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Rare Earth Intermetallics as Synthetic Ammonia Catalysts[1]

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The rapidity with which rare earth intermetallics absorb hydrogen suggests that they have high catalytic activity for the dissociation of molecular hydrogen and possibly other diatomic molecules such as N_2. Thirty-six intermetallics involving rare earths in combination with Fe, Co, or Ru were studied as catalysts for the formation of NH_3 from the elements. Several of these have specific activities exceeding that of a doubly promoted iron synthetic ammonia catalyst of the type in commercial use, although the actual activity is lower because of the relatively small surface area of the intermetallics. X-ray diffraction patterns of some of the intermetallics, notably the Fe-containing catalyst, showed extensive conversion into transition metal and rare earth nitride. The catalytic activities of these systems may be due mainly to the transition elements.

INTRODUCTION

Recently many rare earth intermetallic compounds have been shown to absorb large quantities of hydrogen rapidly and reversibly under mild conditions of temperature and pressure (*1–4*). Kuijpers and Loopstra showed (*5*) by neutron diffraction measurements on $PrCo_5D_4$ that deuterium is in atomic form in this material. It occupies interstitial sites in the $PrCo_5$ lattice, making it clear that molecular D_2 is dissociated into atoms, or possibly ions, as it enters the solid. The rapidity with which $PrCo_5$ absorbs H_2 (or D_2) makes it clear that the breaking of the H_2 bond is extremely rapid on the surface of this material. From general considerations it seemed likely that, in this respect, $PrCo_5$ is typical of all the rare earth intermetallics which absorb H_2 rapidly and in large quantities. This in turn has suggested that these materials might be effective hydrogenation catalysts.

Ozaki and co-workers (*6*) have shown the addition of alkali metals to transition metals supported on active carbon remarkably enhances the catalytic activities of the transition metal for the synthesis of ammonia from the elements. They ascribed this to electron transfer from the alkali metal to the transition metal. During the past decade or so an enormous amount of attention has been focused on rare earth-transition metal intermetallics (*7*). A portion of these studies has been concerned with the determination of magnetic properties—susceptibility, saturation magnetization, Curie temperatures, etc. These studies have made it abundantly clear that there is electron transfer from the rare earth to the transition element (*8*). In the light of observations of Ozaki *et al.* and the demonstrated surface activity of the rare earth intermetallics for the dissociation of H_2, it seemed of interest to examine them as

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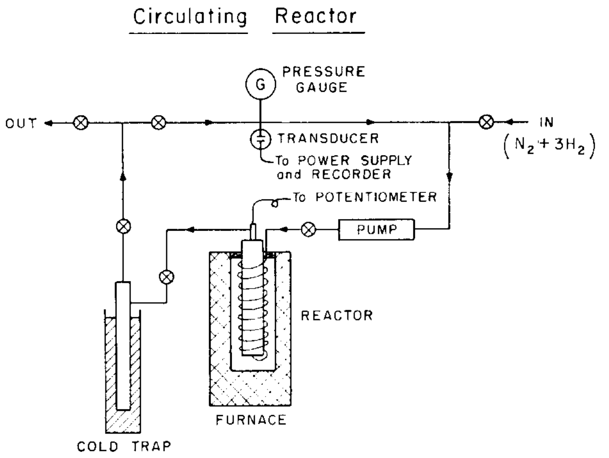

FIG. 1. Schematic diagram of the circulating reactor.

synthetic ammonia catalysts. A number of the rare earth intermetallics has now been examined in this regard and the results obtained are presented in this communication.

EXPERIMENTAL DETAILS

The rare earth intermetallics were prepared by techniques that are now standard in this laboratory. They are formed by induction melting of the component metals in a water-cooled copper boat under an atmosphere of purified argon. In some cases the compound is formed directly upon solidification of the melt. In other cases the compound is formed peritectically from the melt and, hence, an appropriate heat-treatment procedure is required. The particular heat treatments required are established from the phase diagrams for the systems where available. After this, powder X-ray diffraction patterns were taken to establish the presence of the desired compound and the absence of extraneous phases.

The component metals used were the best grade materials obtainable commercially. Purities (exclusive of gaseous contaminants) as stated by the suppliers were as follows: rare earths and ruthenium,

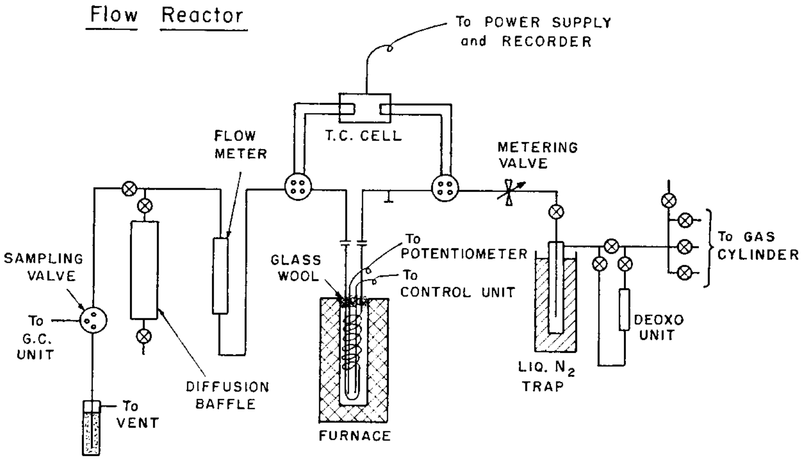

FIG. 2. Schematic diagram of flow system used for surface area measurements.

99.9%; iron, cobalt, and nickel, 99.999%. The manganese was 99.99%.

Apparatus employed for the reaction studies consisted of a stainless steel, closed-circulating system with a dry ice–acetone trap, which can be operated under pressures of up to 70 atm and at temperatures of up to 600°C. The extent of the reaction was monitored by recording pressure change as a function of time. The schematic diagram of the apparatus is shown in Fig. 1. The pressure gauge used was a Matheson Test gauge (1000 PSIG) and the pressure transducer used was a Stathum Universal Transducing Cell (UC3).

TABLE 1

Catalytic Activity of Fe-Containing Synthetic Ammonia Catalysts

Catalyst	Temperature (°C)	100 x[a]	y (% NH_3)[b]	ml[c] NH_3/m^2·min
Cat. 416	300	0.23	0.12	0.15
2.77 g	350	0.98	0.49	0.62
S = 14.42 m^2	406	2.31	1.17	1.49
	428	2.78	1.41	1.79
	465	3.05	1.55	1.97
	490	2.78	1.41	1.79
$CeFe_2$	360	0.13	0.07	0.71
4.0 g	440	0.42	0.21	2.14
S = 1.80 m^2	500	0.75	0.38	3.87
	513	0.77	0.39	3.97
Ce_2Fe_{17}	430	0.45	0.23	
3.57 g	490	0.63	0.32	
	520	0.87	0.44	
$GdFe_3$	365	0.01	0.00	
3.24 g	430	0.01	0.00	
	515	0.10	0.05	
$TbFe_3$	403	0.07	0.03	
3.05 g	450	0.14	0.07	
	480	0.28	0.17	
$DyFe_3$	350	0.02	0.01	
3.21 g	435	0.04	0.02	
	480	0.08	0.04	
$HoFe_3$	430	0.04	0.02	
3.20 g	502	0.14	0.07	
	520	0.13	0.06	
$ErFe_3$	390	0.22	0.11	
3.14 g	448	0.27	0.14	
	517	0.31	0.16	
$ThFe_3$	457	0.25	0.12	1.01
3.93 g	514	0.44	0.22	2.03
S = 2.35 m^2				

[a] x is the fraction of the reactant gases which are converted for each pass through the catalyst.

[b] y is the percentage of NH_3 in the gas exiting from the catalyst bed.

[c] Milliliters at STP.

TABLE 2

Catalytic Activity of Rare Earth Intermetallics Containing Ce and Pr

Catalyst	Temperature (°C)	100 x[a]	y (% NH_3)[a]	ml[b] NH_3/m^2·min
$CeRu_2$	340	0.32	0.16	2.47
3.62 g	382	0.55	0.28	4.35
S = 1.18 m^2	405	0.71	0.36	5.59
	460	1.32	0.66	10.25
	500	1.81	0.91	14.13
$Ce_{24}Co_{11}$	330	0.15	0.08	
3.30 g	410	0.23	0.12	
	500	0.51	0.26	
$CeCo_2$	332	0.24	0.12	1.01
3.30 g	400	0.66	0.33	3.02
S = 2.00 m^2	450	0.94	0.47	4.31
	490	1.01	0.51	4.67
	530	0.99	0.49	4.49
$CeCo_3$	390	0.32	0.16	7.15
3.50 g	450	0.78	0.39	17.43
S = 0.41 m^2	505	0.84	0.42	18.77
	530	0.96	0.48	21.45
Ce_2Co_7	314	0.03	0.02	1.02
3.30 g	374	0.10	0.05	2.54
S = 0.36 m^2	431	0.28	0.14	7.12
	477	0.44	0.22	11.20
	503	0.56	0.28	14.25
$CeCo_5$	395	0.27	0.14	3.33
3.66 g	450	0.45	0.23	5.47
S = 0.77 m^2	503	0.67	0.34	8.09
$PrCo_2$	362	0.04	0.02	0.32
3.04 g	421	0.11	0.06	0.97
S = 1.14 m^2	449	0.15	0.08	1.29
	479	0.23	0.12	1.94
$PrCo_3$	394	0.08	0.04	1.87
3.14 g	420	0.12	0.06	2.80
S = 0.39 m^2	450	0.14	0.07	3.27
	480	0.22	0.11	5.14
$PrCo_5$	330	0.07	0.04	1.22
3.05 g	423	0.29	0.15	4.58
S = 0.60 m^2	464	0.43	0.22	6.72

[a] For definitions of x and y see footnotes to Table 1.

[b] Milliliters at STP.

The synthesis gas mixture was obtained commercially, and the purity of gas was better than 99.99%. The ratio of nitrogen and hydrogen gas was close to 1:3 (25.1% N_2 in H_2). Catalysts were powdered in the air by a mortar and pestle and then introduced into the reactor.

Catalysts used weighed about 3.3 g, having a volume of ~1 cm^3. The reactor was first evacuated by a mechanical pump

TABLE 3

Rank Ordering for NH_3 Synthesis (at 450°C)

	Yield $\left(\frac{NH_3(ml)}{m^2 \text{ of cat. min}}\right)$
$CeCo_3$	17.4
$CeRu_2$	13.5
Ce_2Co_7	9
Ce_2Fe_{17}	6.7*
$PrCo_5$	6
$CeCo_5$	5.5
$CeCo_2$	4.3
$Ce_{24}Co_{11}$	4.3*
$PrCo_3$	3.3
$ErFe_3$	3.3*
$CeFe_2$	2.3
416	1.8
$TbFe_3$	1.7*
$PrCo_2$	1.3
$ThFe_3$	0.9
$DyFe_3$, $HoFe_3$	0.5*

* Surface area of these systems was not measured. Calculations were made assuming their areas per gram were the average of the intermetallics studied.

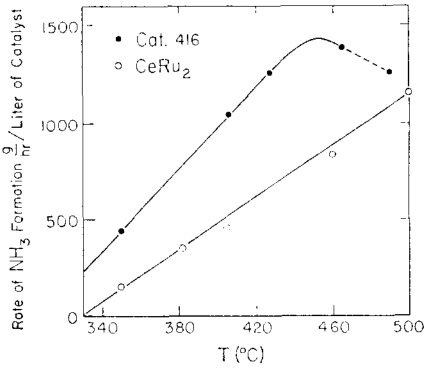

FIG. 3. Rate of formation of NH_3 from the elements over Catalyst 416 (●) and $CeRu_2$ (○) at various temperatures. Pressure, 50 atm, space velocity, 120,000 hr^{-1}.

(10^{-3} Torr) and a small amount of synthesis gas was admitted into the reaction system. This process was repeated several times to clean the reactor and the catalyst. The synthesis gas mixture was then introduced into the reactor up to a pressure of 70 atm. The temperature of the catalyst bed was raised gradually to 400°C while the gas was circulated through the cold trap. Catalysts were seen to absorb hydrogen gas at low temperature, which was indicated by a very rapid drop in the system pressure. As the temperature of the catalyst bed is raised to higher temperature, a gradual pressure drop was noted, indicating ammonia formation. The catalyst bed was kept at 400°C until a steady pressure drop was obtained. Formation of NH_3 was confirmed by taking the ir spectra of the product caught in the trap.

Surface areas of some of the catalysts were measured after reaction runs by the continuous flow method of Nelsen and Eggertsen (*9*). The schematic diagram of this equipment is shown in Fig. 2. The thermal conductivity cell and the power supply were obtained from Gow-Mac Instrument Co. This setup was so designed that the reaction kinetics of the process could also be determined in a single pass experiment and at pressures ~1 atm. Provisions were made for surface areas to

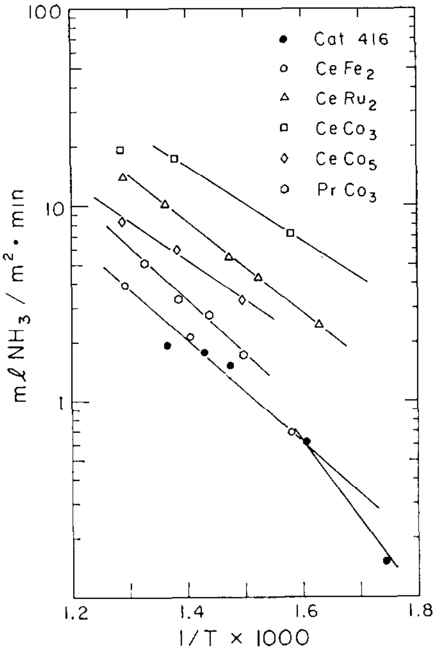

FIG. 4. Specific rate of formation of NH_3 over Catalyst 416 (●), and several representative rare earth intermetallics. Pressure, 50 atm. Space velocity, 120,000 hr^{-1}.

TABLE 4

Apparent Activation Energies for NH_3 Synthesis

Catalyst	E_a (kcal $mole^{-1}$)
416	20.5
$CeFe_2$	13.2
Ce_2Fe_{17}	8.0
$ErFe_3$	12.3
Er_2Fe_{17}	9.0
$ThFe_3$	10.6
$CeRu_2$	10.3
$Ce_{24}Co_{11}$	9.4
$CeCo_2$	5.8
$CeCo_3$	8.7
$CeCo_5$	9.3
CeNi	14.5

be determined on the sample *in situ*. This part of our study will be reported in more detailed manner in the near future. The gas mixture used for the surface area measurement was 25% nitrogen in helium or 5% argon in helium.

The fraction of the reactants, which is converted per pass, is designated $x(P, t)$. For the ammonia formation this was obtained in the following manner: The equation of the reaction is

$$N_2 + 3H_2 \rightarrow 2NH_3.$$

As noted above, the ammonia formed is trapped out. Since the volume of the entire system is constant, the pressure will decrease as ammonia is formed and frozen out; $x(P, t)$ is given by the expression

$$x(P, t) = -\left[\frac{V_R}{V_G}\left(\frac{\partial P}{\partial t}\right)_T\right]_{P,t},$$

where V_R = volume of the entire system, V_G = volume of gas circulated in a unit time, and T, P, and t denote temperature, pressure, and time, respectively. Thus, x can be established from the rate at which the pressure decreases.

Using $x(P, t)$, the percentage of ammonia in the gas mixture exiting from the catalyst bed, y, is given as

$$y = 100x/(2 - x).$$

At the space velocity used ($\sim 120{,}000 V_g \cdot V_c^{-1} \cdot hr^{-1}$) and with catalysts having activity in the range of Cat. 416 (*Vide infra*), the expected conversion per pass is at most 0.04 or $y \sim 2$ at 50 atm and 450°C. Therefore, we may assume that the reaction was run in a quasi-steady flow reactor, although the reactor is intrinsically of a transient nature.

The experiments were carried out over a period of 1 or 2 weeks. There was no detectable decrease in the activity of any of the catalysts over this period of time.

RESULTS AND DISCUSSION

In Tables 1 and 2, the yield of $NH_3(y)$ and the conversion per pass (x) are shown for the 17 most active catalysts out of 36 rare earth intermetallics which have been studied to date. In addition, for purposes of comparison data are supplied for a standard high activity synthetic ammonia catalyst (designated as Cat. 416). Catalyst 416, kindly supplied by Prof. P. H. Emmett, consisted of 0.97% Al_2O_3, 0.65% K_2O, and the balance iron oxide. It was reduced by the reaction gas mixture prior to use.

Nineteen other intermetallics were studied. They had lower activities than the intermetallics shown in Tables 1 and 2˙ The other systems studied were: (a) R_2Fe_{17} with R = Th, Gd, and Er; (b) $HoFe_2$; (c) $TbMn_2$ and $HoMn_2$; (d) $CeCu_5$ and $LaCu_5$; (e) Y_6Mn_{23} and Tb_6Mn_{23}; (f) CeNi, $CeNi_5$, CeC_2, Ce_2In, $CeOs_2$, and $CeRe_2$; (g) $HoCo_2$; and (h) $DyCo_3$.

Specific activities (expressed as ml NH_3(STP)/m^2 min) are given in Tables 1 and 2 for most of the intermetallics studied and for Cat. 416. Because of its large surface area, Cat. 416 is the most effective of the materials studied; the rare earth intermetallics have surface areas an order of magnitude or more lower than Cat. 416.

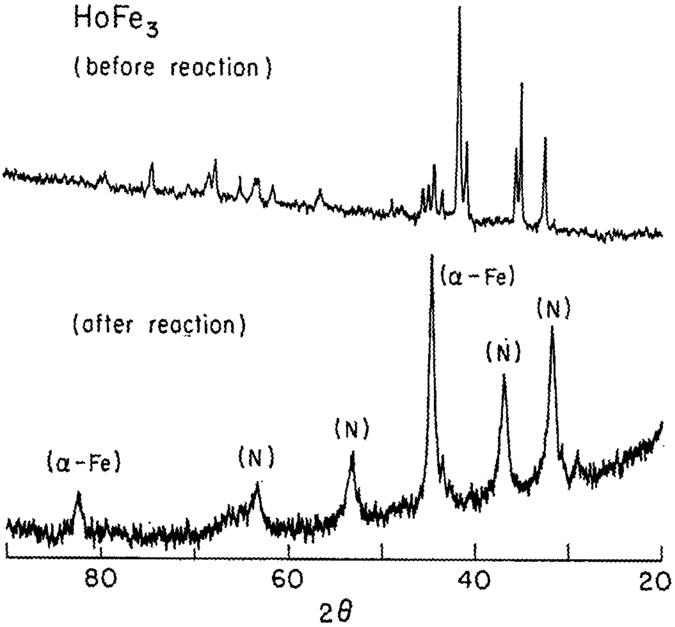

FIG. 5. X-ray diffraction patterns of $HoFe_3$ before and after the reaction run. Peaks marked (N) are from HoN.

However, when expressed as specific activity (see Table 3), many of the rare earth intermetallics are substantially superior to Cat. 416.

The relative effectiveness of several of the catalysts is shown in Figs. 3 and 4. The maximum in yield for Cat. 416 at higher temperatures is the result of the influence of equilibrium conditions. It is clear from Table 3 and Fig. 4 that the specific activity of a number of intermetallics substantially exceeds that of

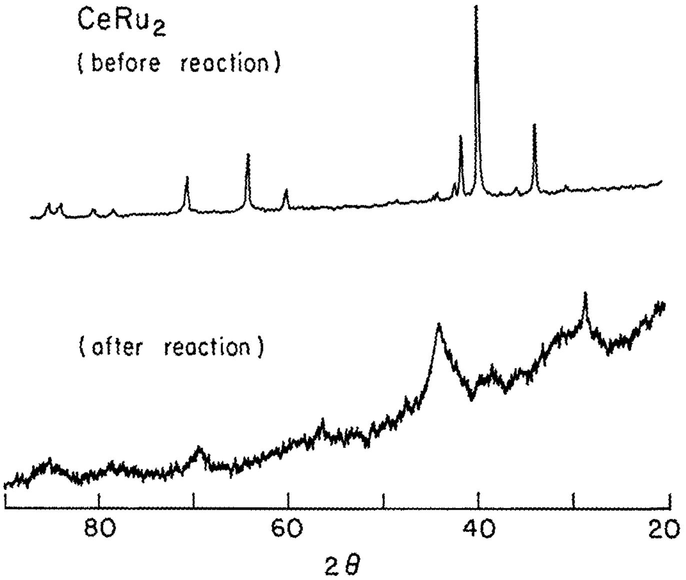

FIG. 6. X-ray diffraction patterns of $CeRu_2$ before and after the reaction run.

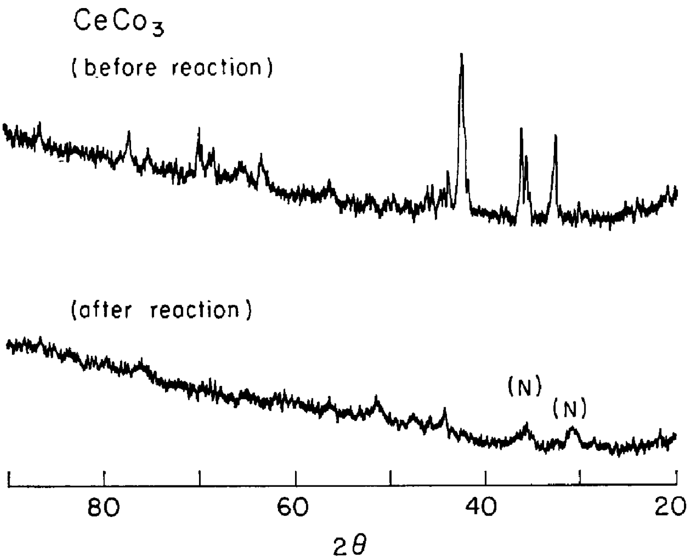

FIG. 7. X-ray diffraction patterns of $CeCo_3$ before and after the reaction run. Peaks marked (N) are from CeN.

Cat. 416. The temperature coefficient of the rate of formation of NH_3 (see, for example, Fig. 4) has been used to establish the apparent activation energies which are listed in Table 4.

It is of obvious interest to know the chemical species responsible for the observed catalytic activity. It seems likely that the actual catalyst is the finely divided transition metal formed by decomposition of the rare earth intermetallic under the conditions of the reaction. X-ray diffraction patterns for a few of the catalysts studied are shown in Figs. 5–7, for the initial material and the material after the experiment was concluded. Results for $HoFe_3$ (Fig. 5) show decomposition into αFe and HoN. For $CeCo_3$ (Fig. 7) weak peaks characteristic of CeN are observed. (RN peaks are also clearly observed in the case of $PrCo_2$, $CeCo_2$, and $PrCo_3$.) No CeN peaks are seen in the diffraction pattern of used $CeRu_2$ but decomposition has obviously taken place.

It seems a reasonable surmise to ascribe the catalytic activity to Fe, Co, or Ru formed when the compound decomposes. However, the variable apparent energy of activation (Table 4) and the high specific activities of the rare earth compounds indicate that the rare earth constituent is not without some effect. Further work is needed to clarify the way in which the rare earth makes its influence felt.

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