

NOTES

Volcano Relationship for Catalytic Dehydrogenation of Cyclohexane on Oxides

It has been shown previously that volcano relationships are exhibited by the available data on the catalytic decomposition of N_2O (1); catalytic oxidation of toluene (2), benzene (3), ammonia (4), and carbon monoxide (5); catalytic decomposition of H_2O_2 (5) and catalytic isomerization of butene (5) on a series of oxide catalysts. The object of the present note is to explore whether the existing data on dehydrogenation of cyclohexane can lend to interpretation in terms of the volcano relationship.

The relative order of activity exhibited by various oxides towards the dehydrogenation of cyclohexane as reported by Richardson and Rossington (6) are presented in Table 1 together with $-\Delta H_e$ (magnitude of the M-O bond energy represented by

the equivalent standard heat of formation at 25°C, exothermic) values for the corresponding oxides (7). The activity order is arranged in the increasing order of the rate constants reported. Surface areas were taken into account in determining the rate constants. According to the interpretation of these authors, a correlation of catalyst activity with the 3d electron configuration of the metal ion is that low activity is associated with stable $3d^0$, $3d^5$, and $3d^{10}$ configurations while oxides with the $3d^1$, $3d^2$, and $3d^3$ configurations are progressively more active. This conclusion is drawn from the inspection of the variation of the catalytic activities of the oxides and their electronic configurations. Accordingly, it is observed that for transition metal oxides, Cr_2O_3 is of highest activity, V_2O_3 and Ti_2O_3

TABLE 1
Catalytic Activity of Oxides for Dehydrogenation of Cyclohexane (6)

Oxide	Activity order (in the order of increasing rate constants)	$-\Delta H_e$ (kcal)
MgO	1	71.9
Al_2O_3	2	66.5
CaO	3	75.9
ZnO	4	41.5
TiO_2	5	51.0
Fe_3O_4	6	33.3
MnO	7	46.0
Ti_2O_3	8	61.1
V_2O_3	9	48.3
Cr_2O_3	10	44.9

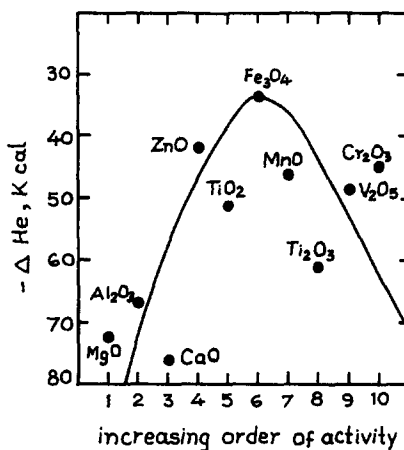


FIG. 1. A plot of the order of activity for the dehydrogenation of cyclohexane on the shown oxides against their $-\Delta H_e$ values; see Table 1.

are intermediates and TiO_2 , MnO , Fe_3O_4 , and ZnO are of lower activity.

An alternative interpretation in terms of volcano plot may be put forward, however. In Fig. 1 the order of activity has been plotted against $-\Delta H_e$ values of the corresponding oxides. A volcano relationship is clearly obeyed. On the ascending (i.e., left) arm of the volcano increasing order of the activity is associated with decreasing M-O bond energy (i.e., lower $-\Delta H_e$ values). On the descending (i.e., right) arm of the volcano, increasing order of activity with increasing $-\Delta H_e$ value is observed.

Although the detailed nature of this volcano plot is different from the Sabatier-Balandin view (8, 9) it is similar to the plot referred for catalytic decomposition of hydrogen peroxide (5). Therefore, the basic conceptual similarity for this plot is also obvious: activity increases with increasing bond energy on one arm of the

volcano, whereas the opposite is true for the other arm.

REFERENCES

1. Vijh, A. K., *J. Catal.* **31**, 51 (1973).
2. Vijh, A. K., *J. Chim. Phys.* **69**, 1695 (1972).
3. Vijh, A. K., *J. Chim. Phys.* **70**, 635 (1973).
4. Vijh, A. K., *J. Chim. Phys.* **70**, 1444 (1973).
5. Vijh, A., *J. Catal.* **33**, 385 (1974).
6. Richardson, P. C., and Rossington, D. R., *J. Catal.* **14**, 175 (1969).
7. Weast, R. C. (Ed.), "Handbook of Chemistry and Physics," 52nd ed., p. D-61. Chem. Rubber Co., Cleveland, 1971.
8. Sabatier, P., *Chem. Ber.* **44**, 2001 (1911).
9. Balandin, A. A., in "Advances in Catalysis" (D. D. Eley, W. G. Frankenburg, V. I. Komaresky, and P. B. Weisz, Eds.), Vol. 10, p. 120. Academic Press, New York, 1958; *Usp. Khim.* **33**, 549 (1964).

M. S. WAGH

*Laxminarayan Institute of Technology
Nagpur University
Nagpur 400 010, India*

Received November 6, 1975