

Catalytic Properties of Rare Earths

► Because they are by-products of atomic piles and titanium production, rare earth elements may soon be abundant. They are promising as catalysts. Neodymium and samarium oxides, reported here, are predominantly alcohol dehydrogenating catalysts and their activity substantially improves with deposition on alumina. In their presence, *n*-heptane and 1-octene can be cyclized and cyclohexane can be dehydrogenated to benzene.

NEW INTEREST has centered in the rare earth elements because of developments in titanium production and because they are essential by-products of atomic piles. As a group, they are more abundant in the earth's crust—in igneous and sedimentary rock—than many common elements such as lithium, copper, zinc, lead, and tin (Table I). They will become readily available materials.

Monazite is closely associated in rocks with rutile and ilmenite, the main natural sources for titanium. It is composed essentially of phosphates of rare earths, with cerium, lanthanum, praseodymium, and neodymium constituting up to 92%. The remaining 8% is distributed between other rare earths and yttrium.

These rare earths commonly known as lanthanons, are usually divided into two subgroups—light lanthanons, comprising elements in the periodic table from lanthanum to gadolinium; and heavy lanthanons, comprising those from terbium to lutecium. Also, there are two other elements, yttrium and scandium, which do not belong in this group but are included because of similarity in chemical properties and their origin in the same minerals.

Rare earths belong to the group called

transition elements characterized by changing valency and paramagnetic properties (ferromagnetic for gadolinium). They crystallize in body- and face-centered cubic systems and close-packed hexagonal systems with ionic radii between 1.0 to 1.22 Å. They form oxides of the general formula R_2O_3 . Their chemical similarity is determined by the similarity of the valence electrons ($6s^2$) and their transition character by the unfilled $5d$ shell. They differ from each other by completeness in filling of the $4f$ shell which is an inner shell screened by the $5s$ and $5p$ shells from regular chemical activity.

Unavailability of rare earths in pure state has prevented systematic study of these materials as catalysts. Most of the work was done with cerium oxide; its application as a promoter to increase luminosity of the thorium mantle (Welsbach mantle) is probably the earliest exhibition of catalytic properties.

Cerium oxide was used extensively as an oxidation catalyst and particularly as a catalyst promoter in various oxidations such as of alcohols and carbon monoxide (2, 3, 5-8). In an extensive work, Cremer (7) studied lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, and yttrium oxides in dehydration and dehydrogenation of ethyl alcohol. Of particular interest is the work of Taylor (9), who found that orthopara hydrogen conversion takes place in the presence of cerium, neodymium, and gadolinium oxide catalysts. Use of rare earths as promoters is cited in existing patent literature (about 75 patents).

Preparation of Catalysts

This study began with an investigation of the action of neodymium and samarium oxides in dehydrogenation. The oxides of 98% purity, obtained from the Société des Terres Rares of Paris, were dissolved in dilute hydrochloric acid. The hydroxides, precipitated with dilute sodium hydroxide, were filtered, washed free of chloride ions, dried at 105° C. overnight, sized to 8 to 10 mesh, and activated in a catalytic furnace in a stream of nitrogen at 550° C.

In contrast to chromia or vanadia catalysts, activation with nitrogen gave catalysts of higher activity than with hydrogen (Table IV). Consequently, in all experiments reported here, nitrogen-activated catalysts were used. Sur-

faces of these catalysts as determined by the Brunauer - Emmett - Teller method were 40 square meters per gram for neodymium oxide and 58 for samarium oxide. Neodymium oxide-alumina catalyst was prepared by coprecipitation—a sodium aluminate solution was added to a solution of neodymium nitrate. The mixed hydroxides were washed, dried, and activated as described before. The final composition was 15% neodymium oxide and 85% alumina.

Apparatus and Materials

The usual catalytic furnace with thermoregulator, automatic constant-dropping buret, water, and ice and dry ice product condensers were used in the experiments. The quantity of catalyst used in each run was 30 ml.

The materials included absolute ethyl alcohol and *n*-octyl alcohol having a boiling point of 194°-195° C., obtained from E. I. du Pont de Nemours & Co.; *n*-heptane, 1-octene, and cyclohexane of 99% pure grade obtained from the Phillips Petroleum Co.

Results and Discussion

Alcohol. The first series of experiments was conducted with ethyl and *n*-octyl alcohols (Table II). As shown by the early work of Cremer (7) with ethyl alcohol, neodymium and samarium oxides exhibited both dehydration and dehydrogenation activity with dehydration predominating in a ratio of 2 to 1. Conversely, in this work, neodymium oxide predominantly catalyzed dehydrogenation of ethyl alcohol to give over-all yields of 45% of aldehyde and 10% of ethylene in a ratio of 4.5 to 1.

The difference in these results from those of Cremer can probably be ascribed to differences in catalyst preparation. These catalysts were prepared by precipitation and not heated above 550° C., whereas Cremer's catalysts were ignited at temperatures of 650° to 700° C. As in the case of chromia, such high temperatures destroy their dehydrogenating activity.

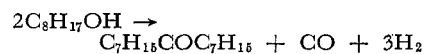
The dehydrogenation action of neodymium oxide was even more pronounced with octyl alcohol. At 400° C. and above, only traces of water were found in the reaction products. The reaction was directed mostly to dehydrogenation to form aldehydes, with consequent condensation to di-*n*-heptyl ketone and evolution of carbon monoxide

Table I. Abundance of Rare Earths and Yttrium

(G./ton of earth's crust)			
Element	G.	Element	G.
Ce	44.0	Yb	2.6
Y	31.0	Er	2.4
Nd	24.0	Ho	1.2
La	19.0	Eu	1.0
Sm	6.5	Tb	1.0
Gd	6.3	Lu	0.7
Pr	5.6	Tm	0.3
Dy	4.3		

PREPARING CATALYSTS IN THE LABORATORY

in a manner similar to the behavior of a chromia catalyst reported by Komarewsky and Coley (4).



At higher temperatures (500° C.), neodymium oxide also acts similarly to chromia. In addition to di-*n*-heptyl ketone small amounts (2%) of xylenol are formed.

Cyclohexane. Experiments with cyclohexane (Table III) were carried out with pure neodymium and samarium oxides and with coprecipitated neodymium-alumina catalyst. With the pure oxide catalysts, formation of aromatics was first detected at 545° C. However, coprecipitated neodymium oxide-alumina was an active aromatization catalyst with 59% yields at temperatures as low as 500° C.

n-Heptane, 1-Octene, and Propane.

The main part of this experimental work was carried out with aliphatic hydrocarbons (Table IV). Dehydrocyclization of *n*-heptane and 1-octene occurred at 525° C. in the presence of neodymium and samarium oxides. Coprecipitated neodymium oxide-alumina was more active than neodymium oxide. Higher yields of cyclized products were obtained with 1-octene than with *n*-heptane using both pure and coprecipitated oxide catalysts. Dehydrogenation of propane in the presence of a coprecipitated neodymium oxide-alumina catalyst was initiated at 540° C.

At 525° C., neodymium and samarium oxides are active as dehydrogenation catalysts for paraffins but not for cycloparaffins. In this respect they differ with chromia and vanadia catalysts which are active in dehydrogenation of both products at this temperature. Thus, these rare earth oxides are selective catalysts for dehydrogenation of paraffins in natural hydrocarbon mixtures.

Table II. Alcohol Experiments with Neodymium Oxide (Nd₂O₃) Catalyst

Alcohol Charged	T, ° C.	Space Velocity Ml./Ml./Hr.	Product, Wt. % of Charge
Ethyl	350	0.25	Ethylene traces; aldehyde, 10 ^a
	400	0.25	Ethylene, 10.5; aldehyde, 45.4 ^a
Octyl	400	0.1	Water traces; di- <i>n</i> -C ₇ ketone, 20 ^b
	450	0.15	Water traces; di- <i>n</i> -C ₇ ketone, 50 ^b
	500	0.16	Water traces; di- <i>n</i> -ketone 49 xyleneol, 2 ^c

^a Products determined by analyzing gas and water formed in reaction.

^b Products identified by distillation and melting point of ketone (4).

^c Xyleneol determined by literature method (10).

Table III. Cyclohexane Experiments with Neodymium and Samarium Oxide and Coprecipitated Nd₂O₃-Al₂O₃ Catalysts

Catalyst	T, ° C.	Space Vel., Ml./Ml./Hr.	Product, ^a Wt. %	Refractive Index, n _D ²⁰
Nd ₂ O ₃	500	0.25	No reaction	1.4235
Sm ₂ O ₃	525	0.25	No reaction	1.4232
Nd ₂ O ₃	545	0.25	Aromatics, 14.7	1.4370
Sm ₂ O ₃	545	0.25	Aromatics, 12.7	1.4360
Nd ₂ O ₃ -Al ₂ O ₃	500	0.25	Aromatics, 59.0	1.4699

^a Analyzed by separation in chromatographic column (SiO₂) and identification of benzene by physical constants.

Summary

Rare earth elements appear promising as catalysts. Neodymium and samarium oxides are predominantly alcohol dehydrogenation catalysts and their activity substantially improves with deposition on alumina. In their presence, cyclohexane can be dehydrogenated to benzene at 545° C.; *n*-heptane and 1-octene can be cyclized and dehydrogenated at 525° C.

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Table IV. Aliphatic Hydrocarbon Experiments with Neodymium and Samarium Oxides and Coprecipitated Nd₂O₃-Al₂O₃

Hydrocarbon	Catalyst	Temp., ° C.	Space Vel., Ml./Ml./Hr.	Liq. Recovery, Vol. of Charge	Analysis of Product				
					Liquid ^a		Gas ^b		
					Aromatics	Olefin	Hydrogen	Paraffin	Olefin
<i>n</i> -Heptane	Nd ₂ O ₃	500	0.15	95.0	°	°	°	°	°
	Nd ₂ O ₃	525	0.15	78.2	11.4	15.7	52.7	27.1	20.2
	Nd ₂ O ₃	525	0.15	79.0	9.0	12.3	°	°	°
	Nd ₂ O ₃ ^d	540	0.15	44.0	19.0	16.0	°	°	°
	Nd ₂ O ₃ -Al ₂ O ₃	500	0.15	89.0	11.6	4.2	64.8	20.4	14.8
		525	0.15	71.8	21.9	10.3	64.8	22.9	12.3
	Sm ₂ O ₃	500	0.15	95.0	°	°	°	°	°
	525	0.15	70.0	12.6	7.4	°	°	°	
1-Octene	Nd ₂ O ₃	525	0.25	59.0	49.0	°	°	°	°
	Sm ₂ O ₃	525	0.15	60.0	50.0	°	°	°	°
	Nd ₂ O ₃ -Al ₂ O ₃	500	0.15	70.0	59.0	°	°	°	°
Propane	Nd ₂ O ₃	540	0.25	°	°	°	°	°	17.0
	Sm ₂ O ₃	540	0.25	°	°	°	°	°	18.5
	Nd ₂ O ₃ -Al ₂ O ₃	540	0.3	°	°	°	°	°	5.0

^a Separated by chromatography (SiO₂) and identified by physical constants.

^b Analyzed by mass spectrograph. ^c No reaction. ^d Hydrogen activated. ^e Not analyzed