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Effects

Certain named Effects are well entrenched in the vocabulary of catalysis (Table 1). Each describes a nominally simple variation in the microscopic composition or structure of a sample that can give rise to a variation in catalytic activity or selectivity. However, while it is commonplace to discuss the existence of Effects, operational definitions involve constraints that are difficult to attain (*1*). For example, in the investigation of support effects, varying the composition of the support while keeping the size and shape and location of the supported metal particles constant appears to be achievable (*2–4*) but only if considerable attention is paid to all the steps in the preparation procedure. Thus, as has been pointed out (*1, 5*), many claims for the identification of certain Effects are in fact rather poorly deconvoluted from other possible causes for the observed variations in activity or selectivity. Still, since Effects will continue to figure in our literature, it would seem useful to devise a definition which includes a way to assign them magnitudes and signs.

Mathematically, a particular Effect, E_i, could be defined appealingly in terms of how a change in just one independent variable, v_i, affects a postulated activity relation, $C(\vec{v})$, which depends functionally on the nature and extent of all the variables, $\vec{v}$, that describe the molecular and electronic structure of the sample. The activity function might be a measure of turnover rate, site concentration, activation energy, etc.—the choice need not be specified for the general discussion of this preliminary communication. To first order, the natural way to express the magnitude of this Effect is the partial derivative of C with respect to v_i:

$$E_i \equiv \frac{\partial C(\vec{v})}{\partial v_i} \tag{1}$$

$$\Delta C = \sum_i E_i \times \Delta v_i. \tag{2}$$

Thus, if E_i is large, a given variation in the associated variable, Δv_i, causes a large change in the activity of the sample. Of course the derivative in Eq. (1) and its higher order and mixed order counterparts can only be sampled at discrete points since, for example, there is no element that interpolates between Pt and Pd and no support that truly interpolates between SiO_2 and Al_2O_3.

There are two interesting consequences of applying this definition of an Effect to one particular functional form for C: the Balandin Volcano Curve (Fig. 1). First, it is possible to suggest that samples displaying the maximum activity should *not* be used to look for any first-order Effect whose associated variable influences C as does the one shown in the figure. The reason is simple; at the maximum, such an Effect would have zero magnitude according to the proposed definition. Indeed, although most measured volcano curves have cusp-like maxima, the slopes of the curves are comparatively smaller near the top than along the steep sides. Thus the latter comprise regions where one would expect the Effect to be larger in magnitude even though these regions contain samples displaying lower activity. This reasoning is embodied in a piece of catalysis lore which suggests that Effects are best proved using poorer catalysts instead of better ones.

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TABLE 1

Examples of Some Named Effects and Early References to Them

Effect	Reference
Steric	Langmuir, 1916[a]
Geometric	Burk, 1926[b]
	Zelinsky and Balandin, 1927[c]
Ensemble	Kobozev, 1940[d]
Electronic	Roginskii and Schulz, 1928[e]
	Rideal and Wansbrough-Jones, 1929[f]
Support	Schwab, 1959[g]
Particle size	van Hardeveld and Montfoort, 1966[h]
	Poltorak and Boronin, 1966[i]
Ligand	Sachtler and van Santen[j]

[a] Langmuir, I., *J. Amer. Chem. Soc.* **38,** 2221 (1916).

[b] Burk, R. E., *J. Phys. Chem.* **30,** 1134 (1926).

[c] Zelinsky, N. D., and Balandin, A. A., *Z. Phys. Chem.* **126,** 267 (1927).

[d] Kobozev, N. I., *Acta Physicochim. USSR* **13,** 469 (1940).

[e] Roginsky, S., and Schulz, E., *Z. Phys. Chem.* **A138,** 21 (1928).

[f] Rideal, E. K., and Wansbrough-Jones, O. H., *Proc. R. Soc. London* **A123,** 202 (1929).

[g] Schwab, G. M., Block, J., and Schultze, D., *Angew. Chem.* **71,** 101 (1959).

[h] van Hardeveld, R., and Montfoort, V., *Surf. Sci.* **4,** 396 (1966).

[i] Poltorak, O. M., and Boronin, V. S., *Russ. J. Phys. Chem.* **40,** 436 (1966).

[j] Sachtler, W. M. H., and van Santen, R. A., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 26, p. 69. Academic Press, New York, 1977.

A second consequence of the proposed definition concerns Ligand Effects. It follows from the change in sign of E_i when v_i traverses $v_{\max}$ and from the observation that, at least for metallic samples, there is a general trend in the way that the positions of points on volcano curves track with the atomic numbers of the metals. Present day electronic theories, admittedly simplistic, about the effects of supports, promoters, or poisons suggest that they can act by withdrawing or donating electrons to and from the valence orbitals of catalysts, thereby altering the activity of a particle of an element toward that of its left or right neighbor in the periodic chart. Such transmutation arguments have been awkward to defend, particularly in view of the apparent difficulty in manifesting strong Ligand or Electronic Effects in catalysis by metallic alloys where some sort of bonding between metal and ligands is guaranteed (*6, 7*). The point here is that a good test of such chemical theories would be to attempt to generate the Support Effect or Promoter Effect in two samples, the first containing a metal chosen from those lying on the left side of the volcano and the second containing a metal from the right side. If the Effect is present and is adequately explained on the basis of shifts in electron populations then the same change, Δv_i, which increases the activity of the first sample should decrease the activity of the other. Of course, by the prescription developed above, both metals should be chosen from the steepest respective regions in order to manifest the Effect most clearly.

Unfortunately, available data stop short of providing this test. Of the reactions studied completely enough to afford volcano curves (e.g., ethylene hydrogenation (*8, 9*), ammonia synthesis (*10*), methanation (*11*), formic acid decomposition (*12–14*), hydrodesulfurization (*15*), toluene oxidation (*16*), etc.), ethylene hydrogenation, being nearly structure-insensitive (*1*), ought to permit a reasonably clear examination of Ligand Effects. Indeed, there is qualitative evidence that low surface concentrations of sulfur

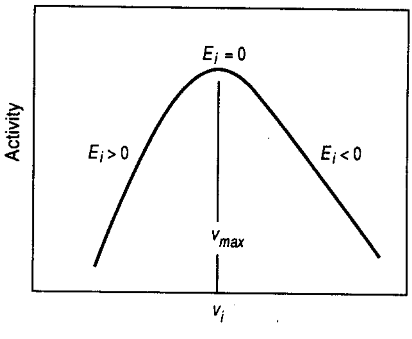

FIG. 1. A prototypic volcano curve.

(*17*) or oxygen (*18*) and the environment within the pores of acidic zeolites enhance the activity of platinum, purportedly by withdrawing electron density from the metal and thus modifying its behavior toward that of metals with a higher percentage *d* character in the valence levels (*19, 20*). Moreover, inferences from selectivity measurements suggest that adsorption of ammonia decreases the activity of platinum and palladium for olefin hydrogenation (*21*). However, each of these tests pertains to elements from just one side of the volcano curve in Fig. 1. The analogous tests with sulfur, oxygen, ammonia, or supports have not been done for elements like W or Ta, although the activities of the carbides of those metals for ethylene hydrogenation are higher than those of the metals alone (*22, 23*), which is in the indicated direction if the valence electrons of the carbon are donated to the metal according to the Zintl concept (*24*) as suggested by Levy and Boudart (*25*).

It appears to be a pattern in the literature that available data describing the influences of promoters or poisons or supports permit direct estimation of Effects for only one side of the associated volcano curve. Perhaps this stems from an appropriate wariness—there is reason to extrapolate catalytic reactions cautiously since observed rates represent only an average over the distribution of the rates of the parallel network of reaction sequences associated with the distribution of active sites that are produced by the reaction conditions and each sequence might be affected differently by the imposed variation in the sample. Certainly complications from side reactions would arise in applying the ideas developed here to the influence of surface structure on hydrogenolysis reactions or the influence of surface composition on selective oxidation reactions. Nonetheless, this use of the proposed definition is offered as a necessary but not sufficient condition for establishing the existence of electronic or ligand effects, at least for less complicated reactions.

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REFERENCES

1. Boudart, M., and Djéga-Mariadassou, "Kinetics of Heterogeneous Catalytic Reactions." Princeton Univ. Press, Princeton, 1984.
2. Foger, K., and Anderson, J. R., *J. Catal.* **54,** 318 (1978).
3. Gallezot, P., *Catal. Rev. Sci. Eng.* **20,** 121 (1979).
4. Tzou, M. S., Teo, B. K., and Sachtler, W. M. H., *J. Catal.* **113,** 220 (1988).
5. Ponec, V., *in* "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.), p. 63. Elsevier, Amsterdam, 1982.
6. Sachtler, W. M. H., and van der Plank, P., *Surf. Sci.* **28,** 62 (1969).
7. Ponec, V., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 32, p. 149. Academic Press, New York, 1983.
8. Schuit, G. C. A., and van Reijen, L. L., *in* "Advances in Catalysis" (D. D. Eley, W. G. Frankenberg, and V. I. Komarewsky, Eds.), Vol. 10, p. 242. Academic Press, New York, 1958.
9. Beeck, O., *Discuss. Faraday Soc.* **8,** 118 (1950).
10. Bond, G. C., "Heterogeneous Catalysis." Clarendon Press, Oxford, 1974.
11. Vannice, M. A., *J. Catal.* **37,** 449 (1975).
12. Fahrenfort, J., van Reijen, L. L., and Sachtler, W. M. H., *in* "The Mechanism of Heterogeneous Catalysis" (J. H. de Boer, Ed.), p. 23. Elsevier, Amsterdam, 1960.
13. Mars, P., Scholten, J. J. F., and Zweitering, P., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 14, p. 35. Academic Press, New York, 1963.
14. Trillo, J. M., Munuera, G., and Criado, J. M., *Catal. Rev. Sci. Eng.* **7,** 51 (1972).
15. Chianelli, R. R., and Pecoraro, T. A., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 1426. Elsevier, Amsterdam, 1981.
16. Vijh, A. K., *J. Chim. Phys.* **69,** 1695 (1972).
17. Barbouth, N., and Salame, M., *J. Catal.* **104,** 240 (1987).
18. Amariglio, A., and Amariglio, H., *J. Catal.* **78,** 44 (1982).
19. Figueras, F., Mencier, B., de Mourgues, L., Naccache, C., and Trambouze, Y., *J. Catal.* **19,** 315 (1970).
20. Dalla Betta, R. A., and Boudart, M., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1329, North Holland, Amsterdam, 1972.

21. Barbier, J., *in* "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.), Vol. p. 293. Elsevier, Amsterdam, 1982.
22. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59,** 472 (1979).
23. Kojima, I., Miyazaki, E., Inoue, Y., and Ysaumori, I., *J. Catal.* **73,** 128 (1982).
24. Hoffmann, R., "Solids and Surfaces." VCH Publishers, New York, 1988.
25. Levy, R. B., and Boudart, M., *Science* **181,** 547 (1973).

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