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The Catalytic Properties of the Lanthanide Oxides and the Application of the Inclined W Theory

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Sinha [1–4] has recently been able to correlate the properties (P_i) of the lanthanides and actinides with their free ion orbital quantum number (L) applying the inclined W theory:

$$P_i = w_i L + k_i \qquad (i = 1\text{–}4) \qquad (1)$$

In most cases the properties considered are those of the free ions (*cf.* ionization potentials [2, 3]) or the aquo ions [1]. Some success of this theory in correlating the properties of the condensed phase (crystallographic parameters) [1, 4, 5] has also been demonstrated.

Systematic studies on the catalytic properties of the oxides of the lanthanide series are sparse, although several individual ones have been investigated in some details [6]. The present communication attempts to examine some of the available data of the catalytic properties of the M_2O_3 type lanthanide oxides in the light of the inclined W theory. The data on the dehydrogenation of cyclohexane [7, 8], tetralin(tetrahydronaphthalene) [7] and isopropanol [7], dehydration of isopropanol [7], and the bond energies of the interaction of hydrogen [7] with the catalyst surfaces have been analyzed.

Several authors [7–9] have already tried to correlate the catalytic properties of the lanthanide oxides with various central ion parameters like atomic numbers, ionic radii, magnetic moments *etc.* But no unique explanation of the activity is forthcoming. Hence it is of interest to examine whether the catalytic activities of the lanthanide oxides fit the inclined W systematics.

In Fig. 1 a two-way classification of the data on the dehydrogenation of tetralin has been attempted by plotting the activation energy of the process (i) against the atomic numbers (Z) of the lanthanides as in a classical plot and (ii) against the free ion total angular quantum number (L) as in the inclined W plot. Interestingly the activity *vs.* Z plot does not exhibit the so called tetrad effect. The inclined W parameters (w_i and k_i) together with the correlation coefficients (r) in per cent for this and other systems are tabulated below:

Tetralin Dehydrogenation

First tetrad (La–Nd)*: $w_1 = -0.6613$, $k_1 = 51.558$, r = 57%; Second tetrad (Pm–Gd): $w_2 = -0.0605$,

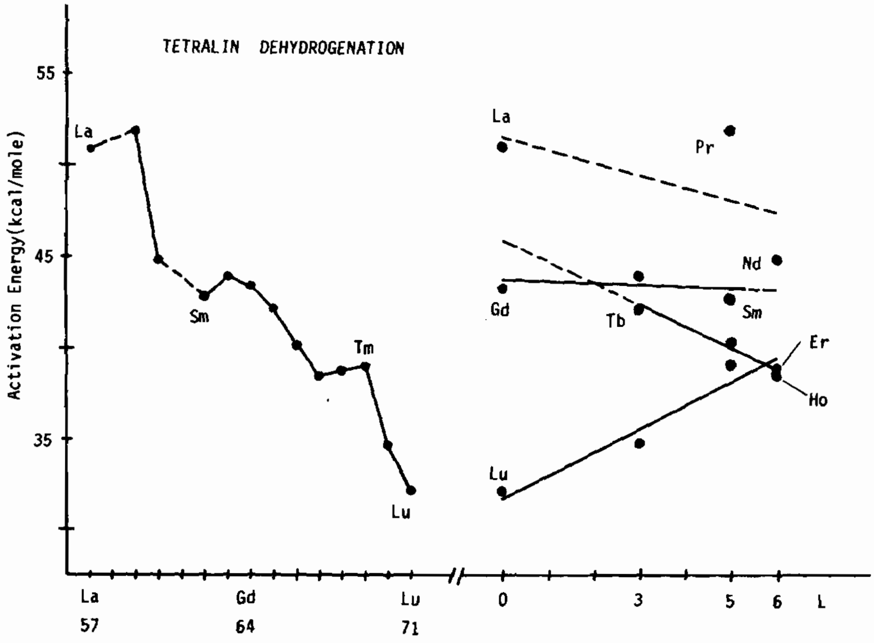

Fig. 1. A two-way representation of the activation energy (kcal/mol) of the dehydrogenation of tetralin (i) against the atomic numbers (Z), (ii) against the free ion orbital angular quantum numbers (L) of the lanthanides.

k_2 = 43.495, r = 34%; Third tetrad (Tb–Ho): w_3 = –1.1929, k_3 = 45.000, r = 99%; Forth tetrad (Er–Lu): w_4 = 1.2071, k_4 = 31.800, r = 97%.

Cyclohexane Dehydrogenation:

First tetrad (La–Nd): w_1 = 0.4371, k_1 = 34.330, r = 99%

Isopropanol Dehydrogenation:

First tetrad (La–Nd)*: w_1 = –1.3661, k_1 = 23.976, r = 93%; Second tetrad (Pm–Gd): w_2 = 0.9868, k_2 = 13.968, r = 84%; Third tetrad (Tb–Ho): w_3 = –0.7929, k_3 = 17.600, r = 99.9%; Forth tetrad (Er–Lu): w_4 = –1.1548, k_4 = 23.667, r = 96%

Isopropanol Dehydration:

First tetrad (La–Nd)*: w_1 = –0.2645, k_1 = 28.103, r = 83%; Second tetrad (Pm–Gd): w_2 = 0.0842, k_2 = 25.642, r = 92%; Third tetrad (Tb–Ho): w_3 = –0.4786, k_3 = 28.100, r = 72%

Oxide Catalyst–H Bond energy:

First tetrad (La–Nd)*: w_1 = 0.0914, k_1 = 47.547, r = 10%; Second tetrad (Pm–Gd): w_2 = –0.6474, k_2 = 55.330, r = 82%; Third tetrad (Tb–Ho): w_3 = –0.250, k_3 = 58.500, r = 95%; Forth tetrad (Er–Lu): w_4 = 0.7095, k_4 = 51.717, r = 97%.

It is quite remarkable that the catalytic properties fit reasonably well the inclined W scheme. The cerium point cannot be considered in this scheme because of its tetravalent state in the oxide (CeO_2) employed (Table I of Ref. 7). We also feel that the sample of Pr_2O_3 used may contain some amount of Pr^{4+} ion causing increased activity [7] and showing largest deviation within the first tetrad. Hence in this analysis the confidence level for the first tetrad is questionable.

It is normally believed that only a small fraction of the catalyst surface is responsible for the activity (active sites) and that these sites are dramatically different from the bulk. If this is universally true, one would not expect any correlation of the catalytic properties of the lanthanide oxides (M_2O_3) with the L–values of the unperturbed M^{3+} ions.

In the case of tetralin dehydrogenation the second tetrad shows considerable scatter (correlation coefficient, r = 34%). This may be due to the liberation of considerable amount of conjugation energy during the conversion of tetralin (tetrahydronaphthalene) to naphthalene and thereby partially reducing the surfaces of samarium and europium oxides. Some scatter for the second tetrad is also evident from the dehydrogenation of isopropanol (r = 84%).

Further complication in this region could be expected due to the presence of the polymorphic forms of M_2O_3 (B and C forms) having different crystal structures and metastability [10] at lower temperature range (600–800 °C). But in fact, the cell parameters (a(Å)) for the cubic M_2O_3 type (C-oxides) lanthanide oxides [11] exhibit extremely good inclined W systematization: Second tetrad (Pm–Gd): w_2 = 0.02416, k_2 = 10.8036, r = 97.5%, predicted a for Pm_2O_3 is 10.948 Å; Third tetrad (Gd–Ho): w_3 = –0.03268, k_3 = 10.8169, r = 98.9%; Forth tetrad (Er–Lu): w_4 = 0.02448, k_4 = 10.3788, r = 95.6%. A similar systematization of the two cell parameters a and c is also obtained for the hexagonal A-type La_2O_3, Pr_2O_3 and Nd_2O_3. For (La–Nd) tetrad, cell parameter (a): w_1 = –0.01758, k_1 = 3.9311, r = 99.4%; cell parameter (c): w_1 = –0.02355, k_1 = 6.1197, r = 99.9%; predicted value for A-type CeO_2 a = 3.88, c = 6.05 Å.

Thus, for the inclined W scheme to work, one must make certain that the reaction within a given tetrad (at least) proceed via the same type of mechanism. The dehydration process of alcohol probably does not proceed via one particular mechanism with all M_2O_3 type lanthanide oxides. An analysis of the activation energies of the desorption process of water (E_{dw}) from the catalyst surface (see also Fig. 9 of Ref. 7) indicates that the value of E_{dw} for Sm, Ho and Yb are rather low (~13 kcal/mol). Hence the process of desorption of this entity cannot be the rate determining step in the dehydration of alcohol. However, the value of 22.8 kcal/mol for E_{dw} of Dy_2O_3 compares favourably with the measured activation energy of the dehydration reaction. Hence it is more likely that the mechanism of dehydration reaction may differ from one oxide to another, thus offsetting the inclined W systematization.

Of the reported catalyst surface–X (where X = hydrogen, oxygen, carbon) bond energies, only the surface–H bond energy is reliable (this being the measured quantity). Other reported values [7] have been calculated by difference and throw considerable doubt as to their limits of error. Beside the obvious limitation in the first tetrad (as discussed previously), the third and the fourth tetrads show extremely good correlations. There is, however, considerable deviation within the second tetrad (r = 82%) and again this is probably due to easy reducibility of the catalyst surface in the case of Sm and Eu oxides.

The reasonably good correlation of the catalytic properties of the lanthanide oxides with L-systematization presented here, implies that at least in these systems the catalytic activity is mainly dependent on the free ion properties, rather than it being a collective property of the oxide as a whole.

We have now extended the inclined W systematization to cover the catalytic properties of the lanthanide oxides, bringing it to the attention of the workers in the catalytic field.

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*For these first tetrads the uncertainty is rather large as explained below.

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