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Semiconductivity in Eu_2O_3 and Gd_2O_3, and Exchange Interaction in the System MnO–MgO, as Possible Criteria for the Catalytic Decomposition of Ammonia

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This work was part of an attempt to characterize more precisely the structural characteristics associated with catalytic activity in certain classes of solids. It was found that Eu_2O_3 in H_2 atmosphere at 800°C was an *n*-type semiconductor with a conductivity 19 times greater than that of Gd_2O_3 under similar conditions. But no difference could be detected in the rate or activation energy for ammonia decomposition over these oxides.

It was found that dilution with MgO did not alter the catalytic activity of MnO for the ammonia decomposition although, as was previously known, exchange interaction between Mn^{2+} ions is diminished by such dilution.

It appears from these results that neither semiconductivity nor exchange effects are directly related to catalytic activity in these solids, under the conditions described.

I. INTRODUCTION

Many studies in recent years have tended to establish a correlation between catalytic activity and electrical conductivity in transition metal oxides. One type of study consists of measuring the rates of a single reaction over a variety of oxides. Thus, for instance, Stone (*1*) and, more recently, Saito *et al.* (*2*) have shown that *p*-type semiconductors such as Co_3O_4 and NiO are more active for the decomposition of N_2O and the oxidation of CO, than are *n*-type semiconductors such as ZnO and Fe_2O_3. A second kind of study has shown that activity may be altered if the conductivity is altered by pretreatment in a selected gaseous atmosphere. Thus Voltz and Weller (*3*) enhanced the activity of Cr_2O_3 for the H_2–D_2 exchange at −78°C by pretreatment in H_2; Gray and Darby (*4*) modified the activity of NiO for H_2 oxidation by pretreatment in O_2.

The most abundant evidence for a possible relationship between conductivity and catalysis is to be found in those studies in which the conductivity of an oxide is altered by the familiar doping techniques. Thus, for example, Hauffe *et al.* (*5*) and Cvetanovic and Dewing (*6*) show that the activity of NiO for N_2O decomposition is much increased by doping NiO with lithia, with an attendant increase of conductivity amounting to many orders of magnitude, while doping with gallia produces an opposite effect. Examples of such effects described in the literature could be multiplied almost indefinitely.

In spite of all this evidence, it is possible to raise a serious objection to most of it. A transition metal oxide such as NiO exhibits the phenomenon of exchange interaction between nearest-neighbor (or next nearest-neighbor) cations.* If, to such an oxide there is added a diamagnetic ion (Mg^{2+}

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* A substantial portion of the work described was done in the Chemistry Department of Northwestern University.

* This phenomenon, which has been known for many years, has recently been treated in elegant detail by Goodenough (*7*).

would be an example) the exchange interaction is broken down and ultimately, at high magnetic dilution, virtually disappears. This effect is most strikingly shown by the increasing magnetic susceptibility per transition metal ion with increasing dilution. While most studies of the magnetic dilution effect have been made on systems such as MnO–MgO, Cr_2O_3–Al_2O_3, and the like, yet there seems no question that the doping of NiO (ref. *7*, pp. 25, 120, 238–239) with lithia greatly modifies the exchange relationships in this substance. Similar effects have been observed, or may certainly be expected, in almost all transition metal oxides doped (or "promoted" in catalytic terminology) with foreign atoms or ions. It appears, therefore, that in virtually all of the work tending to relate conductivity to catalysis in transition metal oxides there is at least one (the exchange effect), and possibly other parameters which change simultaneously with the conductivity whenever a doping agent is added. In the absence of a truly convincing theoretical basis for the relationship it is impossible to say that catalytic activity is more closely related to the one parameter than to another.

The purpose of the present work was to examine, so far as possible, each of the parameters separately. This involved finding a system in which semiconductivity might be made to change (preferably to increase), and to do this independent of appreciable modification of exchange effects, as measured by the magnetic susceptibility. Then the problem required finding a system in which exchange effects would be altered to an important degree without extensive modifications of the conductivity.

The first such system is approximated in the rare earth oxide, Eu_2O_3. This oxide is similar in almost all respects to the neighboring oxide, Gd_2O_3, except for one less electron in the 4*f* shell, and the consequent possibility of reduction to the 2+ oxidation state. Furthermore, owing to the shielding of the outer electrons, exchange effects are minimized in these oxides, especially at the elevated temperatures employed. No previous studies on relative electrical conductivities of Eu_2O_3 and Gd_2O_3 in a reducing atmosphere appear to have been made. But it was thought that the Eu_2O_3 would show an appreciably greater conductivity under these conditions and this proved to be the case. Under the circumstances it may then be said that the Eu_2O_3 and the Gd_2O_3 are about as nearly identical as two catalytic solids can be, except for the difference in conductivity. This pair of oxides was therefore selected for the first series of tests.

A contrasting system, in which conductivity effects are minimal but exchange effects are strong, is readily found. The solid solutions of MgO in MnO are nearly ideal for examination of this property. Although the degree of exchange interaction between Mn^{2+} ions is appreciably diminished by substitution of Mg^{2+} in the MnO lattice, as shown by Bizette (*8*), the electrical conductivity remains nearly constant throughout the series of solutions from pure MnO to pure MgO. Furthermore, MnO and MgO are isomorphous, with lattice parameters differing only moderately; hence they form a complete series of homogeneous solutions. Neither the MnO nor the MgO are further reduced in hydrogen at the elevated temperatures. The MgO–MnO solid solution system was, therefore, selected for examination of the possible influence of exchange interaction, uncomplicated by conductivity effects, on catalytic action.

II. EXPERIMENTAL ON RARE EARTHS

a. Preparation of catalyst samples. The rare earth samples were obtained from Lindsay Chemical Division, American Potash and Chemical Corporation, and stated to be 99.9% pure. The maximum single impurity in the Eu_2O_3 was 0.024% La_2O_3; and that in the Gd_2O_3 was 0.024% Sm_2O_3. These oxides were dissolved in nitric acid, precipitated with ammonium hydroxide, and ignited at 900°C in air. Resistance measurements were made on this material after it had been pressed into cylindrical pellets 6 mm wide and 3 mm long, at 3100 atm. The pellets were ignited in air before the measurements were made.

Pellets used in the catalytic studies were prepared with stearic acid as a binder prior to ignition. Surface areas on all samples were obtained by the BET (N_2) method.

b. Conductivity measurements. Pelleted samples were pressed between gold electrodes covered with platinum under a 600-g weight, all enclosed in Vycor tubing. Oxygen and hydrogen were dried over silica gel at −78°C, and the latter was first freed from oxygen in a De-Oxo unit. The resistances were measured on a DC bridge. Reproducibility of conductivity data was to about 1% on a given sample pellet.

A simple measurement of this type on polycrystalline samples is strongly influenced by the electrode contacts, by interparticle resistance, and by surface conductivity. The procedure used was believed to be justified because the interest was in the relative conductivities of each sample in oxygen and in hydrogen. It is, of course, often stated that the surface conductivity is of primary interest in connection with catalytic activity.

c. Thermal emf measurements. In these experiments the pelleted sample was placed near the end of a tubular furnace. The temperature gradient was measured with Pt, Pt-Rh thermocouples. The thermal emf was obtained from 10-mil Pt wires wrapped around the cylindrical pellet. The emf was measured on a Keithley millimicrovoltmeter. While the accuracy of the measurements was not high, it was quite adequate to give the sign of the carrier as well as a good estimate of the gap energies for conduction.

d. Catalytic activity. It was necessary to choose a reaction in which the atmosphere would be strongly reducing. The decomposition of ammonia appeared to meet all required conditions, and this reaction was used throughout. The apparatus used is shown in Fig. 1. Each gas was brought to 25°C and manually controlled at 15 cc/min as measured on capillary flow meters. This gave a space velocity of the ammonia of about 3 per min. The catalyst was placed in a 15-mm Vycor tube with an enclosed chromel-alumel thermocouple junction just above the sample. The furnace temperature was controlled to ±2°. The product gases were cooled to 25°, and their flow rates were measured on a third flow meter.

Inasmuch as the flow meter readings in

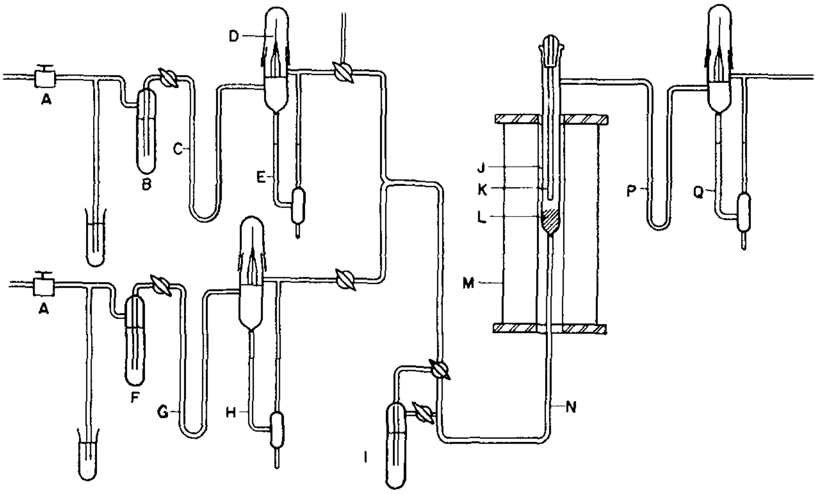

FIG. 1. Catalytic activity apparatus for NH_3 decomposition. A, High pressure valves for ammonia and hydrogen. B, CaO filled trap. C, G, and P, U-tubes filled with glass beads. D, Capillary for ammonia flow meter. E, H, P, Dibutyl phthalate manometers for flow meter. F, Silica gel trap for hydrogen. I, Silica gel trap for hydrogen (during pretreatment). J, Vycor catalyst tube. K, Thermocouple well. L, Catalyst pellets. M, Furnace. N, Glass tubing filled with glass beads.

such a system are dependent both on gas volume and viscosity, the following procedure was adopted. Hydrogen and ammonia, each at 15 cc/min were mixed, passed over the catalyst, through the exit flow meter, and then through a bubble flow meter. At sufficiently low catalyst temperature the total flow rate was, of course, 30 cc/min, but as the catalyst chamber temperature was raised, the exit gas volume V was related to the initial gas volume V_0 by $V = V_0\ (1 + \frac{1}{2}\ \alpha) = 30$ cc/min $+ (\alpha \times 15$ cc/min), where α is the fractional decomposition of the ammonia. In this way it was possible to obtain α as a function of the pressure difference on the exit flow meter.

In view of the high temperatures required to obtain measurable rates of reaction (and electrical conductivities), it was essential that no appreciable homogeneous decomposition occurred under the experimental conditions. It was found that with no catalyst in the reaction chamber the amount of decomposition at 800°C was negligible, and that with quartz chips in the chamber the reaction was very slight.

The procedure used in obtaining activities in each case was to heat the catalyst for 1 hr in oxygen at 850°C, to evacuate, then to heat for about 10 hr in hydrogen at 850°. The temperature was lowered to 800° and the reaction mixture was allowed to flow over the catalyst for 45 min prior to the start of measurements. Subsequently, measurements at lower temperatures were made, but it was found that the curve of α vs temperature was the same for decreasing and increasing temperature, provided the preliminary heat treatment had been made as described.

III. Results on Rare Earths

The electrical resistances R of Eu_2O_3 and of Gd_2O_3 in O_2 and in H_2 are given as functions of temperature in Figs. 2 and 3. The plots of log R vs $1/T$ gave straight lines, the slopes of which equal $E_g/2kT$ where E_g is the gap energy of the semiconductor. Table 1 contains conductivities at 800°C and values of $E_g/2$ in O_2 and in H_2 for several rare earths. For all oxides except Eu_2O_3 the resistance in H_2 increased considerably over that in O_2. However, for Eu_2O_3 the resistance in H_2 was less than that in O_2 by a factor of 5.2. Comparing the conductivity of Eu_2O_3 in H_2 with that of its neighbor Gd_2O_3 in H_2 at 800°C, we see that the conductivity of Eu_2O_3 is greater by a factor of 19.0. The gap ener-

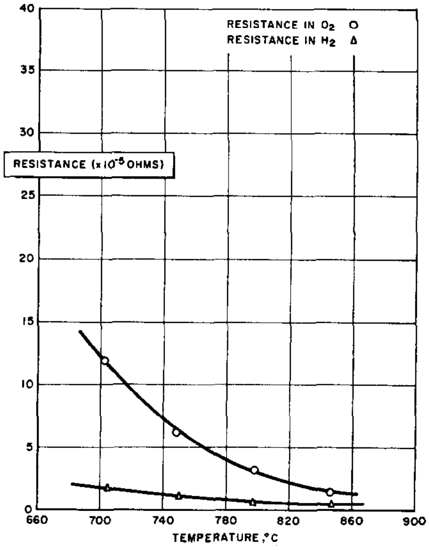

FIG. 2. Electrical resistance of Eu_2O_3 in O_2 and in H_2 as a function of temperature.

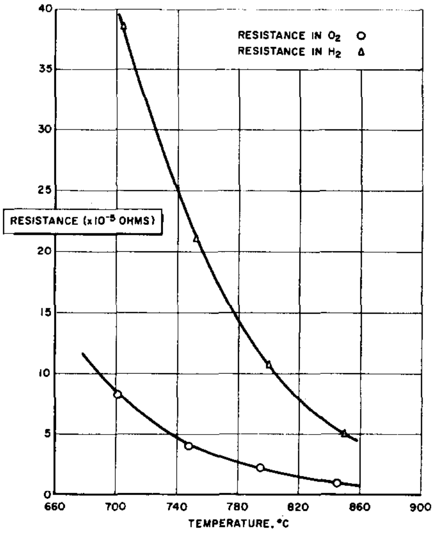

FIG. 3. Electrical resistance of Gd_2O_3 in O_2 and in H_2 as a function of temperature.

TABLE 1

Conductivities (σ) and Gap Energies ($E_g/2$) in O_2 and in H_2 for Several Rare Earths at 800°C[a]

Oxide	σ in O_2	σ in H_2	$E_g/2$ in O_2	$E_g/2$ in H_2
La_2O_3	7.09	1.52	1.305	1.242
Eu_2O_3	5.16	24.60	1.210	0.943
Gd_2O_3	6.40	1.29	1.185	1.246
Yb_2O_3	1.45	0.87	1.071	1.115
Lu_2O_3	2.11	1.08	1.330	1.128

[a] Conductivities are given in units of 10^{-6} ohm^{-1} cm^{-1}; gap energies in electron volts.

gies of all the oxides except Eu_2O_3 are the same in H_2, with a precision of 5%, whereas the gap energy of Eu_2O_3 in H_2 is 21% lower than this average.

Results of the thermoelectric measurements on Eu_2O_3 are given in Table 2. In the final column are the activation energies for conduction calculated from the formula, $QT = (E_c - E_f) + 2kT$ for electrons where E_c is the conduction band energy and E_f the Fermi energy. For holes the activation energy is $(E_f - E_v)$ where E_v is the valence band energy. Quantitative results were difficult to obtain in oxygen atmosphere because of the very high resistance. In a final series of results not shown in Table 2 the temperature difference, (ΔT), across the sample was increased but no change of Q was observed. All oxides proved to be p-type in O_2 and n-type in H_2. The activation energies are higher than those from conductivity measurements, which is not unusual when one considers that the temperature is 200°C higher.

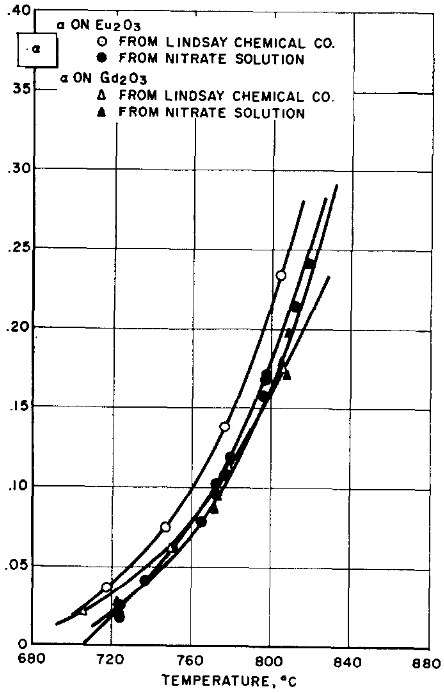

Fig. 4. Catalytic activity for NH_3 decomposition over Eu_2O_3 and Gd_2O_3 (from the Lindsay Chemical Company, and from precipitation with ammonia from a nitrate solution).

Catalytic activity data for Eu_2O_3 and for Gd_2O_3 are shown in Fig. 4. The other rare earths tested gave similar results. Previous work on the same reaction over calcium oxide, quartz, and transition metal nitrides (*9–11*) all shows a first order reaction at high temperature, and the same process probably occurs over the rare earths.

Assuming a first order reaction of the form $A \rightarrow \nu P$, where $\nu = 2$, one can derive

TABLE 2

Thermoelectric Power (Q) and Derived Energy Gap ($E_g/2$) for Eu_2O_3 in O_2 and in H_2 Near 950°C

Sample	ΔT (°C)	Q (mv/deg)	QT (ev)	$2\,kT$ (ev)	$(E_c - E_f)$, $(E_f - E_v)$ (ev)
Eu_2O_3[a] in O_2	3.6	+1.69	+2.081	+0.212	1.869
Eu_2O_3[a] in H_2	4.7	−1.38	−1.685	−0.210	1.475
Eu_2O_3[b] in O_2	5.0	+1.40	+1.70	+0.209	1.491
Eu_2O_3[b] in H_2	7.9	−1.27	−1.52	−0.206	1.314

[a] Pure Lindsay oxide.

[b] Lindsay oxide precipitated from nitrate solution with NH_3 and pressed under 3100 atm. Doubling the pressure had a negligible effect.

the rate equation for a flow reactor according to the method of Hougen and Watson (*12*). The number of moles of reactant changed in the reactor volume element dV can be expressed as Fdn, where F is the flow rate in terms of total mass of fluid per unit time and n is the reactant concentration in moles per unit mass. This is equal to the material reacted on the catalyst surface,

$$-Fdn = k'S'\rho ndV \tag{1}$$

where

$$\rho = \rho_0 \left[\frac{1}{1 + (\nu - 1)(n_0 - n/N_0)} \right] \tag{2}$$

ρ_0 = fluid density at the reactor inlet;
n_0 = reactant concentration at the inlet;
N_0 = the total fluid concentration at the inlet, moles/unit weight;
S' = catalytic surface area/unit volume.

Integrating over the total catalyst volume and the total change in n, we obtain

$$\frac{k'S'\rho_0 V}{F} = \left[1 + \frac{(\nu - 1)n_0}{N_0} \right] \ln \left(\frac{n_0}{n} \right) - \frac{(\nu - 1)}{N_0}(n_0 - n) \tag{3}$$

In the present system where $\nu = 2$ and the initial mole fraction of the reactant is 0.5, this equation becomes

$$\frac{k'S}{q_0} = \frac{3}{2} \ln \left(\frac{1}{1 - \alpha} \right) - \frac{\alpha}{2}$$

where $q_0 = F/\rho_0$, the volumetric flow rate; S = the total surface area.

Table 3 lists the values of $k'S/q_0$ for the various oxides, as well as the final values of k', the intrinsic first order rate constant. The rate constants according to a second order reaction were calculated by a similar method and the variation from sample to sample was found to occur in the same way as for the first order constants. Therefore, any conclusion based on these data will not rest on the particular order chosen.

The activation energies are given in Table 3. These were obtained from the slope of log k' vs $1/T$. Experiments using pelleted and 20-mesh La_2O_3 showed no increase of activity for the smaller particles, and hence, no diffusion limitation. Further calculations confirmed this.

IV. CONCLUSIONS ON RARE EARTHS

The electrical conductivity of Eu_2O_3 at elevated temperatures, in H_2 atmosphere, is substantially greater than that of Gd_2O_3 or of any other rare earth, under the same experimental conditions. Furthermore, it has been shown that electrons are the charge carriers primarily responsible for this effect in Eu_2O_3. In contrast, the conductivities of Yb_2O_3 and Lu_2O_3 are nearly the same in both O_2 and H_2 atmospheres. This is apparently due to the oxidation potential for the reaction $Yb^{2+} \rightarrow Yb^{3+} + e^-$ being substantially larger than that for the corresponding reaction in europium. It is to be noted that in all cases except that of Eu_2O_3 the conductivity in O_2 is greater

TABLE 3

RATE DATA kS/q_0, INTRINSIC FIRST ORDER RATE CONSTANT k', AND ACTIVATION ENERGY E_a, FOR AMMONIA DECOMPOSITION OVER SEVERAL RARE EARTHS (800°C)

Oxide sample	Per cent decomposition	kS/q_0	Surface area (m^2)	k' ($\times 10^6$) (cm min^{-1})	k'' (cm^4 min^{-1} $mole^{-1}$)	E_a (kcal/mole)
Eu_2O_3[a]	17.4	0.201	27.20	7.98	8.04	49.6
Gd_2O_3[a]	16.2	0.184	43.00	4.61	4.69	49.6
Eu_2O_3	21.5	0.258	18.90	14.40	9.54	48.9
Gd_2O_3	15.8	0.180	8.41	24.20	23.10	42.2
Er_2O_3	17.3	0.200	9.04	24.90	24.20	45.7
Yb_2O_3	17.3	0.200	7.78	27.80	28.20	47.6
Lu_2O_3	19.5	0.229	13.49	18.35	19.02	47.2

[a] These two samples were precipitated from the nitrate solution with ammonia. The others were used as received from Lindsay Chemical Company.

than in H_2. This is evident also from the recent results of Noddack (*13*) on La_2O_3, CeO_2, Gd_2O_3, and Yb_2O_3 in O_2 and in vacuum, and in the results of Foëx (*14*). This possibly occurs because oxygen acts as a surface trap for electrons, and this increases the electron hole concentration in these intrinsic semiconductors. Noddack's conductivity data are higher than those reported here by about one order of magnitude. This is possibly due to the higher ignition temperature (1300°C) used by Noddack. The results of Foëx on La_2O_3 agree with those reported here within a factor of 2. The activation energies are less sensitive to particle size and contact area, and are consequently in better agreement. Noddack reports values ranging from 1.05 to 1.53 ev in O_2. Foëx gives 1.47 for Sm_2O_3 and 1.60 for La_2O_3 in O_2.

The catalytic activities of Eu_2O_3 and Gd_2O_3 may be considered to be the same, within experimental error, for the decomposition of ammonia. The activation energies for this reaction on several samples, prepared in different ways, agreed within 2 kcal/mole. In contrast to many results on oxides of the first transition series where conductivity and activity seem clearly to be related, it is found that a change in conductivity of 19.0 (in Eu_2O_3 over that in Gd_2O_3) produces no observable difference in catalytic activity. Certainly it cannot be thought that the surface of the catalyst is saturated at the high temperature employed. The only conclusion which may be drawn is that in these systems, in which variations in all properties except conductivity have been minimized, there is no observable relation of catalytic activity to conductivity. It appears, then, that the correlations frequently observed in other systems may actually be related to other properties which have been altered simultaneously with the conductivity. Of these, the exchange interaction is one possibility.

VI. EXPERIMENTAL ON MNO–MGO SYSTEM

a. Preparation of catalyst samples. The MnO and its solid solutions with MgO were prepared by decomposition of the oxalates as described by Bizette (*8*). The oxalates were coprecipitated in ammoniacal solution with excess oxalic acid. The precipitate was filtered, pressed into pellets 6 mm × 3 mm, and heated in dry H_2 at 550°C for 6 hr. The temperature was then slowly raised to 1200°C and held for 12 hr. According to Jay and Andrews (*15*) MgO is completely soluble in MnO at 1150–1350°C, but becomes less so at lower temperatures. Rapid cooling is, therefore, to be preferred and this was done. The green product pellets were 3 mm × 1.5 mm. Pure reagent grade MgO was used as indicated, without further treatment except for heat treatment in H_2 at 1100°C. The surface areas of these samples averaged 0.4 m^2/g.

The solid solutions were all analyzed for manganese content by oxidation to permanganate by potassium persulfate, followed by iodimetric titration. Confirmation of true solid solution formation was obtained from X-ray powder diffraction measurements.

b. Magnetic susceptibilities. Susceptibilities of the several samples were obtained by the method of Gouy. The pelleted samples were evacuated at 400°C, then sealed without exposure to air. Measurements were made at several fields to detect any ferromagnetic impurity but the susceptibilities obtained were independent of field. All susceptibility measurements were made at room temperature.

c. Catalytic activity. The measurement of activity was the same as for the rare earth series already described, except that a moderately lower temperature was used. The reason for this was that the MnO–MgO system proved to be a somewhat better catalyst for ammonia decomposition than any of the rare earths studied.

VII. RESULTS ON MNO–MGO SYSTEM

Table 4 gives chemical analysis data and MnO concentrations derived from the X-ray diffraction data. The latter are not very accurate, but they show that the MgO was present in solid solution. Table 4 also shows that this conclusion is confirmed by the magnetic data—the susceptibility per

TABLE 4
COMPOSITION, X-RAY DATA, AND MAGNETIC SUSCEPTIBILITIES FOR THE MnO-MgO SYSTEM

Mole % MnO (chemical analysis)	Mole % Mn (X-ray)	Susceptibility $\chi_{MnO} \times 10^3$
100	100	4.91
79.3	81.4	—
78.3	82.8	5.90
75.3	66.9	—
64.4	66.9	—
62.1	73.0	6.79
58.5	63.1	—

mole of MnO increasing with progressive dilution. Although the molar susceptibility for pure MnO agrees well with Bizette's value 4.88×10^{-3}, yet the susceptibilities for the diluted samples are somewhat higher than his. In any event, it is clear from the X-ray and the magnetic data that solid solutions have been formed, and from the magnetic data it is established that exchange interaction between Mn^{2+} ions is progressively diminished by the presence of the MgO.

The catalytic activities of the MnO-MgO system, up to 41.5% MgO, are given in Fig. 5, in terms of α as a function of temperature. Above 750°C the curve of α vs T begins to level off, indicating the approach to equilibrium. The first order constants are included in Table 5. A comparison of the rate constant on pure MgO (specific surface 19 m^2) with that on pure MnO shows that the MgO is less than 1% as active as MnO. One sample consisting of pure MnO mixed mechanically with pure MgO, having about the same total surface area, gave the same rate constant as pure MnO alone. It is clear, therefore, that the MgO on the surface of the solid solution samples contributes only a negligible pro-

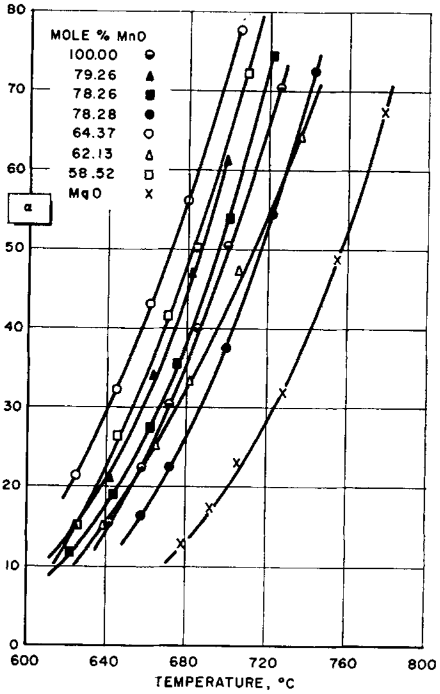

FIG. 5. Catalytic activity for NH_3 decomposition over MnO, MnO–MgO, and MgO as a function of temperature.

TABLE 5
RATE DATA FOR AMMONIA DECOMPOSITION OVER MnO-MgO AT 690°C

Mole % MnO	Per cent decomposition	kS/q_0	Surface area (m^2) of MnO	$k'(\times 10^3)$ (cm min^{-1})	$k''(\times 10^{-2})$ (cm^4 min^{-1} mole^{-1})	E_a (kcal/mole)
100	48.7	0.755	1.222	5.99	7.90	44.7
79.26	62.0	1.148	0.970	11.41	18.80	45.6
78.26	56.0	0.955	0.823	11.28	16.48	46.0
75.28	38.5	0.540	0.926	5.65	6.41	45.9
64.37	57.0	0.985	0.745	12.81	19.03	45.5
62.13	32.4	0.427	0.660	6.26	6.63	41.0
58.52	48.0	0.738	0.960	7.46	9.70	45.7
MnO + MgO[a]	52.0	0.843	1.222	6.69	9.21	47.0
MgO (pure)	13.7	0.151	(20.4)	0.72	0.064	45.9

[a] This was a mechanical mixture.

portion to the activity observed. The effective surface of MnO in the catalysts, if one may assume a homogeneous distribution of MgO, is simply the total surface area times the mole fraction of MnO. Again, calculations on diffusion effects on various samples revealed that the reaction was outside the diffusion-limiting range, despite the rate constants being considerably higher than for the rare earth series. The rate constants indicate that there is no trend in activity with increasing MgO in MnO.

The activation energies determined for a first order reaction confirm these results, giving an average value of 45.6 ± 0.3 kcal/mole (omitting the value for 62.13% MnO).

VIII. CONCLUSIONS ON MnO–MgO

There is ample evidence that dilution of an oxide such as MnO with a diamagnetic diluent such as MgO diminishes the exchange interaction between neighboring positive ions. A few examples of other similar systems in which this effect has been observed include Cr_2O_3–Al_2O_3, CoO–MgO, and UO_2–ThO_2. Evidence concerning the effect of diluting, or doping, NiO with Li_2O is less clear—some authors (*16*) claiming that the dilution process has results analogous to that observed in MnO–MgO, but others reporting some ferro- or ferrimagnetism as being observed (*17*). But there can be no doubt that the presence of Li_2O in NiO makes a serious *change* in the exchange interaction between adjacent nickel ions.

Few attempts have been made to investigate the effect of altered exchange interaction in catalytically active solids, even though in many such systems the exchange effects are no less readily observed than are the conductivity effects. Stone and De (*18*) have recently attempted such a study in connection with the H_2–D_2 reaction on the isostructural oxides, Ti_2O_3, V_2O_3, and Cr_2O_3. While markedly different reaction rates on these oxides were observed, and while it is well known that exchange effects are strongly altered on going through the Néel point, yet these results do not unequivocally establish any relationship of the kind sought. The reason for this is that the conductivities of these oxides, under the experimental conditions, vary from metallic to semiconductive.

An alternative approach is found in the study of small (supported) catalyst particles (*19*). The familiar catalyst system Cr_2O_3–Al_2O_3 is one example where altered exchange effects lead to an increase of magnetic susceptibility in the very small particles of Cr_2O_3 normally present. There is no question that catalytic activity, as for the dehydrocyclization of *n*-heptane, is greater (per mole of Cr_2O_3) if the Cr_2O_3 particles are small. But there are so many other variables in such a catalyst system that it is impossible to establish a unique correlation between activity and exchange effects.

The MnO–MgO solid solution system appears to avoid most of the complications mentioned above. No lattice defects are introduced, the conductivity does not vary markedly, and the specific surface may be maintained approximately constant. The only serious change in the surface is that as the MgO is added the number of nearest Mn^{2+} neighbors to each Mn^{2+} is decreased. The electrons which would ordinarily interact with electrons on adjacent Mn^{2+} ions are restricted to one ion. Energetically these electrons are at a higher level than if they were coupled to other electrons. Such an effect might have been expected to yield a measurable change, probably an increase, of catalytic activity.

The activation energies and rate constants for the decomposition of ammonia have been found to be independent of MgO dilution in MnO, in the concentration range 0–50% MgO. Certainly the exchange effects at this dilution are diminished. It must, therefore, be concluded that in this system the degree of exchange interaction does not influence the rate of reaction for ammonia decomposition, over the concentration range studied.

IX. SUMMARY

The rare earth Eu_2O_3 is an *n*-type semiconductor in H_2 at 700–800°C, and its conductivity is greater, under similar conditions, than that of Gd_2O_3 by a factor of 19.0 at 800°C. The rate of decomposition of ammonia and the activation energy for this reaction are the same over Eu_2O_3 and Gd_2O_3. As these two oxides are so nearly alike in all respects except in the reducibility of the Eu^{3+} ion, and as exchange effects are minimal in rare earths at these temperatures, it appears that there is no correlation between semiconductivity and catalytic activity for this system.

The solid solution system MnO–MgO does not change appreciably in conductivity with changing MgO content, but exchange interaction effects are large. Here again, no alteration of catalytic activity for ammonia decomposition was observed. It appears, therefore, that neither semiconductivity nor exchange interaction is of significance for catalytic activity in the systems, and for the reaction, studied.

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