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On Subdivision of the Classification of Demanding Reactions

Two main problems with supported metal catalysts have been the object of numerous investigations, namely the influence of metal crystallite size and of the support on the specific catalytic activity. Significant progress in understanding these problems has come in recent years from recognition of the importance of considering specific catalytic activity and of determining metal surface area by techniques such as hydrogen chemisorption. The need for thinking in these terms can be considered to have been crystallized by Boudart with his classification of reactions as either facile or demanding (*1*). The classification essentially divides all reactions into two categories: (a) "structure insensitive" reactions which as originally defined (*1*) include reactions for which the specific catalytic activity of the catalyst is independent of its mode of preparation and (b) "structure sensitive" reactions for which conversely the specific activity of the catalyst depends significantly on its mode of preparation. The latter category includes all reactions which are not "structure insensitive" and as such would appear to admit to subclassification. Boudart (*2*) has recently discussed several special cases, and Oliver, Wells and Grant (*3*) suggest an extension of the demanding reaction definition to cover parallel reactions. Recent work in our laboratory on ammonia oxidation indicates the need for explicit subdivision of the demanding category, and we suggest that the understanding of supported metal catalysts will be further advanced as a result. Below we outline the proposed subdivision and detail our reasoning.

The specific catalytic activity for certain reactions such as neopentane hydrogenolysis (*4*), deuterium exchange of benzene (*5*) and of cyclopentanes (*6*) is highly dependent on the metal crystallite size and on the catalyst pretreatment. These reactions appear to require special sites, e.g., B_5 sites, triplet sites or multiplet sites, composed of more than two surface atoms. Changes in specific catalytic activity are due to changes in the number of such special sites with crystallite size or pretreatment, and such reactions can be used to probe the surface structure of a catalyst and provide fundamental information on the nature of these catalytic sites. We propose that such structure sensitivity be called *primary structure sensitivity.*

In other reactions involving supported platinum and hydrocarbons and those involving supported platinum and oxygen classification is complicated. The literature suggests that those involving oxygen are not facile reactions and therefore must be structure sensitive. Boudart *et al.* (*1*) observed in cyclopropane hydrogenation that addition of a small amount of oxygen to a platinum catalyst in a hydrogen environment at 0°C resulted in about a twofold decrease in specific activity for a large crystallite catalyst and almost a 100-fold decrease in specific activity for a catalyst containing very small crystallites. Resultant specific catalytic activity increased by a factor of about 50 as crystallite size increased indicating apparent structure sensitivity for a reaction which is *insensitive to structure* under normal conditions. Mitrofanova, Boronin and Poltorak (*7*) observed for cyclohexane dehydrogenation, normally a structure insensitive reaction (*8*, *9*) that "oxygen alters the catalytic properties of platinized silica gels in different ways depending on the degree of dispersion" and that "in order to compare the specific activities of platinized silica gels associated *solely with differences in the degree of dispersion of platinum particles,* it is necessary to employ catalysts with a "clean" (i.e., degassed and regenerated in a vacuum at a high temperature) platinum surface." Dorling, Eastlake and Moss (*10*) observed apparent crystallite size effects in ethylene hydrogenation associated with the methods used to vary the metal crystallite size and with a self-poisoning of the small platinum areas. Schlatter and Boudart (*11*) described another type of poisoning. Others (*1, 12–14*) have observed self-poisoning in hydrocarbon reactions over platinum. Joyner, Lang and Somorjai (*15*) observed that self-poisoning carbon formation on platinum single crystals does not adversely affect activity on certain crystallite planes, but on others it does, indicating structure sensitivity in the poisoning which could result in a crystallite size dependent self-poisoning. Mitrofanova, Boronin and Poltorak (*7*) observed a crystallite size dependent self-poisoning in cyclohexane dehydrogenation causing an apparent dependence of specific activity on crystallite size. Oxidation reactions over platinum also show marked crystallite size effects (*16*). This effect may be due more to a crystallite size dependent self-poisoning than to primary structure sensitivity of the reaction. We propose that such structure sensitivity be referred to as *secondary structure sensitivity.*

A third type of structure sensitivity may also exist, that associated with the number of metal atoms in very small crystallites. Wilson and Hall (*17*) observed that the stoichiometry of oxygen chemisorption on platinum crystallites changes as the crystallites become very small indicating a possible size effect although Freel (*18*) suggested that this may be more due to surface structure equilibration than to crystallite size. Molecular orbital calculations predict that as metal atom clusters become very small their metal and electronic properties, and bonding interactions with chemisorbed species change solely due to the decreasing number of atoms present (*19, 20*). Very small clusters of metal atoms should exhibit properties more similar to semi-conductors than to metals. This suggests that catalytic activity in certain reactions should depend on the number of metal atoms in the cluster. Although the importance of such size effects awaits further calculations and experimental proof, we propose that such structure sensitivity be called *primary size sensitivity.*

We feel that these are important distinctions. The original concept of structure sensitivity considered essentially only primary structural effects resulting from the presence and relative numbers of certain sites or geometrical arrangements of surface atoms or from the altered reactivity of surface sites composed of atoms of decreasing average coordination number as crystallite size decreases. Specific catalytic activity may be altered by factors which are not purely geometrical or structural, e.g., impurity stabilized surface reconstructions, selective poisoning of specific sites or of crystallites of certain sizes, or intrinsic activity changes due purely to the number of metal atoms present. Support effects may be considered in terms of the three subclassifications indicated depending on whether the support affects specific catalytic activity by affecting resultant crystallite surface structure (a primary effect), by affecting crystallite size dependent sensitivity alteration by reactants or other substances (a secondary effect), or by affecting further those catalytic properties of very small metal clusters which are dependent only on the number of atoms present (*21*). Carefully distinguishing between these different effects should promote a more careful examination of these factors and a clearer understanding and interpretation of "structure sensitive" reactions.

Data obtained by Ostermaier (*22*) in our laboratory illustrate our point. The work involved the catalytic oxidation of low concentrations of ammonia (0.5–5%) with oxygen (1–5%) in helium at temperatures below 200°C in a continuous flow microreactor operated differentially (conversion $< 10\%$). Typical results for two Pt/Al_2O_3 catalysts each containing 1% Pt but having average platinum crystallite sizes of 27 and 155 Å are given in Table 1. The work is discussed in detail elsewhere (*23*). Initial rates were obtained by extrapolating to zero time and indicate the presence of a crystallite size effect which appears to be due to primary structure sensitivity. Self-deactivation is present which leads to a temperature dependent and crystallite size dependent deactivation to steady-state activity. The 27 Å crystallite catalyst undergoes approximately twice the deactivation of the 155 Å crystallite size catalyst (Table 1). This results in approximately a doubling of the ratio of specific catalytic activities for the two crystallite size catalysts. This added enhancement of the crystallite size effect is due to secondary structural sensitivity and represents half of the total difference in specific catalytic activity observed at steady-state.

We speculate that of the large differences in specific catalytic activity observed in oxidation reactions (*16*) secondary structure sensitivity constitutes a large fraction. Failure to recognize and differentiate between the various effects may lead to misleading speculation about the presence, nature, and concentration of special sites as a function of crystallite size and even hinder progress in supported metal catalysis research. Future studies should note carefully the effect of pretreatment conditions, and if any activity changes are observed, initial specific catalytic and specific catalytic activity at steady-state should be determined to aid more fully in defining in nature of specific activity difference in demanding reactions.

TABLE 1

Dependence of Deactivation and Specific Catalytic Activity on Platinum Crystallite Size[a]

Temp (°C)	Catalyst % Pt	Catalyst Å	r_I/r_{ss}	$\left(\frac{r_{155Å}}{r_{27Å}}\right)_I$	$\left(\frac{r_{155Å}}{r_{27Å}}\right)_{ss}$
120	1	27	21.6	3.7	6.6
	1	155	12.2		
140	1	27	9.9	3.7	7.8
	1	155	4.5		
160	1	27	4.1	3.5	8.8
	1	155	1.6		

[a] Feed composition: 1% NH_3; 3% O_2 in helium; I = initial rate, ss = steady-state rate, 155 and 27 Å subscripts indicate rates of NH_3 oxidation for catalysts having these crystallite sizes.

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William H. Manogue*
James R. Katzer†

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

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* Experimental Station, E. I. duPont de Nemours and Co., Wilmington, DE.

† Correspondence concerning this manuscript should be with James R. Katzer, Department of Chemical Engineering, University of Delaware, Newark, DE 19711.