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Adjacency of Molybdenum Redox Sites and the Oxidation of Butene

There is long-standing evidence from the unique catalytic behaviors of certain metal oxides and their crystalline surfaces that partial oxygenation of organic molecules requires complex surface moieties in order to achieve the necessary geometry and ease of reducibility (*1*). Observations of singular specificities of oxidation reactions with respect to composition, crystalline face, or bulk crystallographic properties have engendered the idea that partial oxidation reactions are structure sensitive (*2–9*).

There is also growing evidence that a site containing only one metal cation (and its oxide ligands) is sufficient to activate the C–H bonds that break during oxidative dehydrogenation and that are involved in the kinetically significant steps of other oxidations of organic molecules. Examples can be found in the oxidative dehydrogenations of alkanes, (*10*), alkenes (*10–12*), and methanol (*13–16*). In these cases it has been demonstrated that the turnover frequency per surface metal ion varies weakly with the superficial concentration (*12–14*) or adjacency of the redox sites ((*16*); however, see (*17, 18*) for a contrary view). These reactions might be termed structure insensitive in order to emphasize their weak dependence on composition and geometry beyond the first coordination sphere of the redox site.

Evidently, there is need to combine information from experiments that probe different scales of structure. The approach we have adopted here descends from the operational method of ascertaining structure sensitivity as it was originally defined in the study of catalysis by metals: a reaction can be inferred to be structure insensitive if its turnover frequency remains constant when measured across a set of catalysts in which the size of the metal crystallites, d, varies over a range (typically $1 \text{ nm} < d < 10 \text{ nm}$) that produces significant changes in the set of coordination sites available at the surface (*19*). An earlier attempt to apply this approach to an oxidation reaction (oxidative dehydrogenation of butene on iron oxide (*20*)) clearly showed a particle size effect on the selectivity of the overall conversion, but could not establish the origin of the effect or the structure sensitivity of the oxidative dehydrogenation alone, because of difficulties in synthesizing and characterizing catalyst particles smaller than about 10 nm.

We have attempted to determine the structure sensitivity of C–H activation and oxygen insertion during the oxidation of 1-butene by measuring how the rates of the reactions depend on variations in the sizes of *very* small ensembles of redox centers in a catalyst. We have employed polyoxometalate cluster compounds (*21–28*) in which 3 or 12 of the tungsten ions initially present in a Keggin framework were replaced with molybdenum ions. As in our previous work with methanol oxidation (*16*), the catalyst derived from the parent Keggin anion, $[PW_{12}O_{40}]^{3-}$, was only slightly active for oxidation reactions, making it possible to attribute the activity for the oxidation reactions catalyzed by the substituted samples to the Mo ions and their oxygen ligands.

The heteropolyacids, $H_3PW_{12}O_{40}$, $H_3PMo_3W_9O_{40}$, and $H_3PMo_{12}O_{40}$, were prepared according to literature recipes (*29, 30*). Aqueous solutions of the sodium salts, prepared by elution of the acids through an Amberlite ion-exchange column, were adjusted to pH 2 with nitric acid and then used to load 15 wt% of the anions onto HS-5 Cabosil (230 m^2/g) by incipient wetness im-

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pregnation (0.7 cm^3 of solution per g of support). Portions of the catalyst dried overnight at 393 K were pressed into wafers at 10,000 psig (55 MPa) and then crushed and sieved to form 0.25–0.59 mm particles. Redried samples (0.5 g) were loaded into a Pyrex flow reactor described previously (*16*) and heated to 623 K for 1 h in a 100 cm^3/min stream of 25% dioxygen (Airco, 99.6%) and helium (Airco, 99.995%). The standard reactant stream consisted of 2% 1-butene (Matheson, C.P.) and 25% dioxygen diluted with helium flowing at 2.50 cm^3/s (STP). Products were analyzed by gas chromatography with either a Porapak QS column (dioxygen, methane, carbon dioxide, water, formaldehyde, acetaldehyde, butene, furan, acetic acid, tetrahydrofuran, and maleic anhydride) or a picric acid/Carbopack C column (acetaldehyde, 1-butene, *cis*-2-butene, *trans*-2-butene, butadiene). Unfortunately, limitations on equipment prevented us from analyzing for carbon monoxide which we estimate contributed 10–15% of the carbon balance.

The rate and selectivity patterns of 1-butene conversion became steady after about 200 min of operation following an initial drop in the overall rate to about half its original value most likely due to coking of the catalysts. We did not check spectroscopically for the persistence of the Keggin structures in the catalyst samples but we were careful not to expose the samples to temperatures higher than 623 K, which appears to be safely below the decomposition temperature of the clusters, even under reaction conditions (*16, 21, 22, 28, 31–36*). We have shown previously (*16, 36*) that the available rates of mass and heat transfer do not disguise the kinetics of comparably fast and comparably exothermic reactions (oxidative dehydrogenation and etherification of methanol) catalyzed by silica-supported heteropolyanions in this reactor. Conversion under the standard conditions over a blank of 0.5 g of the Cabosil support was slight (≲1%) consisting mainly of CO_2 (and presumably CO) plus small quantities of *cis*- and *trans*-2-butene and butadiene.

At a loading of polyoxometalate of 15 wt%, the anions form agglomerates small enough that nearly all of the clusters remain exposed (*34, 36–38*). Therefore it is convenient to express the rates of the reactions catalyzed by the cluster-based samples as turnover frequencies normalized by the amount of each cluster present in the reactor (Fig. 1). Conversion over PW_{12}, the sample derived from the parent tungsten cluster, was significant (8%) but consisted almost exclusively (≳95%) of the isomers of 2-butene. This catalyst also produced small quantities of CO_2 and butadiene in amounts comparable to those yielded by the silica support. PMo_3 and PMo_{12}, the samples derived from $Na_3PMo_3W_9O_{40}$ and $Na_3PMo_{12}O_{40}$, produced 2-butene, carbon oxides, and butadiene with the inlet flow rate adjusted to achieve 7% conversion of the 1-butene. PMo_{12} also catalyzed the production of oxygenates (acetaldehyde, furan, formaldehyde, and a minor amount of tetrahydrofuran; see Fig. 1). Table 1

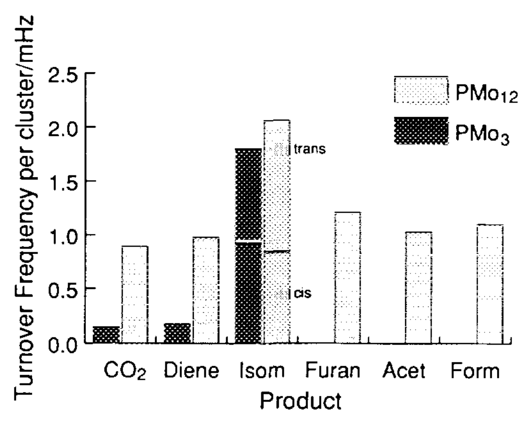

FIG. 1. Comparison of reaction rates during the conversion of 1-butene over supported Keggin ions; conditions: 623 K, 2% butene, 25% O_2, balance He, 7% conversion of 1-butene. Product abbreviations: 2-butenes (Isom), butadiene (Diene), acetaldehyde (Acet), formaldehyde (Form). The bar representing the rate of isomerization is divided to further display the turnover frequency for producing the *trans*- (top portion) and *cis*-isomers (bottom portion).

TABLE 1

Turnover Frequencies per Molybdenum for Reactions of 1-Butene[a]

Sample	Symbol	N/Mo/mHz	
		Butadiene	CO_2
$Na_3PMo_3W_9O_{40}/SiO_2$	PMo_3	0.060	0.04
$Na_3PMo_{12}O_{40}/SiO_2$	PMo_{12}	0.081	0.074
MoO_3[b]	—	0.043	0.078
MoO_3 (100) and (010)[c]	—	0.023	≈0.01

[a] Measured at 623 K, 2% butene, 25% O_2, 7% conversion of butene.

[b] Extrapolated to 623 K, from the data obtained by Gill and Ozkan (*43*). Activation energies for conversion to butadiene (100 kJ/mol and for CO_2 (90 kJ/mol) were calculated from their results.

[c] Extrapolated to 623 K from the data obtained by Tatibouët *et al.* (*9*). The rate of production of butadiene is attributed to the (100) face and that for CO_2 to the (010) face.

presents the rates of the oxidation reactions normalized by the amounts of molybdenum in the catalysts. Maleic anhydride was not produced under these relatively mild conditions, again, chosen to guard against decomposition of the clusters.

The selectivity of the cluster catalysts towards isomerization of 1-butene is consistent with their known activity as Brønsted acid catalysts (*21, 37, 39–42*), protons being introduced either during preparation or evolving from the water that is produced during reaction (*41*). The roughly comparable rates of isomerization catalyzed by all three clusters agrees with an electrostatic model for the acid strengths of Keggin ions that we have proposed elsewhere (*16*). The value we measure for the isomerization rate catalyzed by PMo_{12} compares well with that reported previously by Ai (*31*) when we extrapolate our results to the conditions he employed using first order kinetics and an apparent activation energy of 100 kJ/mol.

From the comparison of the turnover frequencies per Mo cation shown in Table 1, it appears that the production of butadiene from 1-butene scales roughly with the number of molybdenum ions in the cluster from which the catalysts were prepared. Comparable rates per surface molybdenum can be calculated from the work reported by Gill and Ozkan (*43*) and by Taitbouët *et al.* (*9*) who used bulk MoO_3. The total oxidation of 1-butene roughly parallels the rate for oxidative dehydrogenation, a correlation that can be found in other studies of supported and unsupported molybdenum oxide (*11, 43, 44*). However, closer comparison among these reaction rates requires a more detailed examination of the overall reaction network since the intermediate that leads to butadiene most likely also participates in the oxygenation reactions discussed next.

Figure 1 shows that the two Mo-cluster catalysts behave quite differently from each other in the partial oxygenation reactions. PMo_{12} catalyzes a suite of partial oxygenation reactions, the turnover rates of which are comparable to those measured for the oxygenation of butene over catalysts resembling those used commercially (*45*). On the contrary, PMo_3 produces no partially oxygenated products. At first glance it would appear, therefore, that the oxygenation reactions require a catalyst containing larger ensembles of Mo than are available in PMo_3. However, this appealingly simple hypothesis does not take into account the alkali metal ions which we employed to confer thermal stability on the Keggin ions and which are known to act as inhibitors of oxygenation reactions at the concentration levels present in our samples (*26, 31, 35, 41*). Thus we cannot easily deconvolute the effect of ensemble size and from that of the Na : Mo ratio (1 : 1 in PMo_3, 1 : 4 in PMo_{12}) on the turnover frequency of the oxygenation reaction.

To summarize, in the case of oxidative dehydrogenation, and perhaps combustion, we found that the rate of reaction per Mo ion remained approximately constant across a fourfold increase in the local concentration of Mo ions. The turnover frequency we obtained compared well with those measured by others for catalysts comprised of bulk MoO_3. Because of the possibility that the sodium ions may have been more effective in poisoning PMo_3 than PMo_{12}, we are content to summarize the oxygenation results with the prudent statement that the sodium salt of a Keggin ion containing three molybdenum ions does not evolve under these reactions conditions into surface sites capable of catalyzing oxygen insertion; the sodium salt of the permolybdenum Keggin ion does.

These results suggest a cautious use of the term "structure sensitivity" when there is the need to distinguish among sensitivities to (a) the effects of the geometry of the first coordination sphere, (b) the effects of next nearest neighbors, and (c) longer range order that appears as crystallographic anisotropy.

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REFERENCES

1. Kung, H. H., "Transition Metal Oxides: Surface Chemistry and Catalysis," p. 169. Elsevier, Amsterdam, 1989.
2. Volta, J. C., Desquesnes, W., Moraweck, B., and Tatibouët, J. M., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 1398. Elsevier, Amsterdam, 1981.
3. Volta, J. C., Forissier, M., Theobald, F., and Pham, T. P., *Faraday Discuss.* **72,** 225 (1982).
4. Volta, J. C., Tatibouët, J. M., Pitchitkul, Ch., and Germain, J. E., *in* Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 451. Dechema, Berlin, 1984.
5. Volta, J. C., and Portefaix, J. L., *Appl. Catal.* **18,** 1 (1985).
6. Tatibouët, J. M., and Germain, J. E., *J. Catal.* **72,** 375 (1981).
7. Tatibouët, J. M., Germain, J. E., and Volta, J. C., *J. Catal.* **82,** 240 (1983).
8. Tatibouët, J. M., and Germain, J. E., *C.R. Acad. Sci. Paris* **296,** 613 (1983).
9. Tatibouët, J. M., Phichitkul, Ch., and Germain, J. E., *J. Catal.* **99,** 231 (1986).
10. Michalakos, P. M., Kung, M. C., Jahan, I., and Kung, H. H., *J. Catal.*, **140,** 226 (1993).
11. McCormick, R. L., and Schrader, G. L., *J. Catal.* **113,** 529 (1988).
12. Brückman, K., Haber, J., and Wiltowski, T., *J. Catal.* **106,** 188 (1987).
13. Machiels, C. J., and Sleight, A. W., *in* "Proceedings of the 4th International Conference on the Chemistry and Uses of Molybdenum," (H. F. Barry and P. C. H. Mitchell, Eds.), p. 411. Climax Molybdenum Company, Ann Arbor, 1982.
14. Kim, D. S., Tatibouët, J. M., and Wachs, I. E., *J. Catal.* **136,** 209 (1992).
15. Deo, G., and Wachs, I. E., *J. Catal.* **129,** 307 (1991).
16. Sorensen, C. M., and Weber, R. S., *J. Catal.*, in press.
17. Louis, C., Tatibouët, J. M., and Che, M., *J. Catal.* **109,** 354 (1988).
18. Niwa, M., Yamada, H., and Murakami, Y., *J. Catal.* **134,** 331 (1992).
19. Boudart, M., and Djéga-Mariadassou, G., "Kinetics of Heterogeneous Catalytic Reactions." Princeton Univ. Press, Princeton, NJ, 1984.
20. Kung, H. H., and Kung, M. C., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 33, p. 159. Academic Press, New York, 1985.
21. Misono, M., *Catal. Rev. Sci.-Eng.* **29,** 269 (1987).
22. Bolmer, M., Ph.D. dissertation, University of Delaware, 1981.
23. Brückman, K., Haber, J., Lalik, E., and Serwicka, E. M., *Catal. Lett.* **1,** 35 (1988).
24. Serwicka, E. M., Black, J. B., and Goodenough, J. B., *J. Catal.* **106,** 23 (1987).
25. El Ali, B., Brégeault, J. M., Mercier, J., Martin, J., Martin, C., and Convert, O., *J. Chem. Soc. Chem. Commun.*, 825 (1989).
26. Brückman, K., Tatibouët, J. M., Che, M., Serwicka, E., and Haber, J., *J. Catal.*, in press.
27. Pope, M. T., "Heteropoly and Isopoly Oxometalates." Springer, Berlin, 1983.
28. Rocchiccioli-Deltcheff, C., Amirouche, M., and Fournier, M., *J. Catal.* **138,** 445 (1992).
29. North, E. O., Haney, W., and Bailar, J. C., "Inorganic Synthesis," p. 129. McGraw–Hill, New York, 1939.
30. Massart, R., Contant, R., Fruchart, J. M., Ciabrini, J. P., and Fournier, M., *Inorg. Chem.* **16,** 2916 (1977).
31. Ai, M., *J. Catal.* **71,** 88 (1981).
32. Bartoli, M. J., Monceaux, L., Bordes, E., Hecquet, G., and Courtine, P., *in* "New Developments in Selective Oxidation by Heterogeneous Catalysis" (P. Ruiz and B. Delmon, Eds.), p. 81. Elsevier, New York, 1992.
33. Centi, G., Lopez Nieto, J., Iapalucci, C., Brück-

man, K., and Serwicka, E. M., *Appl. Catal.* **46,** 197 (1989).
34. Kasztelan, S., Payen, E., and Moffat, J. B., *J. Catal.* **125,** 45 (1990).
35. Black, J. B., Clayden, N. J., Gai, P. L., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106,** 1 (1987).
36. Sorensen, C. M., Ph.D. dissertation, University of Delaware, 1985.
37. Izumi, Y., Hasebe, R., and Urabe, K., *J. Catal.* **84,** 402 (1983).
38. Mizuno, N., Watanabe, T., Mori, H., and Misono, M., *J. Catal.*, in press.
39. Hayashi, H., and Moffat, J. B., *J. Catal.* **77,** 473 (1982).
40. Hayashi, H., and Moffat, J. B., *J. Catal.* **81,** 61 (1983).
41. Saito, Y., Cook, P. N., Niyama, H., and Echigoya, E., *J. Catal.* **95,** 49 (1985).
42. Viswanathan, B., Omana, M. J., and Varadarjan, T. K., *Catal. Lett.* **3,** 217 (1989).
43. Gill, R. C., and Ozkan, U. S., *J. Catal.* **122,** 452 (1990).
44. Filipek, E., Brzybowska, B., Serwicka, E., Barbaux, Y., Bonnelle, J. P., and Grimblot, J., *in* "New Developments in Selective Oxidation" (G. Centi and G. Trifiró, Eds.), p. 767. Elsevier, Amsterdam, 1990.
45. Misono, M., Miyamoto, K., Tsuji, K., Goto, T., Mizuno, N., and Okuhara, T., *in* "New Developments in Selective Oxidation" (G. Centi, F. Trifiró, Eds.), p. 605. Elsevier, Amsterdam, 1990.

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