagnetic ions is almost certainly owing to the low specific surface of the chromia. The result with this catalyst parallels to some degree that previously reported (21) for the dehydrocyclization of *n*-heptane, on a similar preparation.

The 5.0%  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst represented an attempt, which was successful, to make a catalyst of enhanced activity on the basis of the information gained from the study of the 0.5% systems already described. Particularly effective was the technique of multiple impregnation (14) in obtaining a relatively high concentration of metallic nickel widely dispersed on the surface of the alumina. There seems no reason why an even more active catalyst could not be devised on the basis of this reasoning, but whether it would be a practical catalyst at the normal boiling point of hydrogen is another problem. There is no obvious reason why the 0.5%  $\text{Ni}/\text{Al}_2\text{O}_3$  catalysts should be better than the 5.0%  $\text{Ni(I)}/\text{Al}_2\text{O}_3$  unless the nickel particles in the latter were very much larger than in the former. It is quite possible that this could be the case, because at the temperature of reduction considerable nickel metal particle growth is well known to occur (36).

The 0.5%  $\text{TbO}_2/\text{ZrO}_2$  represented an attempt to prepare a catalyst with high magnetic moment and relatively low ionic radius. The choice of high area zirconia as supported was dictated by the wish to stabilize the +4 oxidation state of the terbium by supporting it on a diamagnetic high area solid in which the positive ion had the same charge (+4) and nearly the

same radius. The principle involved has been described elsewhere (11). There was evidence that the desired stabilization had been achieved but the catalyst was not particularly effective. This preparation might be of interest in catalytic oxidations.

No reason has been developed for the differences, amounting to a factor of three or more, reported by Weitzel *et al.* (9) between the activity of ferromagnetic hydrous ferric oxide and that showing no ferromagnetism. But this, as suggested by Weitzel is probably attributable to accidental factors not related to the ferromagnetism.

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