The Effect of Ionizing Radiations on Catalytic Activity. Hydrogenation and Isotopic Exchange on Inorganic Solids

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Irradiation at −78°C with doses of Co^{60} gamma rays in the range 10^{18} to 10^{20} ev/g increases, from three to several hundred times, the catalytic activity for hydrogen-deuterium exchange of ZnO, ThO_2, $BaTiO_3$, MgO, V_2O_3, $KAlSi_3O_8$, and $CaSiO_3$. The catalytic activity of TiO_2 (rutile) is virtually unaffected by gamma rays at this temperature but can be increased by exposure to neutrons. The activity of several hydrides (LiH, NaH, BaH_2, CaH_2) is decreased by irradiation *in vacuo*, but it is increased (for the two investigated, LiH and BaH_2) by irradiation in 20–30 mm of H_2. The hydrogen-deuterium exchange activity of promoted zinc oxides is virtually unchanged by irradiation, in contrast to the increase with pure ZnO. Activity for ethylene hydrogenation, however, is decreased for both promoted and unpromoted zinc oxides.

INTRODUCTION

Ionizing radiation has been shown to affect markedly the catalytic activity of a number of substances (*1*), and fairly detailed studies have been made of radiation effects in alumina, silica-alumina, and silica gel as catalysts for H_2–D_2 exchange (*2, 3*). Further observations of interest have now been made on several other oxides and other compounds, which are reported herewith.

EXPERIMENTAL

Preparation of the catalyst. Many of the catalysts used in this study were prepared from commercially available reagent grade chemicals.† Thorium oxide was pre-

pared by the Chemical Technology Division of this Laboratory by decomposing thorium oxalate at temperatures above 800°C (*4*). It had a lower surface area (1–10 m²/g) than that of the material used by Holm and Blue (*5*), which was prepared from the hydrous oxide. Promoted zinc oxides were prepared by "reverse coprecipitation" (*6*) and by impregnation (*7*). Precipitated catalysts were prepared by quickly pouring a 1 *M* solution of promoter plus zinc ions into a warm, mechanically stirred excess of sodium carbonate or ammonium bicarbonate solution. The precipitate was washed to neutrality by decantation, dried overnight at 110°C, then calcined stepwise to 350°C. For comparison, a zinc oxide catalyst with no added

feldspar from Kona, North Carolina was supplied by the Consolidated Feldspar Corporation, Trenton, New Jersey. Preliminary experiments on zinc oxide utilized Baker and Adamson "dry process" ZnO, and the magnesium oxide used was a reagent grade. Hydrides were supplied by Metal Hydrides Incorporated. Vanadous oxide was prepared by the hydrogen reduction of reagent grade V_2O_5.

promoter was similarly prepared. Catalysts promoted by impregnation were prepared by immersing Baker and Adamson dry-process zinc oxide in an appropriate amount of $1M$ solution of promoting ion, evaporating to dryness, and calcining as above. Red zinc oxide was prepared from zinc oxide and ammonium nitrate by a deflagrating procedure similar to that described by Kutzelnigg (8).

The catalysts were placed in glass tubes of 20 to 50 cc volume fitted with a stopcock and a standard taper joint. They were activated by pumping overnight at an elevated temperature. Surface areas were measured by nitrogen adsorption.

Catalytic activity measurements. Hydrogen-deuterium exchange activity was assessed by contacting an equimolar mixture of palladium-filtered hydrogen and deuterium at 20–30 mm pressure with the catalyst for a measured time. The gas was sampled by expansion into an evacuated bulb. Analysis was by mass spectrometer. The agreement between duplicate rate measurements was usually no better than ±30%, but the observed effects of radiation were large enough so that this precision was adequate.

The hydrogenation of ethylene was followed manometrically without contacting mercury by using a glass bourdon gage with a balancing pressure measured by a mercury manometer. That the pressure decrease was actually due to ethylene hydrogenation was confirmed by chromatographic analysis of representative gas samples which were compared with standard mixtures.

Irradiation. Gamma irradiation was done in an approximately 800 curie Co^{60} source calibrated by ferrous sulfate dosimetry (9). The dose rate could be varied from 1 to 5×10^{17} ev/g, min. X-ray irradiation was done at 50 ma and 50 kv using a Machlett tube with a tungsten target and a thin beryllium window. Reactor irradiation was done in hole 10 of the O.R.N.L. graphite reactor where the temperature is 25°C and the flux is 1.4×10^{12} neutrons/cm^2, sec; about half of the neutrons are thermal and half are fast. The total dose

rate to water in this position is about 10^{-3} cal/g, sec, with gamma rays contributing about one third. For non–hydrogen-containing materials the total dose rate is lower than for water, with more of it coming from gamma rays than from neutrons.

RESULTS AND DISCUSSION

A summary of the radiation effects upon H_2–D_2 exchange activity of all of the materials studied is given in Table 1, which includes for comparison results previously reported. It is obvious that most of the substances are affected, the majority in the direction of increasing activity. Points of interest are discussed in more detail below.

Thorium oxide. In contrast to oxides first examined (Al_2O_3, ZnO), thoria showed in preliminary experiments no effect of radiation. Measurement of the exchange reaction rate during irradiation, however, demonstrated a faster exchange than without radiation, evidence either for an efficient energy transfer from solid to adsorbate, as found by Caffrey and Allen with pentane on several solids (10), or for a short-lived induced catalytic activity. Thus, a thoria catalyst too inactive to measure readily at 0°C had a rate constant of 1.5×10^{-3} hr^{-1}, g^{-1} at 25°C, but one of 4.3×10^{-2} at 0°C when irradiated during the exchange reaction. A similar sample (k $= 1 \times 10^{-3}$ at 25°C) showed in two successive rate measurements in the radiation field rate constants greater than 1 at 0°C with complete equilibration occurring in both experiments.

Evidence that the enhanced activity of thoria during irradiation was due to induced catalytic activity, and not to energy transfer, was obtained by using a catalyst active enough to measure at a low temperature, where the induced activity did not rapidly anneal. A sample of thoria calcined at 1400°C and degassed at 200°C had a rate constant of 10^{-3} min^{-1}, g^{-1} at −78°C. The rate constant measured during a 2-hr irradiation had increased to more than 2×10^{-2}. Four measurements of activity were then made in the next 6 hr while the catalyst was held at −78°C without further irradiation. The rate con-

TABLE 1

Typical Effects of Irradiation on the H_2-D_2 Exchange Activities of Several Catalysts

Catalyst	Rate constant for unirradiated 1 g sample (hr⁻¹)	at	Irradiation conditions Source	Time	Temp. (°C)	Enhancement factor[a] Minimum	Maximum	Annealing half-time[b]
γ Al₂O₃ (ref. 2)	0.02-8.3	-78°C	G(amma)	1 hr	-78°	0.5	2000	2 hr to 2 days
γ Al₂O₃ (ref. 2)	2.1-4.2	-78°	R(eactor)	1 week	60°	3	10	>14 days[c]
SiO₂ gel (ref. 3)	10⁻³	25°	G	10 min	30°	—	~10,000	~1 day
SiO₂ gel (ref. 3)	10⁻³	25°	R	3 weeks	60°	—	10⁹ est.	~2 months
13% Al₂O₃-SiO₂ (ref. 3)	0.8-1.6	-78°	G	1 day	-78°	50	—	>1 month
13% Al₂O₃-SiO₂ (ref. 3)	—	—	R	—	—	—	>10⁴ est.	>1 month
ZnO, dry process	0.05-0.1	-78°	G	1 day	-78°	3	10	>1 month
ZnO, CO₃²⁻ pptd.	0.23-3.3	-78°	G	1 day	-78°	10	20	Not measured
ZnO, promoted, CO₃²⁻ pptd.	0.0035-46.0	-78°	G	1 day	-78°	0.8	1.4	Not applicable
ThO₂	0.001-10.5	-78°	G	1-4 hr	-78°	2	>100	< ten minutes
TiO₂ (rutile)	0.42	-78°	G	1 day	-78°	1	1.5	Not applicable
TiO₂ (rutile)	0.42	-78°	R	1 week	60°	—	6	1-2 weeks
BaTiO₃	0.008	-78°	G	4 hr	-78°	13	220	1 day
BaTiO₃	0.008	25°	R	1 week	30°	—	20	>1 week
Hydrides (vacuo)	0.02-4.2	-78°	G	1 day	-78°	0.1	1	>1 month
Hydrides (H₂)	0.05-5.2	-78°	G	1 day	-78°	1	10	>1 month
MgO	2.1	-78°	G	1 hour	-78°	3	20	~10 minutes
V₂O₃	0.03	-78°	G	1 day	-78°	5	10	>1 day
KAlSi₃O₈	0.007	25°	G	1½ hr	25°	—	370	Not measured
CaSiO₃	0.15	25°	G	1 day	-78°	—	~5800	~1 day

[a] Rate constant after irradiation/Rate constant before irradiation.

[b] Approximate time required for one-half the radiation-induced catalytic activity to disappear at room temperature after radiation indicated.

[c] Also >14 days after α-particle irradiation. See ref. (2).

stants were all between 1.7 and 2.2×10^{-2}. The sample was annealed for 1 hr at 25°C and cooled to −78°C; the rate constant was then 1.7×10^{-4}. Another irradiation at −78°C *in vacuo* again increased the rate constant (measured after irradiation) to 1.8 to 1.9×10^{-2}. After annealing at −55°C for 1 hr the rate constant had decreased to 1.5×10^{-4} (measured at −78°C).

A wide range of activities was observed for thoria prepared in different ways, suggesting that poisoning might play a role here, as already shown for gamma-alumina (*3*). The experiments summarized in Table 2 show that this is indeed the case. The

400°C and tested for catalytic activity and the effect of irradiation thereon. Within experimental error, overnight gamma irradiation produced no change of catalytic activity at −78°C (*11*). One of these samples was encapsulated in quartz and exposed to neutrons in the O.R.N.L. Graphite Reactor for one week. The rate constant, measured after 7 months of cooling, had increased from 0.4 hr^{-1} g^{-1} to ∼1.9 hr^{-1} g^{-1}. Subsequent measurements showed that the rate constant was decreasing, which made further observations of doubtful use, but the initial increase was undoubtedly real.

It is noteworthy that rutile is particularly resistant to radiation damage by re-

TABLE 2

EFFECT OF POISONING ON RADIATION SENSITIVITY OF THORIA CATALYSTS[a]

Sample I calcined at 800° C		Sample II calcined at 1200° C	
Treatment sequence	Rate constant (min^{-1} g^{-1}, −78° C)	Treatment sequence	Rate constant (min^{-1} g^{-1}, −78° C)
Evacuated 16 hr at 510° C	1.2×10^{-2}	Evacuated 16 hr at 530° C	1.6×10^{-1}
Irradiated 30 min during reaction	3.1×10^{-2}	Irradiated 15 min during reaction	1.5×10^{-1}
Poisoned 16 hr 50 mm dry air[b]	—	Poisoned 16 hr 150 mm CO$_2$, 25° C	1.2×10^{-4}
Irradiated 90 min during reaction	2.6×10^{-2}	Irradiated 45 min during reaction	2.7×10^{-2}
Annealed 25° C, 1 hr	3.0×10^{-3}	Annealed 25° C	3.5×10^{-4}
Irradiated 25 min during reaction	4.4×10^{-2}	Pumped 30 min at 200° C	4.0×10^{-4}
		Irradiated 75 min during reaction	2.4×10^{-2}
		Held at −78°	1.3×10^{-2}

[a] H$_2$-D$_2$ exchange, Co^{60} gammas at 2×10^{17} ev/g, min.

[b] Purified by passage through a liquid nitrogen trap.

initial difference between the two samples shown in Table 2 is probably due to differences in the calcination step. Whether the differences in catalytic activity are due to more thorough removal of poisons or to lattice changes as a result of the higher calcination temperature is, of course, not established, particularly since the difference in final degassing temperature (510 to 530°C) might be significant. The subsequent results on Sample II, however, show unambiguously that the well-pumped, unpoisoned sample is insensitive to radiation, but that the same sample poisoned with CO$_2$ is susceptible to radiation enhancement. Sample I shows a similar but smaller effect of dry, CO$_2$-free air.

Titanium oxide (rutile). Three 1 g samples of rutile were degassed overnight at

actor irradiation (*12*). This apparent resistance may be associated with a lability of radiation-produced defects even greater than that already noted with thoria.

Hydrides. Alkali hydrides, because of their simple structure, should be useful subjects for attempts to characterize radiation damage and relate it to changes in catalytic activity. The findings of Wright and Weller with calcium and barium hydrides (*13*) suggested that the alkali hydrides could be activated for hydrogen exchange by evacuation at 100–300°C. Both sodium and lithium hydrides were thus found to be catalysts, and the activity of these as well as of calcium and barium hydrides was found to be sensitive to radiation. As shown in Table 3, the activities of the four hydrides were lowered by ir-

TABLE 3
EFFECT OF IRRADIATION ON H_2-D_2 EXCHANGE ACTIVITY OF HYDRIDES[a]

Sample	Treatment sequence	Dose (ev)	Reaction temperature (°C)	Rate constant (hr^{-1}, g^{-1})
BaH$_2$	Evacuated 16 hr, 100° C	None	−78°	1.9×10^{-2}
	Aged 10 days Irradiated in 21 mm H$_2$	2.5×10^{20}	−78°	0.9–1.1×10^{-1}
BaH$_2$	Evacuated 220° C, aged Outgassed 1 hr 100° C	None	−78°	6.9×10^{-1}
	Outgassed 1 hr at 100° C Irradiated in vacuo	5×10^{19}	−78°	$<10^{-2}$
CaH$_2$	Evacuated 16 hr, 180° C	None	−78°	0.7–1.0×10^{-1}
	Irradiated in vacuo	2.5×10^{20}	−78°	1.5×10^{-2}
LiH	Evacuated ½ hr, 250° C	None	−78°	1.2–2.0×10^{-2}
	Irradiated in 20 mm H$_2$	1×10^{20}	−78°	5.3×10^{-2}
LiH	Evacuated 2½ hr, 100° C	None	0°	4.0×10^{-1}
	Irradiated in vacuo	1×10^{20}	0°	1.7×10^{-2}
NaH	Evacuated 16 hr, 220° C	None	−78°	1.9×10^{-4}
	Irradiated in vacuo	1×10^{20}	0°	1.7×10^{-1b}

[a] Co^{60} gammas, ca. 3×10^{20} ev/g total dose.

[b] No reaction at −78° C.

radiation in evacuated ampoules containing the few microns of equilibrium H$_2$ pressure always shown by these materials, but was raised for LiH and BaH$_2$, the only two examined in this way, by irradiation in 20–30 mm of hydrogen.

Since the catalytic activity for hydrogen exchange has been shown to depend on a hydrogen deficiency in the lattice (14), one might at first attribute the radiation effect

Lattice hydrogen exchange was observed during gaseous exchange only on freshly prepared samples (Table 4), meaning that all of the exchangeable lattice hydrogen had come to equilibrium with the standard gas mixture within the time of one experiment. Therefore, the lattice hydrogen exchange has at least as great a velocity as the catalytic exchange. It is likely, therefore, that some of the catalytic exchange

TABLE 4
EXCHANGE OF HYDRIDE HYDROGEN WITH $H_2 + D_2$ GAS[a]

Sample (Weight)	H/D at zero time	H/D after exchange	No. atoms D exchanged	Fraction of catalyst H$^-$ exchanged
LiH (0.95 g)	0.95	1.29	5.0×10^{18}	5.4×10^{-5}
LiH (0.55 g)	0.95	1.10	2.4×10^{18}	4.6×10^{-5}
NaH (0.60 g)	1.00	1.17	2.6×10^{18}	1.6×10^{-4}
CaH$_2$ (2.7 g)	1.10	1.22	1.6×10^{18}	1.9×10^{-5}

[a] 20 mm of $H_2 + D_2$ in 50 cc volume contacted with samples overnight at −78° C.

to a removal or restoration of hydride hydrogen in the lattice surface. However, irradiation in hydrogen increased the activity, while Wright and Weller's results indicated that the removal of hydrogen favors catalytic activity. Thus, it is unlikely that irradiation changes the catalytic activity of hydrides by a simple adjustment of the lattice hydrogen content.

proceeds through lattice exchange, a mechanism not possible with catalytic oxides. If this mechanism of catalytic exchange is predominant, the radiation effect may be of little use for correlation with that of the oxides, but this can hardly be determined without more extensive experimentation.

Zinc oxide. The most striking observation made with zinc oxide is that the

H_2–D_2-exchange activity of a pure sample is sensitive to radiation while that of promoted samples is not. "Red zinc oxide" behaves in this respect as if it were promoted, and the excess zinc which it contains may fill the role of promoter. The

or more in initial activity showed an unmistakable increase on irradiation.

Unlike the case of H_2–D_2 exchange, impurities do not eliminate the effect of gamma rays upon ZnO as a catalyst for the hydrogenation of ethylene, as shown

TABLE 5

H_2-D_2 EXCHANGE AND RADIATION EFFECT ON ZINC OXIDE CATALYSTS[a]

Sample	Mole % promoter	Temp. of preparation	Surface area (m²/g)	Initial rate constant (hr⁻¹, g⁻¹, at −78° C)	Radiation effect[b] (k final/k initial)	Remarks
1	1.0 Ti⁴⁺	420	—	1.4×10^{-3}	—	Impregnation prepared
2	1.0 Na⁺	400	—	3.5×10^{-3}	1.0	Na₂CO₃ precipitated
3	0.023 Zn	420	—	4.5×10^{-2}	1.0	"Red" zinc oxide
4	None	460	4.1	4.6×10^{-2}	8.0	Baker's dry process
5	1.0 Na⁺	460	—	1.4×10^{-1}	1.2	Na₂CO₃ precipitated
6	None	400	20.3	2.3×10^{-1}	20.0	Na₂CO₃ precipitated
7	1.0 Cd²⁺	350	—	4.1×10^{-1}	1.1	NH₄HCO₃ precipitated
8	1.0 Al³⁺	350	39.9	5.0×10^{-1}	0.8	NH₄HCO₃ precipitated
9	1.0 Ga³⁺	350	—	6.9×10^{-1}	1.3	NH₄HCO₃ precipitated
10	None	415	30.8	3.3×10^{0}	10.0	NH₄HCO₃ precipitated

[a] Co⁶⁰ gamma rays, ca. 3×10^{20} ev/g total dose.

[b] Largest value observed.

inhibitory effect of several promoters at 1% concentration is shown in Table 5, and the growth of the effect with concentration of a single promoter in Table 6. Both the marked difference between the unpromoted samples and the others in Table 5 and the

in Table 7. This invariability and the large doses required to produce the decrease in activity suggest that the radiation effect for this reaction may result from atom displacement, which would of course not be prevented or much altered by moderate

TABLE 6

INFLUENCE OF PROMOTER CONCENTRATION UPON RADIATION EFFECT ON ZINC OXIDE CATALYSTS[a]

Sample	Mole % promoter (Al³⁺)	Temp. of preparation (°C)	Initial rate constant (hr⁻¹, g⁻¹, at −78°)	Radiation effect[b] (k final/k initial)
10	None	415°	3.3	10.0
11	1×10^{-6}	375°	1.0	10.0
12	1×10^{-4}	400°	1.0	4.5
13	0.01	365°	3.5	3.2
14	0.01	365°	6.9	3.8
15	1.0	355°	46	1.4

[a] H_2-D_2 exchange, Co⁶⁰ gamma rays, ca. 3×10^{20} ev/g total dose.

[b] Largest value observed.

trend with concentration in Table 6 attest to the reality of the effect. It is also especially convincing that promoted samples with initial activities differing by a factor of about 200 agreed in showing no radiation effect (within 30%), whereas unpromoted samples differing by a factor of 10

amounts of impurities. If the apparent greater effect in the presence of impurities (0.15 versus 0.4) is real, there is probably an effect associated with trapped electrons as well.

Three other observations of interest were made on zinc oxide. First, in a series of

zinc oxide samples with different impurities the depth of color nearly parallels the increasing valence of the impurity, the order of color being $Na^+ <$ pure $ZnO < Ti^{4+} < Cd^{2+} < Al^{3+} < Ga^{3+}$. The samples with Ga^{3+} and Al^{3+} are a visible yellow at room

TABLE 7

EFFECT OF IRRADIATION ON
ETHYLENE HYDROGENATION ACTIVITY
OF ZINC OXIDE CATALYSTS[a]

Number	Promoter mole %	Initial rate constant (hr^{-1}, g^{-1})	Radiation effect[b] (k final/k initial)
10	None	6.9×10^{-1}	0.4
13	0.1 Al^{3+}	1.4×10^{-1}	0.18
15	1.0 Al^{3+}	4.1×10^{-2}	0.15

[a] Co^{60} gamma rays, ca. 2×10^{21} ev/g total dose.
[b] Largest value observed.

temperature, and the differences between the lighter-colored ones can be seen by heating them, since, like pure ZnO, all of the impure samples became darker yellow on heating. Catalytic activity for H_2–D_2 exchange, so far as it has been measured (7) parallels the order of increasing valence. The anomalous order of Ti^{4+} as to color may result from inhomogeneity. Incidentally, the activities reported here (Table 5) should not be correlated with promoter type since the temperature of activation (evacuation) was adjusted to avoid large differences in initial activity that might mask radiation-induced changes.

Second, irradiation of zinc oxide with low energy X-rays can also produce an increase in hydrogen-deuterium exchange activity. A small (0.2 g) catalyst sample was irradiated for 3 hr through a thin glass window with 50 kv X-rays at 50 ma at ambient temperature, and then cooled to −78°C. The rate constant, when measured, had increased fivefold. A further 1 hr irradiation produced a further increase to 7.7×10^{-2} min^{-1}, g^{-1}, a factor of 7 over the original value. Dosage was not measured, but the experiment showed qualitatively that ionizing radiation of energy too low to cause an appreciable number of displacements can produce the same effect as gamma radiation.

Third, rather direct evidence has been

obtained for ethylene retention on zinc oxide that has been exposed to the reaction mixture ($2 H_2 : 1 C_2H_4$) and then evacuated at room temperature as usual between runs. Such samples were observed to turn gray or black if heated to 300–400°C, and to be restored to white by heating in oxygen. It seems almost certain that the color is the result of carbonization of residual ethylene, and radiation action on residual ethylene is therefore a possible explanation for the fall in hydrogenation activity observed on irradiation of zinc oxide. However, the semiquantitative arguments against this mechanism (15) seem valid in the absence of convincing experiments on catalysts not exposed to ethylene before irradiation.

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