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LETTER TO THE EDITORS

Volcano Relationships in Catalytic Reactions on Oxides

Vijh (*1*) has shown that in the case of several catalytic reactions on a series of oxides the plot of catalytic activity against metal–oxide bond energy yields a volcano-shaped curve very similar to that involved in the Sabatier-Balandin views on heterogeneous catalysis. His statements about the appropriate representation of the metal–oxide bond energy were later criticized by Criado (*2*).

In this Letter we should like to dispute other aspects of Vijh's work. We have two comments, both criticizing the forced search for analogies which lead to functions and conclusions with no clear physical meaning.

i. In our opinion the discussion of the isomerization of butene within the framework of this study is injustified. The oxygen–metal bond rupture or formation were assumed to be the rate determining step of the isomerization (*1*). This reaction has been thoroughly studied by a series of experimental methods and a detailed description of the mechanism was possible on several oxide catalysts (*3–7*). No mechanism, however, involves the rupture or forming of a metal–oxygen bond. It is not very reasonable, therefore, to correlate the metal–oxide bond energy with the catalytic activity. There may exist, of course, a correlation between these quantities since the metal–oxide bond energy may change in parallel with other physical properties influencing the activity. The electronegativity or the acid–base properties of the oxide surface can be mentioned as examples (*8*).

ii. Vijh remarks as a curiosity that the Sabatier-Balandin volcano-shaped curves represent the activity as a function of the bond energy, while in his discussions in some cases he had to exchange the abscissa and ordinate axes to obtain volcano-shaped curves.

We consider that when representing correlations between parameters and phenomena which are controlled by them the choice of the independent and dependent variable is not arbitrary. The independent variable (cause) should be the parameter, and the dependent variable (effect) should be the phenomenon. In this case the independent variable is evidently the metal–oxide bond energy and on this basis some of these functions are not volcano-shaped but double-valued ones [see Figs. 2, 3, 5, and 6 in Ref. (*1*)]. Double-valued functions are very rare in physics and chemistry, and it can be seen that their physical meaning is not clear in this case, either. Let us consider, for example, Fig. 6 in Ref. (*1*). We find there two different activities rendered to the same metal–oxide bond energy, viz, the pairs NiO–MnO and V_2O_5–CuO. This is in contradiction with the premise of the whole discussion, namely, the supposition that the metal–oxide bond energy controls the activity, clearly showing that other parameters are involved.

REFERENCES

1. Vijh, A., *J. Catal.* **33**, 385 (1974).
2. Criado, J. M., *J. Catal.* **37**, 563 (1975).
3. Shannon, I. R., Lake, I. J. S., and Kemball, C., *Trans. Faraday Soc.* **67**, 2760 (1971).

4. Kokes, R. J., and Dent, A. L., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 22, p. 1. Academic Press, New York, 1972.
5. Burwell, R. L., Haller, G. L., Taylor, K. C., and Read, J. F., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 20, p. 1. Academic Press, New York, 1969.
6. Hattori, H., Yoshii, N., and Tanabe, K., *Proc. Int. Congr. Catal., 5th, 1972*, p. 233 (1973).
7. Hightower, J. W., and Hall, W. K., *J. Phys. Chem.* **71**, 1014 (1967).
8. Tanaka, K., and Tamaru, K., *Bull. Chem. Soc. Japan* **37**, 1862 (1964).

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