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A. A. Tolstopyatova and Academician A. A. Balandin

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Abstract

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On Regularities in the Catalytic Properties of the Rare Earths

In view of the fact that pure rare earths have recently become available, the question arises of investigating their catalytic properties. From a theoretical standpoint this question is of interest, in particular because the lanthanides constitute a large series consisting of 14 elements, differing in that the number of electrons in their $4f$-shell gradually increases. As is known, with change in atomic number the properties of rare-earth elements change according to two limiting types: continuously (monotonically) and periodically. Continuous change occurs under the influence of the increase in nuclear charge (ionic radius, their heat of hydration, etc.); periodic change occurs as a consequence of the special stability of configurations with 0, 7, and 14 f-electrons (anomalous valence, atomic radius of the metals, magnetic moment, color, etc.). From a practical standpoint the question is of interest because in the chemical industry the use of rare earths appears to be most economical precisely as catalysts.

For the prediction ([1]) of catalytic activity, an important property of solids is the energy of their bonds with reacting atoms of organic molecules. Therefore we undertook the systematic determination of bond energies by the kinetic method ([2]) for rare earths, in continuation of our studies on the dependence of the catalytic properties of elements on their position in Mendeleev's periodic system of the elements ([1,3–5]).

In the indicated direction, the following worked under our supervision: Yu Tsiyu'an' (La, Pr, Nd, Sm, Er), Pyn Bi-syan (Gd, Dy, Tu, Tb), L. S. Revenko (La, Pr, Sm, Ho, Er), K. A. Dulitskaya (Nd), and K. D. Tarlykova (Gd).

Experimental procedure and results obtained. The procedure used was that adopted in our laboratory for studying the kinetics of heterogeneous-catalytic reactions in a flow system ([3,6]). All catalysts were prepared by one and the same method, starting from commercial rare earths containing more than 99% oxide. The exceptions were Ho_2O_3 (98.2% purity) and Dy_2O_3 (97.7% purity), the impurities consisting mainly of other rare earths. The oxides were dissolved in chemically pure HNO_3, d 1.16—1.20 (20°), diluted with distilled water until a 30% solution of the nitrate salt was formed. The hydroxide was precipitated with 20% ammonia at 60°. The hydroxide, washed by decantation, was dried at 120°, then gradually heated to 550° in a stream of air over 10–12 hr, until nitrogen oxides and water vapor were completely removed. For work,

7-12 g of oxide were taken.

Over these catalysts the kinetics of dehydrogenation of various hydrocarbons, as well as the dehydrogenation and dehydration of alcohols, was studied. Detailed data will be presented in separate articles; some of them have been published ([6,7]). Below are given the results for the most systematically investigated cases—for the dehydrogenation of tetralin to naphthalene, and for the dehydrogenation and dehydration of isopropyl alcohol respectively to acetone and propylene. The kinetics of these reactions was studied under conditions ensuring the course of the reaction in the kinetic region.

with respect to zero order, in the temperature interval 350-450° for isopropyl alcohol and 480-525° for tetralin. The gaseous and liquid reaction products were analyzed by chromatographic and chemical methods. Side processes were insignificant. The experimental data obeyed the Arrhenius equation. The results obtained for all the rare earths we studied are given in Table 1. The activation energies

Table 1

Activation energies ϵ (kcal/mole) and bond energies Q (kcal/mole) for rare-earth catalysts

Atomic number of element	Catalyst	Tetralin, ϵ_1	iso-C_3H_7OH, ϵ_2	iso-C_3H_7OH, ϵ_3	Q_{HK}	Q_{CK}	Q_{OK}
57	La_2O_3	51.0	24.3	28.0	47.5	17.2	64.9
59	Pr_2O_3	51.6	15.2	27.4	52.9	11.4	72.0
60	Nd_2O_3	44.8	17.4	26.0	52.8	16.0	64.7
62	Sm_2O_3	42.9	20.6	26.0	51.3	18.8	60.6
64	Gd_2O_3	43.3	14.7	25.6	54.8	15.0	65.2
66	Dy_2O_3	42.0	17.3	28.8	55.7	15.0	60.1
67	Ho_2O_3	38.4	12.8	24.7	57.1	16.0	62.2
68	Er_2O_3	38.6	15.5	26.5	56.5	16.5	59.4
69	Tu_2O_3	38.8	18.3	27.0	54.9	18.0	57.4
70	Yb_2O_3	34.7	20.6	25.1	53.4	22.1	53.0

for the dehydrogenation of tetralin are denoted by ϵ_1, for the dehydrogenation of isopropyl alcohol by ϵ_2, and for the dehydration of isopropyl alcohol by ϵ_3. The bond energies of H, C, and O with catalyst K were calculated from formulas following from multiplet theory ([2]):

$$Q_{HK} = \frac{1}{3}(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + 62.0,$$

Fig. 2

Figure 1: Fig. 2

$$Q_{\mathrm{CK}} = \frac{1}{3}(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + 36.7,$$

$$Q_{\mathrm{OK}} = \frac{1}{3}(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + 48.8. \quad (1)$$

Fig. 1. Q_{HK}, Q_{OK} (in kcal) and μ (in Bohr magnetons) as functions of n

For the bond energies C–H, C–O, and C–C, data of V. N. Kondrat' ev ([8,9]) were taken: 98.1; 85.5 and 110.8 kcal, respectively.

Discussion of results. We find that for different rare-earth catalysts the bond energies of the reacting atoms Q_{HK}, Q_{CK}, and Q_{OK} differ markedly from one another.

It turns out that the bond energies Q_{HK}, Q_{CK}, and Q_{OK} belong to the number of periodic functions (see above). It is observed that Q changes in parallel with the effective magnetic moment μ. In the latter, as is known, the periodic properties of rare-earth elements are manifested especially clearly. For Q_{HK} this parallelism is seen from Fig. 1, on which the atomic numbers of the rare-earth elements are plotted along the abscissa, and along the ordinate–the values of Q_{HK} from

Table 1 and the values of μ from paper ([10]). For Q_{OK} an analogous, but less distinct, regularity is observed. Possibly the scatter of the points is due to the fact that, as previous investigations ([4]) with other oxides show, Q_{OK} always proves to be much more sensitive to various extraneous influences than Q_{HK} and Q_{CK}. Dy_2O_3 falls outside the regularity found, apparently owing to the presence of 1.3% impurities (see above). The bond energies Q_{CK} vary antibatically (Fig. 2).

Let us turn to the change in the activation energies ε. The activation energy of dehydrogenation of isopropyl alcohol, ε_2, varies periodically and antibatically to μ, similarly to Q_{CK} (Fig. 2). However, the change in the activation energy of tetralin dehydrogenation, ε_1, with change in atomic number n proceeds differently, approaching the continuous type and varying symbatically, for example, with the ionic radius r (see Fig. 3; values of r taken from ([10,11])). The activation energy of alcohol dehydration, ε_3, is the most constant; it gradually decreases (from 28.1 kcal for La_2O_3 to 25.1 kcal for Yb_2O_3; deviations for Dy_2O_3 and Tu_2O_3, see Table 1).

Fig. 2. Q_{CK} (in kcal), ε_2 (in kcal/mole), and μ (in Bohr magnetons) as functions of n

Fig. 3

Figure 2: Fig. 3

Fig. 4. ε_1 (in kcal/mol) as a function of a (in Å).

Figure 3: Fig. 4. ε_1 (in kcal/mol) as a function of a (in Å).

The regularities found show that the bond energies (which depend on the electronic structure) are more primary properties for catalysis than the activation energies. Indeed, all three quantities, Q_{HK}, Q_{CK}, and Q_{OK}, vary regularly and periodically and are clearly symbatic or antibatic to the same quantity μ, whereas ε_2 varies periodically and antibatically to μ, and ε_1 and ε_3 vary continuously with some deviations. If ε were the more primary property, it would be incomprehensible why, for example, in alcohol dehydrogenation ε_2 changes periodically with change in n, while in the analogous reaction of tetralin dehydrogenation ε_1 gradually decreases.

Fig. 3. ε_1 (in kcal/mole) and r (in Å) as functions of n

It is also of interest to approach the results obtained from the structural side. Most of the rare earths crystallize ([12]) in a complex cubic lattice D_{53}, the cell of which contains 16 molecules. The lattice parameter a (the edge of the elementary cube) is proportional to d, the smallest interatomic distance Me–Me. We find that an approxi-

a linear dependence was found between the activation energy of tetralin dehydrogenation (ε_1) on rare-earths of structure $D5_3$ and their lattice parameter a (see Fig. 4). Fig. 4 is analogous to Fig. 1 in (13), illustrating the linear dependence of the activation energy of dehydrogenation of isopropyl alcohol on Co, Ni, Cu, Pd, Ag, Pt on d. It should be noted that in Fig. 1 of paper (13) the interval of variation of d is larger (16%) than for the rare-earths in Fig. 4 (9%). Both cases are explained by the principle of conservation of the valence angle.

The regularities described in the present work are important not only for the chemistry of the rare-earth elements, since the catalytic properties of the latter have been little studied, but also for the theory of catalysis. First, for multiplet theory, because the existence of the above-mentioned regularities in Q confirms the correctness of its energy equations (cf. equations (1)) and of the principle of conservation of the valence angle based on this theory. Second, for the electronic theory of catalysis, from the standpoint of which the literature has considered the existing scattered experimental data on the connection between catalysis (in particular, the high-temperature mechanism of the o–n conversion of H_2, not to mention its low-temperature mechanism) and the magnetic properties of other, non-rare-earth elements (14-17).

Fig. 4. ε_1 (in kcal/mol) as a function of a (in Å)

The results obtained show that the electronic structure (in this case, of the inner f-shell) affects the outer valence electrons (in this case, the $5d$ and $6s^2$ electrons), altering the chemical property of the elements determined by the latter—the energy of their bond with the atoms of the reacting molecules. Thus, the change in electronic structure considered in the electronic theory affects catalysis by changing the energies of the bonds with the catalyst considered in multiplet theory.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Moscow State University
named after M. V. Lomonosov

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