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Irradiation Induced Effects in Magnesium Oxide Catalysts

by

J. Hoigne⁽¹⁾ and D. Ballantine
(Brookhaven National Laboratory, Upton, New York)

It has been known for some time that high energy radiation can produce changes in the catalytic activity of heterogeneous catalysts^(1,2). However, a good correlation has not yet been established between changes in the catalytic activity and changes in the physical and chemical structure of the catalytic materials. The present study was undertaken with the hope of generating additional data which might help clarify the picture of this complex and poorly understood field.

This paper describes the effect of gamma radiation from a cobalt-60 source on the activity of magnesium oxide catalysts in the ortho to para hydrogen conversion reaction. Under similar irradiation conditions measurements were also made of surface area, hydrogen adsorption and electron spin resonance spectra.

The choice of magnesium oxide as the subject material was dictated by a number of considerations. Magnesium oxide has a relatively simple lattice, only one crystalline modification is known and irradiation effects on its single crystals have been described. Furthermore, it had been shown by Kohn⁽³⁾ that irradiation effects are reasonably stable in refractory oxides. The transition elements of the iron groups in the 2+ and 3+ valence state have an ionic radius which is similar to that of Mg 2+ ions and can thus be incorporated into the magnesium oxide lattice. These impurities often have an E.S.R. line and electron transfer reactions can thus be studied.

It was reasonable to expect that irradiation might produce one or more of the following effects on the pure oxide:

1. production of new surface sites and lattice defects.
2. changes in surface stoichiometry.

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(1) Present address: E.T.H., Zurich, Switzerland.

3. changes in electronic structure.

Where impurities were present, one might get in addition:

4. enhanced surface cleaning or radiolysis of the impurities and the formation of surface adsorbed radicals.

5. electron transfer between impurity ions.

Most of these changes or effects will be interrelated and, in fact, previous authors have explained their results by invoking one or more of these effects.

(1) Kohn and Taylor⁽⁴⁾ discussed their irradiation effects on silica catalysts using the framework of this first effect. They have shown that the production of even a few sites can produce a large enhancement of catalytic activity. While magnesium oxide has a much stronger ionic lattice in which neutron irradiation produces even fewer displacements than in silica⁽⁵⁾, it is possible that surfaces of quenched powders are unstable and more easily affected by irradiation. Adamson⁽⁶⁾ was able to produce a 12% surface decrease in rutile (TiO_2) when he exposed it to X-rays for a dose of 7×10^{22} ev/g H_2O .

(2) It is known that magnesium oxide can exist in non-stoichiometric compositions. Mansfield⁽⁷⁾ measured a positive sign for the thermoelectric power of sintered magnesium oxide. He explained the observations made by Lempicki⁽⁸⁾ on the reduction of conductivity of single crystals during heat treatment by assuming a decrease in the excess of oxygen. Yamaka⁽⁹⁾ studied the photo-induced Hall effects which result from excess of magnesium and oxygen. Houghton and Winter⁽¹⁰⁾ reported a very slow oxygen desorption from partly covered surfaces, even at elevated temperatures.

(3) Gamma irradiation can change the semiconductivity by changing the number of defects and raising electrons to higher band levels. Bragg⁽¹¹⁾ explained reactor irradiation effects on zinc oxide catalysts in terms of semiconductivity changes. Wertz⁽¹²⁾ produced F centers in single crystals of magnesium oxide by neutron irradiation and in quenched powders by exposure to X-rays. Trapped holes seem to play a predominant role when pure crystals are subjected to ultra violet or

X-irradiation since these are easily formed and are relatively stable⁽¹³⁾. These bulk changes will in turn affect surface semiconductivity and catalytic activity and the paramagnetic centers themselves may act as catalytic centers if they are located near the surface. Kohn⁽¹⁴⁾ in studies on silica gel has reported a relationship between hydrogen adsorption and the disappearance of electronic holes.

(4) Magnesium oxide holds the last traces of water and carbon dioxide with great tenacity^(15,16,17) and Goodman⁽¹⁸⁾ has observed the decomposition of magnesium hydroxide crystals under the X-ray bombardment in an electron microscope. Therefore, if irradiation could clean a catalyst surface without the adverse annealing effects reported for heat treatment, this method could possibly result in an efficient catalyst activation process.

(5) Wertz^(19,20) and Clarke⁽²¹⁾ have reported an electron transfer between elements of the transition groups which are incorporated as impurities into a magnesium oxide lattice. Some of these electrons go to traps which are sufficiently deep so that the resulting disorder is stable even at room temperature. These changes may also influence surface semiconductivity, generate new catalytic centers, e.g. paramagnetic centers, or produce mechanical stresses in the lattice.

Experimental

Materials

Magnesium oxide catalysts: The magnesium oxide used in these studies was A.R. grade and the per cent impurities in two batches used in these studies were as follows:

	Batch 1	Batch 2
Fe	0.05	0.002
Cr	0.01	0.001
Mn	0.001	0.001
Cu	0.008	0.008
SiO ₂	0.05	0.05

The catalyst was prepared by wetting the magnesium oxide, stirring the slurry to homogeneity and predrying at 110° . This material was then ground and calcined by heating in vacuum for 46 hours at 500° . Before all experiments small samples of catalysts were reactivated by heating overnight at 500° at a pressure of 2×10^{-5} mm. The surface area determined using nitrogen and the BET method was found to be $95 \text{ m}^2/\text{g}$.

Helium: Commercial helium was passed over titanium metal turnings at about 600°C .

Nitrogen: Prepurified grade (99.99% Matheson Co.) was passed through a small glass wool-filled trap at liquid nitrogen temperature.

Hydrogen: Prepurified grade (99.9% Matheson Co.) was passed through a "Deoxo" catalytic purifier (Engelhard Industries) and through a charcoal trap at liquid nitrogen temperature.

Oxygen: C.P. grade (99.8% Matheson Co.)

Carbon Monoxide: C.P. grade (99.5% Matheson Co.) was passed through a cold trap.

Apparatus and Procedures

Hydrogen Conversion in a Static System

The apparatus shown in Figure 1 was used to make batchwise ortho-para hydrogen conversion measurements between 5 and 100 mm. pressure. Briefly, the 150 cm^3 reaction bulb containing the catalyst under study was charged with pure* ortho or para hydrogen and the conversion determined after various times. The conversion was determined by measuring the conductivity in a thermal conductivity cell and comparing with the heat conductivity of pure ortho and para hydrogen. The detection unit contained 2 cells (one for a reference gas and one for the reaction gas) with a pair of matched glass coated thermistors. Both cells were contained in a copper thermostated block.

*The term "ortho hydrogen" will here be used for a mixture of about 50% ortho hydrogen, corresponding to the equilibrium composition at liquid nitrogen temperature and the term "para hydrogen" for the 75% para hydrogen gas corresponding to the 25°C equilibrium composition.

The operating procedure was as follows. The reference cell was filled with reference hydrogen gas and closed. The rest of the system was evacuated and the reaction bulb containing the catalyst under study was filled with ortho or para hydrogen at a convenient pressure. The reaction bulb was closed and the rest of the system re-evacuated. After a time interval, corresponding to a 30-70% conversion, the reaction bulb was opened and the reaction gas let into the gas burette. Then the reaction bulb was reclosed and the heat conductivity measured at about 5 pressures near 30 mm. The amount of conversion was calculated from the ratio of distances between the three parallel approximately straight conductivity vs pressure lines measured for ortho and para and the converted hydrogen.

In practice considerable attention was given to the possible effect of experimental variables such as the duration of evacuation periods, the sequence and time interval of measurements as well as the pressure of hydrogen in the reaction bulb. A satisfactory procedure was established and all runs reported here were conducted at hydrogen pressures of 20 ± 1 mm.

Hydrogen Conversion in a Flowing System

A simplified schematic of the flow system is shown in Figure 2. The catalyst was contained in a glass tube (1 cm diam.) between two glass frittes and sealed into the loop of the flexible copper tube gas circuit. The flexible tubing permitted lowering of the catalyst within a dewar into the Co^{60} gamma source. The loop containing the catalyst could be closed by two valves and detached from the system. It was outgassed in vacuo at 500° and without opening to the air was afterwards connected into the conversion system.

In practice three tubes were set up in parallel with independent continuous hydrogen gas flow rates. The catalyst activity was measured intermittently by diverting the gas flow to the detection system. The index of catalytic reactivity was the

* The statistical significance of these variables is reported in Brookhaven Nat. Lab. Report BNL 686 (T - 233) 1961.

hydrogen gas flow rate required to give 50% of the theoretical conversion at the temperature of measurement. Measurements were made of the conversion ratio at two flow rates near 50% conversion and the flow rate for 50% conversion was derived by interpolation. After a measurement which usually required about two minutes, the flow rate was readjusted to its initial continuous value. The degree of the conversion was determined from measurement of the thermal conductivity of the hydrogen using the detector system of a Perkin Elmer Gas Chromatograph Model 154-C. Reference points for the ortho and para hydrogen were measured by bypassing the catalyst.

Gas Adsorption Measurements

The adsorption isotherms were measured in a simple BET apparatus. The magnesium oxide was contained in a quartz or glass sample bulb which was sealed to the system and evacuated overnight at $500 \pm 10^\circ\text{C}$ except where otherwise mentioned. The measurements were only started if the vacuum reading in the morning was less than 2×10^{-5} mm. The sample size was 0.6 - 1.2 g for the surface area and the carbon monoxide adsorption isotherms. These tubes were fitted with breaker seals so that after initial adsorption measurements they could be removed from the adsorption apparatus, irradiated and then resealed into the system. Care was taken to keep samples at a low temperature during all manipulations.

Electron Spin Resonance Measurements

Irradiation induced paramagnetic centers were measured with a Varian V 4500 EPR Spectrometer (X band, 9.4 kilomegacycles) at room temperature.

The samples were placed in a spherical bulb which had a side arm capillary tube and a 6 mm glass tube for attachment to a vacuum line. After heating for about 14 hours at 500° the bulbs were attached to a vacuum line pumped to a pressure of 2×10^{-5} mm and then sealed off. After gamma irradiation, the capillary tube was annealed to remove any paramagnetic centers in the glass and the sample tapped into the capillary. This

capillary was then inserted into the spectrometer cavity.

Experimental Results

Static System Studies

The 50% conversion time showed a great variation between different samples, but on a single sample the reproducibility of a series of measurements gave a standard error of 6% if care was taken to maintain the same sequence of treatments. The rate of conversion showed a small dependence on the pressure of the hydrogen so that for comparative studies a constant pressure of 20 ± 1 mm was used.

Data on conversion rate for a number of samples fitted a first order rate equation. A typical value for 50% conversion time was 6 minutes for 10 mg (about 1 m^2 surface area) and 150 cm^3 of hydrogen at 20 mm pressure.

On some samples the conversion rates were measured at different temperatures and the activation energy estimated. Only those series of experiments were used in which there was no experimental drift. This means that a final check at the initial temperature gave a repeat measurement within the experimental error. The values calculated from the Arrhenius equation were 1.70 ± 0.29 kcal/mol. between -124 and -78° (4 different samples) and 1.49 ± 0.14 kcal/mol. between -78 and 25° (5 different samples).

The data from static experiments are summarized in Figure 3, where one can see that the temperature of outgassing, pretreatment with oxygen and irradiation all affect the catalyst's activity.

(a) Samples which were outgassed at 675° showed little or no irradiation effect. (Irradiation up to 60 min., intensity 270,000 rad/hr., -78° and 25°C.) See Fig. 3a.

(b) There was little difference between samples outgassed at 600° and 500° . Irradiation to a dose of 0.25 Mrad enhanced their activity by factors of 2 or 3, but the increase decayed within a few measurements. Re-irradiation

restored the activity when samples were tested which had not been totally poisoned. The decay was only qualitatively reproducible and no activation energy could be evaluated. (See Fig. 3b).

- (c) The post irradiation effect was the same when the samples were irradiated under hydrogen pressure (60 mm) or in vacuum. (See Fig. 3c).
- (d) Samples pretreated with oxygen showed a lower activity to start with, but the irradiation effect was much larger. (See Fig. 3d-3e).
- (e) Magnesium oxide samples doped with vanadium ions also did not show an irradiation effect when outgassed at 675°C.

Studies in a Flowing System

Experiments in the flow system were performed with hydrogen at 1 atmosphere and magnesium oxide that had been outgassed at 500°. The following characteristic behavior was observed.

- (a) Unirradiated samples were poisoned within a few hours.
 - (b) Simultaneous gamma irradiation (about 260,000 rad/hr) enhanced the conversion rate by a factor of 10-30.
 - (c) Partially poisoned catalysts could be reactivated by the gamma irradiation, whereas totally poisoned catalysts did not show any reactivation.
 - (d) Catalysts which were irradiated during the reaction were, as long as they were irradiated, poisoned at a slower rate than unirradiated catalysts.
 - (e) Lowering of the flow rate brought the catalytic activity to a higher value.
- The quantitative reproducibility was extremely bad.

The behavior was similar at

liquid nitrogen, dry ice and room temperature.

Surface Area and Adsorption Studies

The surface areas were measured for all magnesium oxide batches used. The

areas for regularly treated samples were always between 90 and 100 m²/g. The calculation was based on the slope of the BET curve in the range of p/p_0 between 0.1 and 0.3. The effect of the preactivation treatment was determined by reheating individual samples. It was found that the nitrogen adsorption isotherm did not change when a sample outgassed at 500° for a few hours was reheated for 16 hours to the same temperature. Only when the succeeding heating was performed at a higher temperature could an annealing effect be observed. Fig. 4 shows this effect on a sample which was repeatedly reheated to different temperatures.

A 2×10^6 rad irradiation dose did not change these adsorption isotherms.

Hydrogen adsorption measurements before and after irradiation were tried at room temperature, -78°, -124°, -183° and -196°, but data could only be obtained at the two lower temperatures. Since the adsorption was small, the experiments were repeated on larger samples (17.3 g). These results are shown in Fig. 5. An arbitrary choice of points taken on three different days have been plotted which give an idea of the variations involved.

The hydrogen adsorption isotherm in the range 0 - 300 mm. pressure fitted the equation

$$V_{\text{ads}} = 7.5 \pm 0.2 \times 10^{-3} \text{ cm}^3/\text{mm}^2 p + 50 \pm 20 \times 10^{-3} \text{ cm}^3 \text{ at } -196^\circ\text{C}$$

and

$$V_{\text{ads}} = 3.6 \pm 0.1 \times 10^{-3} \text{ cm}^3/\text{mm}^2 p + 60 \pm 20 \times 10^{-3} \text{ cm}^3 \text{ at } -183^\circ\text{C}.$$

where p is measured in mm and volume at NTP. These values were determined from the lines calculated to fit with the smallest variation all the readings of different runs. The heat of adsorption derived from these data was 1.5 kcal/mol.

Irradiation for 2 megarad at -183° in vacuum or under hydrogen produced no change in the adsorption process although a similar irradiation dose greatly affected the catalyst's activity for converting ortho-para hydrogen mixtures.

Similar adsorption studies were made with carbon monoxide in the temperature range

-196° to room temperature. No measureable change in carbon monoxide adsorption was found after irradiation doses of 1.08 or 3.78 megarad or after treatment of the magnesium oxide with oxygen (exposure to oxygen at 500° followed by degassing at 200°).

The Electron Spin Resonance Spectra

In all the catalytic powders the chromium (+3) - line ($g = 1.9797$) showed up with a relatively small intensity. The intensity of this line was not changed by 4.3 Mrad irradiation at room temperature. This is in contrast to the chromium line which disappeared in single crystals given a similar treatment. These single crystals, however, contained a much larger amount of transition element impurities.

When the samples were irradiated in a hydrogen atmosphere (pressure: 200-300 mm) a strong resonance line was detected with a g -value of 1.999 and a half width of about 2 gauss. These g -values were determined by comparison with the diphenylpicrylhydrazyl line, $g = 2.0036$, or comparison with magnesium oxide poisoned with vanadium or manganese. The annealing of these lines with time at room temperature is shown in Fig. 6. Stepwise irradiation increased the intensity as represented in Fig. 7. The adsorption curve was not broadened with increasing intensity.

Catalytic powders into which vanadium oxide had been incorporated showed only the 3 vanadium lines after a gamma irradiation.

Discussion

It has been found that irradiation produced an effect on the ability of magnesium oxide to convert ortho and para hydrogen. The magnitude of this effect depended greatly on the pre-irradiation treatment to which the catalyst was subjected. Although it has not been possible to relate the irradiation-produced change in catalytic activity to some defined physical change in the catalyst, some enlightening deductions on the process can be made and certain factors shown to be unimportant.

1. Irradiation did not affect the physical adsorption characteristics of the catalysts and hence this adsorption will not be the rate-determining factor.

2. The post irradiation effects were the same whether the irradiation was performed in vacuum or in a hydrogen atmosphere. This eliminates a mechanism which assumes the adsorption on the catalyst surface of radiation produced hydrogen atoms. Apparently the mechanism in the present magnesium oxide case is different from the results of Maurin (22) on molybdena in which effects were observed only with irradiations in a hydrogen atmosphere.

3. The observed overall low activation energy of 1.5 Kcal/mol. and the adsorption energy of only 1.5 Kcal/mol. do not fulfil the minimum requirement of 7 Kcal/mol. necessary for a Rideal mechanism (23) which involves

4. Since the paramagnetic center with g-value 1.999 is only produced by irradiation in hydrogen atmosphere it cannot be responsible for the catalytic activity increase which was observed even under vacuum irradiation.

5. The fact that only those samples were activated which were pretreated below 675° stresses the possibilities of lattice displacements or radiation induced cleaning of the surface. Well annealed surfaces might be less subject to surface lattice changes. The surface area measured by the nitrogen adsorption was 90 to 100 m²/g for the magnesium oxide samples outgassed at 500° while heat treatments even as low as 600° produced a surface shrinkage. Reheating of samples at the same temperature produced no additional surface shrinkage so that surface annealing depends primarily on the temperature and the time of heating has little or no effect. Likewise catalysts heated for several days showed a similar radiation effect as samples heated for only a few hours. These two observations emphasize the possible importance of the annealing effect.

6. The large effect of the oxygen pretreatment is not specific for any mechanism. Houghton and Winter (10) established that the rate of oxygen desorption, from a surface

partly covered by a small gas pressure at 484°C , was slow even at 540° . Therefore, our oxygen treatment at 500° and subsequent evacuation at 200° will probably leave a surface partly covered with oxygen. Electrons raised from low lying donor levels to the conduction band would be accepted by the physically adsorbed oxygen. Such an oxidation may change the characteristics of any transition element impurities as well as produce holes. The irradiation treatment could reasonably be expected to have an effect on these processes.

Our measurements do not contradict a mechanism in which the irradiation frees oxygen which is covering potential catalytic centers by initiating a migration of oxygen over the surface to non-catalytic sites. Furthermore, oxygen is known to decrease the plasticity of magnesium oxide drastically. The observed oxygen effect will also fit into a framework of radiation induced formation of catalytic sites by lattice displacements.

Obviously the results of these studies do not permit, as had been hoped at the outset, the painting of any positive mechanistic picture. The results do, however, permit the elimination of several alternative possibilities. The irradiation process produces changes in catalytic activity at least as specific as the classical physical and chemical treatments and should prove an interesting tool in studying surface phenomena.

It is perhaps discouraging that while it is not too difficult to produce changes in catalytic activity by irradiation it is always difficult to explain clearly the results. In this discouragement the radiation chemist can find consolation among the surface and catalytic chemists who have long faced this problem. It is hoped that the generation of new data, of negative as well as positive character, will form a sufficiently firm basis from which meaningful mechanisms may be developed.

ABSTRACT

An attempt has been made to find a model system in which to study irradiation effects on heterogeneous catalysts. Pre-irradiation with gamma rays from cobalt-60 enhanced the rate of hydrogen conversion over magnesium oxide catalysts, especially when the oxide was pretreated with oxygen at elevated temperature. No correlation could be found between the catalytic activity and the formation of paramagnetic centers observed in the electron spin resonance spectra at room temperature. Irradiation produced no detectable change in the adsorption properties of magnesium oxide for hydrogen and carbon monoxide. While the results do not permit the establishment of a positive reaction mechanism they do permit the elimination of several of the possible alternatives.

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Fig. 1

Fig. 2

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Fig. 3

Fig. 4

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Fig. 5

BNL Neg. No. 3-38-6

Fig. 6

BNL N₆₉ No. 3-39-61

Fig. 7

BNL Neg. No. 3-40-61

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