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Abstract

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APPLICATION OF RARE-EARTH ELEMENT OXIDES IN CATALYTIC SYNTHESIS

(Presented by Academician A. A. Balandin, March 29, 1964)

In recent years A. A. Balandin, A. A. Tolstopyatova, and their co-workers (1–5) have studied, by the kinetic method, the dehydrogenating and dehydrating properties of rare-earth element oxides as catalysts and determined their bond energies. Kh. M. Minachev and co-workers (6–10) studied the catalytic conversion of hydrocarbons in the presence of Nd oxides.

We investigated and established the possibility of using oxides of the rare-earth elements Er, Pr, La, Ce, Sm, Dy, and others* for obtaining ketones of complex esters, olefins, and cycloolefins, as well as the possibility of applying the indicated oxides in isomerization, oxidation, and other reactions.

The work was carried out on a standard automated flow-type precision apparatus. The oxides were deposited on asbestos, quartz, carbon, silica gel (KSM), and other supports. Below are data obtained under optimum conditions, characterizing the catalytic properties of some of the above-listed oxides in individual reactions mentioned.

Table 1

Yield of symmetrical ketones (in percent) as a function of the nature of the oxides and supports

Ketones	Pr_6O_{11} asbestos	Pr_6O_{11} quartz	Er_2O_3 asbestos	Er_2O_3 quartz	Nd_2O_3 asbestos	Nd_2O_3 quartz	La_2O_3 asbestos	La_2O_3 quartz
Acetone	63	–	64	67	62	63	50	–
Diethyl ketone	89	–	–	–	80	84	39	–
Dipropyl ketone	91	84	88	90	82	86	58	60
Dibutyl ketone	83	77	84	84	78	80	72	76

Ketones	Pr_6O_{11} asbestos	Pr_6O_{11} quartz	Er_2O_3 asbestos	Er_2O_3 quartz	Nd_2O_3 asbestos	Nd_2O_3 quartz	La_2O_3 asbestos	La_2O_3 quartz
Diisobutyl ketone	53	–	44	46	43	45	7	9

Preparation of ketones. Aliphatic symmetrical and unsymmetrical ketones, cyclopentanone, and fatty-aromatic ketones were synthesized on oxides of neodymium, erbium, praseodymium, and lanthanum deposited on asbestos, quartz, and silica gel. On the oxides of neodymium, erbium, and praseodymium deposited both on asbestos and on quartz, aliphatic ketones are obtained with practically equally high yields. In the homologous series of acids—from acetic through butyric inclusive—the yields of ketones (acetone and dipropyl ketone, respectively) on the indicated oxides increase (Table 1). In the case of acetone they amount to 67-65%, and in the case of dipropyl ketone they reach 90-85%. A further increase in the molecular weight of the acids leads to a gradual decrease in the yield of ketones.

The ketone yield falls especially sharply when acids of iso-structure are used. Thus, for dibutyl ketone on the oxides of neodymium, erbium, and praseodymium, the yield ranges from 78 to 85%; for diisobutyl ketone, 45-52%. These same ketones on lanthanum oxide are obtained in lower yields: from 50% for acetone to 76% for dibutyl ketone. However, with an increase in the molecular weight of the acids in this case, the yields of ketones increase. Diisobutyl ketone is obtained in very low yields (up to 10%).

Using as an example the preparation of dipropyl ketone on the oxides of neodymium, praseodymium, erbium, and lanthanum, the influence of supports was studied, and it was shown that the yields of ketones decrease in the series quartz > asbestos > silica gel (Table 2).

Table 2

Yield of dipropyl ketone (in percent) as a function of the nature of the oxides and supports

Supports	Pr_6O_{11}	Nd_2O_3	Er_2O_3	La_2O_3
Quartz	84	86	90	61

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* In this connection we assume that the composition of the catalysts—oxides of Nd, Er, and La under the conditions of our reactions—corresponds to the formulas Ln_2O_3. The composition of cerium catalysts is apparently intermediate between Ce_2O_3 and CeO_2, and that of praseodymium catalysts is Pr_6O_{11}.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Supports	Pr_6O_{11}	Nd_2O_3	Er_2O_3	La_2O_3
Asbestos	91	83	88	58
SiO_2 (KSK)	74	–	–	–
SiO_2 (KSM)	52	35	–	–

Table 3

Yield of unsymmetrical ketones (in percent) as a function of the nature of the oxides (support—asbestos)

Ketones	Nd_2O_3	Pr_6O_{11}	La_2O_3
Methylethyl ketone	35	30	–
Methylpropyl ketone	28	26	10
Propyldiphenyl ketone	82	82	35
n-Butylphenyl ketone	82	82	34
iso-Butylphenyl ketone	35	36	–

On the oxides of neodymium, praseodymium, and lanthanum, unsymmetrical aliphatic and alkylaromatic ketones were obtained (Table 3). Here the same regularity was observed as in the preparation of symmetrical ketones. Alkylaromatic ketones were obtained in higher yields than unsymmetrical aliphatic ketones. This can be explained in part by the fact that, along with unsymmetrical ketones, symmetrical ketones are also formed. In the case of alkylaromatic ketones, diphenyl ketone is not formed.

Fig. 1. Dependence of the yield of butyrates on the structure of the alcohols and the nature of the oxides:
I –Nd_2O_3/asb.; *II* –Pr_6O_{11}/SiO_2 (KSK); *III* –La_2O_3/asb.; *IV* –Ce_2O_3/asb.

Fig. 2. Dependence of the yield of complex esters on the structure of the acids and the nature of the oxides.
1 –HCOOH, 2 –CH_3COOH, 3 –C_2H_5COOH, 4 –C_3H_7COOH, 5 –*n*-C_4H_9COOH, 5′ –*iso*-C_4H_9COOH. *I, II, III, IV* –as in Fig. 1.

Neodymium oxide on asbestos was used for the preparation of cyclopentanone from adipic acid. Cyclopentanone was obtained in a yield of about 70%.

Preparation of complex esters. In the work, the dependence of the yield of complex esters on the structure of the alcohol and acid radicals, and on the nature of the oxides and supports, was investigated. In the esterification of butyric acid with methyl and ethyl alcohols and with alcohols of normal structure (from propyl through octyl inclusive) on the oxides of neodymium, praseodymium, lanthanum, and cerium, we established that with an increase in the molecular weight of the alcohols, the yields of esters for each oxide change little (Fig. 1).

At the same time, the following regularity is observed: esterification of butyric acid with alcohols having an odd number of carbon atoms leads to a higher yield of esters than esterification with alcohols having an even number of carbon atoms. This regularity is especially pronounced on neodymium and lanthanum oxides and is considerably weaker on cerium and praseodymium oxides.

In obtaining amyl butyrate it was found that the highest yields are obtained on neodymium and erbium oxides (72%); further, they decrease from praseodymium oxide to the oxides of lanthanum and cerium (54, 42, and 34%). In addition, oxides deposited on asbestos possess greater activity than those deposited on quartz (Table 4).

Table 4

Yield of amyl butyrate (in percent) as a function of the nature of the oxides and supports

Support	Oxides	Oxides	Oxides	Oxides	Oxides
Support	Nd_2O_3	Er_2O_3	Pr_6O_{11}	La_2O_3	Ce_2O_3
Asbestos	72	71	54	42	34
Quartz	49	51	48	26	–
Charcoal	74	76	–	–	–
SiO_2 (KSK)	–	–	58	–	–
SiO_2 (KSM)	–	–	39	–	–

The dependence of the yield of complex esters on the structure of the acids and on the nature of the oxides was also studied (Fig. 2). Amyl alcohol was subjected to esterification with acids from formic to valeric and isovaleric on neodymium, praseodymium, lanthanum, and cerium oxides deposited on asbestos. From this series of experiments it follows that neodymium oxide in this case as well is the most active catalyst. The yields of esters on neodymium oxide increase from amyl formate (58%) to amyl butyrate (70%), and then gradually decrease. The amyl ester of valeric acid is obtained in a yield of 64%. An especially sharp decrease in ester yield is observed when isovaleric acid is used–the ester yield is only 35%. On lanthanum and cerium oxides the ester yields are considerably lower. In the esterification of acids of normal structure they range from 47 to 33%. In the esterification of isovaleric acid the ester yield on lanthanum oxide is 28%, and on cerium oxide 24%.

Dehydration of cyclohexanol. In this series of work, the degree of dehydration of cyclohexanol over praseodymium oxide deposited on quartz was studied as a function of the reaction temperature. It turned out that this catalyst acts specifically. In its presence, only dehydration of cyclohexanol to cyclohexene occurs. Isomerization of cyclohexene to methylcyclopentene is not observed. The yield of cyclohexene at the optimum temperature of 475° is 53%.

In the presence of Pr_6O_{11} deposited on quartz, only dehydration of cyclohexanol occurs. Isomerization phenomena were not observed. However, the maximum yield of cyclohexene is considerably lower and reaches, even at the higher temperature of 475°, only 53%. The data obtained will be used to study the mechanism of the reactions we are carrying out.

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Note: Figure translations are in progress. See original paper for figures.