JOURNAL OF CATALYSIS 5, 74–80 (1966)

Effect of Neutron Irradiation on Catalysts For the Ortho–Parahydrogen Reaction

AMOS J. LEFFLER* AND BRUCE OSTAR

From Arthur D. Little, Inc.

Received March 30, 1965; revised May 18, 1965

A study was made of the effect of neutron irradiation on chromium and nickel oxides, coated on boron-containing alumina, in their ability to catalyze the para- to orthohydrogen conversion at 77°K. It was found that irradiation increased the activity of poor catalysts but either did not appreciably alter or decreased the activity of good catalysts. In addition it was found that the activity of irradiated catalysts decreased with the passage of hydrogen through the material.

INTRODUCTION

The use of radiation to alter the properties of catalysts has been extensively studied but there have been only a few reports on the effect of radiation on the ortho-parahydrogen reaction. Kohn and Taylor (*1*) examined the effect of gamma rays and neutrons on silica and found a large increase in activity that decreased with time. Hoigne and Ballantine (*2*) showed that gamma radiation of magnesium oxide increased conversion ability and a slower decline in catalyst activity resulted when irradiation took place during reaction than when only preirradiated. Schwab and Konrad (*3*) examined the effect of neutrons on alumina between room temperature and 230°C and found a decrease in activity with irradiation. In the present work the effect of neutron preirradiation on alumina coated with boric oxide or sodium tetraborate and transition metal oxides was examined at 77°K as a function of method of preparation of the catalysts, hydrogen pressure, and flow rates.

EXPERIMENTAL

A. *Apparatus*

The apparatus used in this study was similar to that described in the literature for ortho–parahydrogen conversion studies (4) and is shown in Fig. 1. It differs only in the liquid hydrogen was used as the source of parahydrogen. The system was run at 140 psig, which was just below the relief valve setting on the Dewar. Before entering the catalyst chamber, the hydrogen from the Dewar was cooled to 77°K in a 20-ft stainless steel coil immersed in liquid nitrogen. Because the catalysts had to be irradiated in the nuclear reactor, a special catalyst opener was designed, as shown in Fig. 2. The catalyst was activated, sealed in a quartz capsule, and irradiated in the nuclear reactor. The capsule was then placed in the crusher, which was then attached to the system, and flushed with helium, which is assumed to be nonadsorbed at any temperature. Finally the capsule was thoroughly crushed, cooled to 77°K, and the helium purged with hydrogen. The use of helium avoided any chance of the hydrogen being chemically sorbed at room temperature and thus deactivating the catalyst. It was found impossible to crush the capsule at 77°K because the Teflon packing in the crusher became so stiff that it tended to score the shaft. To prevent catalyst from being carried around the system, stainless steel sintered discs were placed above and below the capsule.

---

* Present address: Department of Chemistry, Villanova University, Villanova, Pennsylvania.

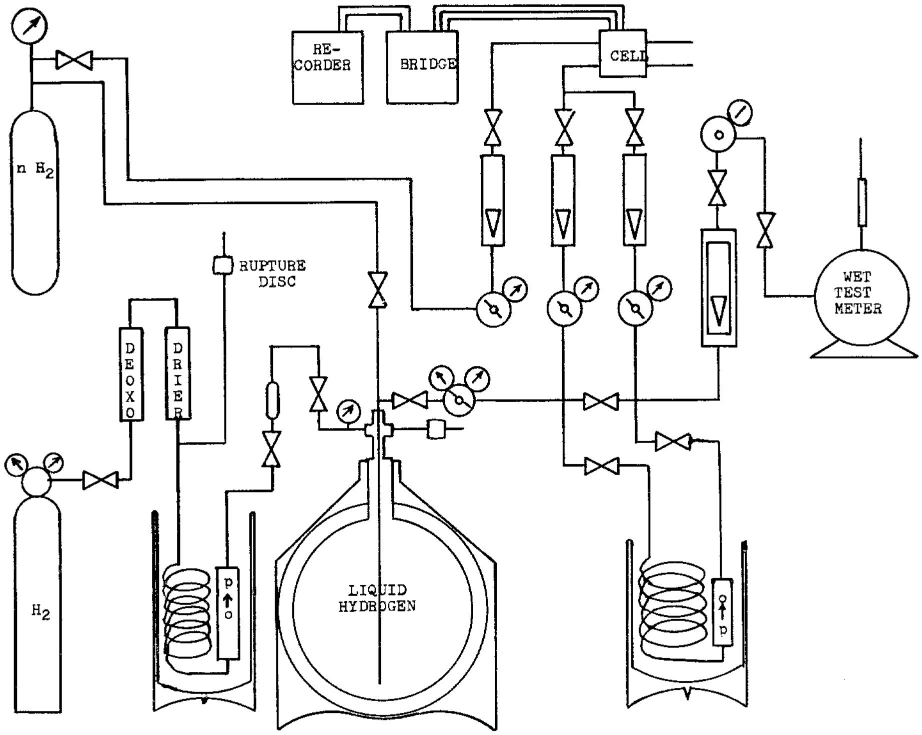

FIG. 1. Schematic design of catalyst measuring equipment.

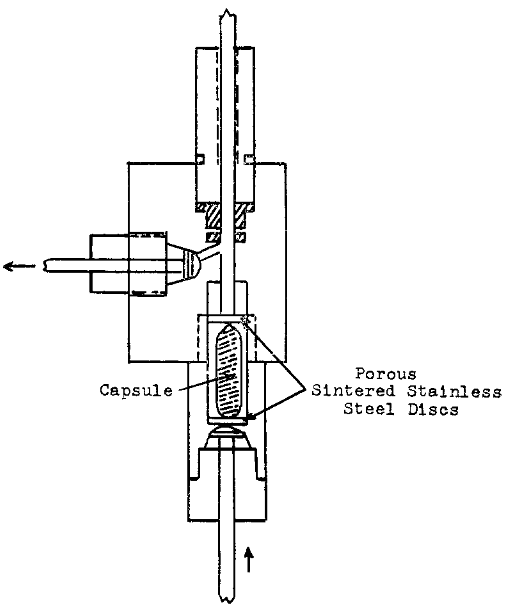

FIG. 2. Crusher reactor for catalyst capsules.

B. Catalyst Preparation

The procedure used for the catalyst preparation was a purpose of this investigation and hence experimental designs were used to obtain the maximum amount of information possible from a given number of catalyst specimens. The substrate used in all cases was H-51* alumina which is an alpha-type alumina having a surface area of 440 m^2/g. Initially the alumina was soaked in the boron-containing material to provide boron for the (n,α) reaction in the nuclear reactor. The slurry was then filtered and sucked dry on a Büchner funnel, and dried at 110°C in an air oven. It was then soaked in the transition metal salt solution, treated as before, and fired at the indicated temperature. Finally the catalyst samples were activated by being placed in an 8-mm quartz tube with a constriction, attached to the vacuum system, pumped, and heated to a specified temperature, and finally sealed off under vacuum. The pellets were then irradiated in the Massachusetts Institute of Tech-

---

* Alcoa Designation. We wish to thank the Aluminum Company of America for a generous sample of this material.

nology Nuclear Reactor for the desired time. Analyses of the catalysts for boron and metal ions were carried out by standard procedures.

C. Catalyst Testing Procedure

After irradiation the capsules were placed in the crusher and opened in the same manner as the unirradiated control specimens. However, specimens irradiated in the nuclear reactor were allowed to stand for at least 48 hours to permit the decay of the short-lived aluminum and silicon nuclides, both of which emit penetrating gamma rays. After this initial radiation disappeared the catalysts were not too active to be handled with ordinary precautions.

After the capsule was placed in the crusher, the system was purged with helium and the catalyst crushed. The system was cooled to 77°K and tested for leaks while under helium pressure. Finally the helium was purged out with hydrogen and the measurements were made at the desired pressures and flow rates. The hydrogen flow through the catalyst was the sum of the flow through the thermal conductivity measuring cell and that through the wet test meter.

D. Experimental Designs and Results

The procedure used for the calculation of catalyst activity was that described by Wakao *et al.* (*5*) and is based on the relation

$$K_{ov} = \frac{2.303 \log [(Y_{eq} - Y_{in})/(Y_{eq} - Y_{out})]}{W/F}$$

where Y is the mole fraction of parahydrogen, W is the weight of catalyst, and F is the flow rate of hydrogen. The units of K_{ov} are g mole H_2/(g cat) (min). A plot of log $[(Y_{eq} - Y_{in})/(Y_{eq} - Y_{out})]$ vs. W/F was made for each value of F, and K_{ov} was taken as the slope as F went to infinity. This procedure eliminated the effect of nonuniform catalyst temperature at low hydrogen flow rates since at high flow rates the amount of hydrogen converted will not appreciably alter the bed temperature.

In Tables 1 through 6 are given the experimental designs, preparative variables, and measured catalyst activities for the systems studied. Only the catalyst activities at 125 psig hydrogen pressure are given, although tests were run at 125, 75, and in some cases 25 psig. The results were always highest at 125 psig and decreased with decreasing pressure.

TABLE 1

DESIGN AND RESPONSES FOR THE CHROMIUM CATALYST EXPERIMENT

Observation	Variable[a] A	B	C	D	E	F	Response K $\left(\frac{\text{moles } H_2}{\text{g cat min}}\right)$
1	0	0	0	0	0	0	0.214
2	1	0	0	0	1	1	0.161
3	0	1	0	0	1	1	0.167
4	1	1	0	0	0	0	0.067
5	0	0	1	0	1	0	—
6	1	0	1	0	0	1	0.132
7	0	1	1	0	0	1	0.0863
8	1	1	1	0	1	0	0.028
9	0	0	0	1	0	1	0.069
10	1	0	0	1	1	0	0.069
11	0	1	0	1	1	0	0.178
12	1	1	0	1	0	1	0.144
13	0	0	1	1	1	1	0.069
14	1	0	1	1	0	0	0.184
15	0	1	1	1	0	0	0.175
16	1	1	1	1	1	1	0.115

[a] A, concentration of metal ion; B, parent compound; C, firing temperature; D, neutron dose; E, standing time after radiation; F, boron concentration.

TABLE 2

ANALYSES OF VARIANCE FOR DESIGN FOR THE CHROMIUM CATALYST

Variable	Degrees of Freedom	Sums of squares	Mean squares	F ratio
A Linear	1	0.00111	0.00111	0.2891
A Quadratic	1	0.00142	0.00142	0.3698
B	1	0.00252	0.00252	0.6563
C	1	0.00521	0.00521	1.3568
D	1	0.00147	0.00147	0.3828
E	1	0.00538	0.00538	1.4010
F	1	0.00006	0.00006	0.0156
Error	7	0.02689	0.00384	
Total		0.04406		

TABLE 3

EXPERIMENTAL DESIGN FOR THE CHROMIUM CATALYST

A. Concentration of Cr

Sample	
1, 5, 9, 13	3.15% Cr.
2, 6, 10, 14	5.2
3, 7, 11, 15	2.3
4, 8, 12, 16	3.1

B. Parent Compound

Level 0 = CrO_3
1 = $Cr(NO_3)_3$

C. Firing Temperature

Level 0 = 300°C
1 = 400°C

D. Neutron Dose

0 = 5 hr @ 8 × 10^{12}/cm^2 sec
1 = 15 hr

E. Standing Time after Radiation

0 = 3 − 5 days
1 = 10 − 14 days

F. Boron Concentration from Boric Acid

0 = 2.1%
1 = 6.5%

Heated to 400°C for 6 hr after being dried at 110°C. All samples were activated by heating in 500 Torr of hydrogen at 400°C for 6 hr.

DISCUSSION

A. Effect of Radiation on Catalyst Activity

The theory of the ortho–parahydrogen on a paramagnetic solid surface has been treated separately.* It predicts that the Cr^{3+} and Ni^{2+} systems will make effective catalysts and this has been confirmed in the present work. An earlier series of catalysts prepared by the deposition of various metal nitrates on alumina and tested at 195°K showed that the activity of the metal was controlled by its electron spin relaxation time and that Fe^{3+}, Cr^{3+}, and Mn^{4+} were good catalysts while V^{3+}, Co^{2+}, and Ni^{3+} were poor catalysts. The aim of the present work was to extend the results to 77°K and to investigate in detail the effect of neutron irradiation on the catalyst activity.

TABLE 4

DESIGN AND RESPONSE FOR THE NICKEL CATALYST EXPERIMENT

Observation	Variable[a] A	B	C	D	Response K $\left(\frac{\text{moles } H_2}{\text{g cat. min}}\right)$ Initial	Final
1	0	0	0	0	0.216	0.135
2	0	0	0	1	0.156	0.115
3	1	1	0	0	—	—
4	1	1	0	1	0.306	0.120
5	1	0	1	1	0.323	0.287
6	1	0	1	0	—	—
7	0	1	1	0	0.403	0.127
8	0	1	1	1	0.196	0.075

[a] A, concentration of metal ion; B, neutron dose; C, mesh size; D, activation temperature.

TABLE 5

ANALYSES OF VARIANCE FOR DESIGN FOR THE NICKEL CATALYSTS

Variable	Degrees of freedom	Sums of squares Initial	Sums of squares Final	F Ratio Initial	F Ratio Final
A	1	0.00686	0.01092	0.8629	6.6585
B	1	0.00735	0.00770	0.9245	4.6951
C	1	0.00992	0.00236	1.2478	1.4390
D	1	0.01104	0.00437	1.3887	2.6646
Error	1	0.00795	0.00164	—	—
Total	5				

TABLE 6

EXPERIMENTAL DESIGN FOR THE NICKEL CATALYSTS

A. Concentration of Ni

Sample		
1, 2	1.55% Ni	0.90% B
3, 4	1.82	0.90
5, 6	1.60	0.80
7, 8	1.40	0.78

The boron source was saturated $Na_2B_4O_7$ while the Ni came from $Ni(NO_3)_2$.

B. Neutron Dose

Level 0 = 0.5 hr, 8 × 10^{12} neut/cm^2 sec
1 = 5 hr

C. Mesh Size

0 = 20 − 30
1 = 40 − 60

D. Activation Temperature

0 = 250°C
1 = 300°C

---

* To be published in the *Journal of Chemical Physics.*

In the Cr catalyst series the most significant variables were found to be activation temperature and standing time after radiation. The other variables, although not so important, showed definite effects. In the Ni catalyst series a complete number of observations were not made and therefore the results are based on an incomplete block design. Calculations were made for the initial and final catalyst activities. The initial results showed activation temperatures and mesh size to be the most significant variables, and metal concentration and neutron dose to be less important. Interestingly enough, the calculations for the final activities showed just the opposite results in that metal concentration and neutron dose were most important and mesh size and activation temperature were of lesser importance.

In the preparation of the catalyst systems, boron was added in the form of boric oxide or sodium tetraborate in order to produce the (n,α) reaction and thus induce lattice damage. This was expected to give a more permeable lattice and therefore higher catalytic activity. In the Cr series the results plainly showed that the concentration of boron did not affect the catalytic activity at the levels used in the present work. It is also evident that the neutron dose (time of radiation) was not significant at the levels used (5 and 15 hr at 8×10^{12} neutrons/cm^2 sec). However, in the Ni series the time of irradiation was shortened to 0.5 and 5 hr to determine whether there is a threshold level of maximum induced activity, and it was found that for the initial activity the time of neutron dose was more significant. Most interesting was the large effect of time (amount) of activation on the final activity. Since the activities obtained were considerably lower than the initial activities, it is evident that the amount of radiation is much more important at lower catalyst activities. From this, it can be concluded that radiation will act to improve an initially poor catalyst to a greater degree than an initially active one. This result is in agreement with that obtained by workers studying other reaction systems.

In the present system, this result can be explained by assuming that neutron activation induces defect structures which exhibit paramagnetism; if the number of induced sites is large enough compared with the number of active sites available, then an increase in activity will be noted. When the number of induced sites is small, or when the defects tend to destroy the activity of sites already present, then radiation will decrease the activity of a catalyst or at least cause little change. The large decrease in activity noted in the two experimental designs was not observed in unirradiated systems. We concluded, therefore, that radiation-activated sites are deactivated (probably by hydrogen adsorption) more easily than unirradiated sites. If we assume that radiation will have a roughly similar effect on all samples of a particular type of catalyst, then it can be seen that the level of initial activity contributed by radiation will be roughly the same. As the activity decreases during the passage of the gas, most of the radiation-activated sites will disappear; only a certain fraction will remain. For a catalyst with only a small number of regular sites, the percentage increase will be much greater than for a catalyst with a larger number of regular sites.

The effect of standing time after radiation is seen to be significant in the Cr series. The reason for this is not completely understood, since the catalysts are insulators and the electronic defects would not be expected to anneal out. The catalysts were sealed under vacuum, but it is possible that the neutron bombardment produced some free gas, either by desorption or by chemical reaction, and that the gas slowly reacted with the active sites on standing. This point needs more investigation before any conclusions can be reached.

B. Decay of Catalyst Activity by Passage of Hydrogen

The fact that a water molecule or perhaps hydrogen atoms may be missing from the coordination sphere of a paramagnetic ion means that there is an electrical and a stoichiometric imbalance. The normal tendency is for such an imbalance to be removed by adsorption or reaction. Thus, hydrogen molecules being adsorbed on a site with a charge deficiency would be expected to be more strongly adsorbed at such a site and thus effectively destroy it. Such a situation will be evidenced by a decrease in catalytic activity as hydrogen is passed through the catalyst bed. This decrease has been observed in the present work. It has been especially evident in the case of irradiated samples, which rapidly decreased in activity to about one-third to one-quarter of their original activities. Neutron irradiation in the presence of boron produces alpha particles of 2.8 meV energy and these decay by the production of "thermal spikes," which are displaced atoms. During the decay process trapped electrons and protons are also produced and thus the material is left with many stoichiometrically unbalanced sites. These are catalytically active but subject to hydrogen adsorption and chemical reaction which will produce a material of much lower activity.

On the basis of the above considerations, the activity of the catalyst can be expected to decay even though there are no impurities present in the hydrogen being used. In Fig. 3 is plotted the change in the percentage of orthohydrogen produced as a function of the amount of hydrogen passed through a particular irradiated catalyst. There are no figures below 60 liters of hydrogen because this amount of gas is necessary to remove the last traces of helium that was used in the opening procedure. It can be seen that the rate of conversion approaches a constant value after a long time, assumedly because the catalytic activity is now confined to the less-active sites.

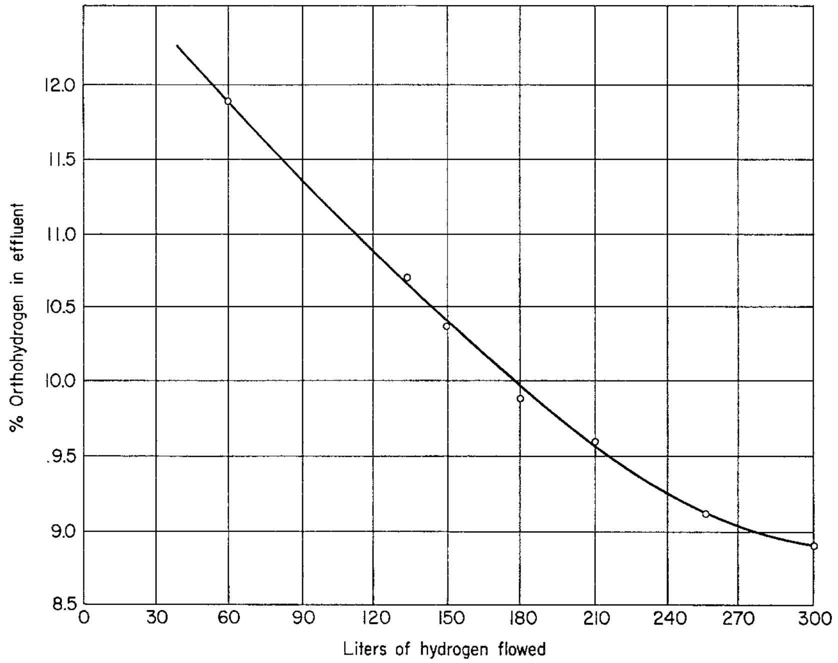

FIG. 3. Plot of orthohydrogen produced by Catalyst No. 2 of Experimental Design I at 3885 ml/min.

A comparison of the results obtained in the present work with those of earlier workers shows general agreement, except for that reported by Schwab and Konrad (*3*). These workers found that neutron irradiation decreased the initial catalyst activity and continued flow of hydrogen gradually increased the rate of conversion. However, the authors note specifically that their samples were exposed to air before and after irradiation, and we believe that exposure of the sample to air drastically affects its catalytic activity. Air molecules would tend to react with surface free radicals and thus deactivate the catalyst. Passage of hydrogen at an elevated temperature would then tend to remove the adsorbed molecules either by chemical reaction to form water or by simple desorption. The removal of the adsorbed gases would then increase the activity of the catalyst, as was observed.

A comparison of the catalyst activities at 77° and 195°K showed that the activity was reduced at the lower temperature, although based on theoretical considerations, the opposite effect would have been expected. It was pointed out* that as the temperature decreases the residence time that an adsorbed molecule spends on the catalyst surface increases until the rate of desorption becomes the controlling mechanism. On a homogeneous surface this can actually lead to a reversal of the temperature coefficient (*6*). The adsorption ability of the catalyst substrate may be one of the more critical factors in catalyst activity. Alumina has long been known to be an effective adsorbant for moisture and a relatively good adsorbant for other gases. Thus, in the present work, alumina, while useful as a diluent for paramagnetic ions to prevent cooperative phenomena, may allow strong adsorption at 77°K and thus prevent unreacted hydrogen from approaching close enough to the active ions to be converted. Since the high surface area of the substrate is important, other materials such as silica may be useful. However, with silica, the lattice structure is unsatisfactory, and some way must be found to modify the silica surface to yield the proper crystal field around the paramagnetic ions to give the long spin relaxation time necessary for efficient catalysts.

---

* Thanks are due to the referee for this point.

ACKNOWLEDGMENTS

We wish to express our appreciation to Mrs. Cordelia Mazuy for performing the statistical analyses. This work was carried out under the sponsorship of the Air Force Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force.

REFERENCES

1. KOHN, H. W., AND TAYLOR, E. H., *J. Phys. Chem.* **63**, 966 (1959).
2. HOIGNE, J., AND BALLANTINE, D., *Intern. J. Appl. Radiation Isotopes* 14(4), 221 (1963).
3. SCHWAB, G. M., AND KONRAD, A., *J. Catalysis* 3, 274 (1964).
4. WAKAO, N., SMITH, J. M., AND SELWOOD, P. W., *J. Catalysis* **1**, 62 (1962).
5. WAKAO, N., SELWOOD, P. W., AND SMITH, J. M., *AIChE J.* **8**, 478 (1962).
6. SANDLER, Y. L., *Can. J. Chem.* **32**, 249 (1954).