# Assessing the concept of structure sensitivity or insensitivity for sub-nanometer catalyst materials

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### ABSTRACT

The nature of the nano-catalyzed hydrogenation of ethylene, yielding benchmark information pertaining to the concept of structure sensitivity/insensitivity and its applicability at the bottom of the catalyst particle size-range, is explored with experiments on size-selected $Pt_n$ (n = 7–40) clusters soft-landed on MgO, in conjunction with first-principles simulations. As in the case of larger particles both the direct ethylene hydrogenation channel and the parallel hydrogenation–dehydrogenation ethylidyne-producing route must be considered, with the fundamental uncovering that at the <1 nm size-scale the reaction exhibits characteristics consistent with structure sensitivity, in contrast to the structure insensitivity found for larger particles. In this size-regime, the chemical properties can be modulated and tuned by a single atom, reflected by the onset of low temperature hydrogenation at T > 150 K catalyzed by $Pt_n$ (n ≥ 10) clusters, with maximum room temperature reactivity observed for $Pt_{13}$ using a pulsed molecular beam technique. Structure insensitive behavior, inherent for specific cluster sizes at ambient temperatures, can be induced in the more active sizes, e.g. $Pt_{13}$, by a temperature increase, up to 400 K, which opens dehydrogenation channels leading to ethylidyne formation. This reaction channel was, however found to be attenuated on $Pt_{20}$, as catalyst activity remained elevated after the 400 K step. $Pt_{30}$ displayed behavior which can be understood from extrapolating bulk properties to this size range; in particular the calculated d-band center. In the non-scalable sub-nanometer size regime, however, precise control of particle size may be used for atom-by-atom tuning and manipulation of catalyzed hydrogenation activity and selectivity.

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## 1. Introduction

Heterogeneous catalysis on metal-oxide supported sub-nanometer size-selected clusters has been shown to exhibit unique characteristic trends that portray dependencies on particle size extending down to the limit of differences in chemical activity caused by size-differences entailing one or two atoms [1–4]. Such observations signal the emergence of a size-regime, where trends observed for extended surfaces and particles of larger sizes, and concepts deduced from such observations, cease to apply, or require essential modifications. In this non-scalable size-regime, small is different in an essential way, and scaling of physical and chemical properties of larger particles to those in the small-size domain, as well extrapolations to small sizes of knowledge gained at larger size-scales, are questionable, and often invalid. In light of ever-growing efforts aimed at the development and characterization of nano-scale catalysts, it is imperative that research endeavors be directed at critical assessment, modification, and reformulation of

concepts used in catalysis research and their validity, when approaching the bottom of the catalysts' size scale. The time-honored, commonly used, concept of structure sensitivity/insensitivity of a catalyzed reaction is a fundamental concept in heterogeneous catalysis, and in this paper we explore it's applicability at the nanoscale. To this end we investigate here experimentally and through first-principles theory simulations, ethylene hydrogenation on size-selected, sub-nanometer-size model platinum cluster catalysts deposited on a single-crystal magnesia surface under ultra-high vacuum (UHV) conditions. Prior to exposition of our investigations we review in the following the development of the structure sensitivity/insensitivity concept over the past half century. This is the period that saw the emergence of our beloved late friend and colleague John T. Yates Jr. as a major force in surface science and heterogeneous catalysis research, first at the then National Bureau of Standards, NBS (now the National Institute for Standards and Technology, NIST), later at the University of Pittsburgh, and last at the University of Virginia). This article celebrates John's magnificent contributions to science and society and is dedicated to his memory.

Since the 1960s, heterogeneously catalyzed reactions on transition metals displaying an activity which was dependent on particle size

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were classified as "*demanding*" and those which were independent of particle size were termed "*facile*" [5–7]. This focus on particle size was based on the fact that the number of atoms exposed on a particle surface compared to the total number of atoms within the particle changes drastically from very small sizes of only tens of atoms to bulk like structures. Quantifying this relation led to the terms "fraction of exposed atoms" [8] or "degree of dispersion" [5] (varying with particle size, approaching unity for very small particles with diameter ≤ 1 nm and taking small values for large particles), and this has been a central guiding theme of research in catalysis for over half a century [8–11]. The application of simple geometric (polyhedral) models initiated the line of reasoning that specific configurations of atoms at metal surfaces were responsible for the varying activities. Indeed, steps, corners and edges, i.e. low coordination sites have all been used extensively to explain varying rates of catalytic reactions [5,8–10]. This line of reasoning has its origins in the concept of *active sites* introduced in 1925 by Taylor, who in the course of investigating formation of nickel carbonyl on a heterogeneous nickel surface concluded that "only a small fraction of the surface is active" and that "the amount of surface which is catalytically active is determined by the reaction catalyzed" [12]. The above led to introduction of the "Taylor ratio" (TR) that gives for a particular reaction the fraction of active sites relative to the total number of sites on the surface of the catalyst; clearly, a value of TR = 1 corresponds to a *facile* reaction, whereas TR < 1 indicates a *demanding* one.

The proliferation of atomic and molecular scale surface science preparation and characterization techniques in the 1970s and onward, focused attention on reactions catalyzed on well-defined single-crystal surface model systems. The classification of reactions as *facile* or *demanding* gave way to the more practical terminology of *structure-sensitive* and *structure-insensitive*, respectively, and this nomenclature continues to be used to this day.

Accumulated evidence from electron and vibration spectroscopies, time-resolved reaction dynamics studies and first-principles quantum-mechanical electronic structure calculations, brought about extensions of the above classification to include factors that reach beyond the pure morphological and structural effects discussed above. These extensions include: (i) size-effects that influence the electronic structure of the catalyst particle — that is energy level organization and spectra of the valence electrons, particularly the frontier orbitals participating in reactive bond-breaking and bond-making and their evolution in the course of a catalyzed reaction, and (ii) temporal effects pertaining to the dynamics of structural reorganization processes and/or the occurrence of reaction intermediates. The latter extension identifies structure sensitive reactions as being those where the time-scale of such dynamical effects are commensurate with the dynamical processes involved in the catalyst's restructuring and/or in the evolution of certain reaction intermediates, whereas for structure insensitive reaction these dynamic processes are either absent, or may occur on a time-scale that leaves the outcome of the reaction unaffected. The most prominent example of a structure sensitive reaction is the ammonia synthesis through the reaction of nitrogen and hydrogen on iron, while ethylene hydrogenation catalyzed by platinum serves as an example of a structure insensitive reaction [13]. The latter fundamental and technological important reaction stands out as the first reaction for which a catalytic mechanistic pathway has been formulated (by Horiuti and Polanyi in 1934), and it forms the focus of our investigation in this paper [14].

The Horiuti–Polanyi (HP) mechanism begins with hydrogen dissociation on the metal catalyst surface and following alkene (ethylene) adsorption hydrogen additions occur in two subsequent steps: first converting the alkene ($C_2H_4$) into a "*half-hydrogenated*" state (ethyl, $-CH_2CH_3$) followed by a second hydrogenation to form the alkane (ethane, $C_2H_6$) product which desorbs from the surface. Sum-frequency generation spectroscopy on single crystal surfaces demonstrated that two strongly bound species are present during the catalytic reaction on Pt(111) and Pt (100) surfaces (although with different relative concentrations) [13]: (i) di-σ ethylene where the carbon atoms of

the adsorbed $C_2H_4$ molecule are σ-bonded (in near $sp^3$ hybridization) to neighboring Pt surface atoms (where two C–Pt bonds anchor the molecule to the surface), and (ii) ethylidyne ($\equiv C-CH_3$), a molecule which may form through several pathways (for a recent discussion see [15]). In this study we favor an ethylidyne formation reaction scheme that starts from adsorbed di-σ ethylene and proceeds through hydrogenation–dehydrogenation reactions with formation of the ethyl molecule (via hydrogenation) followed by two dehydrogenations: the first one converting $CH_2CH_3$ to ethylidene ($CHCH_3$) and the second yielding ethylidyne. Di-σ ethylene and ethylidyne occupy three-fold hollow surface sites (involving reorganization of the neighboring metal atoms); on Pt(111) ethylidyne is readily formed at around 280 K, and both it, and di-σ adsorbed ethylene, are found on *all* platinum surfaces as *stagnant spectators* with respect to the hydrogenation reaction.

The *structure-insensitive hydrogenation* of the ethylene molecule (found in studies on extended platinum surfaces to occur at higher hydrogen pressure and temperature) involves weakly-bound π-bonded ethylene (in a near $sp^2$ hybridization) and the "half-hydrogenated" ethyl ($C_2H_5$) molecule as reaction intermediates [13,16,17]; for a proposed reaction scheme see Fig. 13 in [11]. To summarize: current opinion is that while the adsorption of ethylene is structure sensitive, the *overall hydrogenation reaction is structure insensitive*.

The identification of ethylidyne as a stagnant spectator was shown first by Beebe and Yates in 1986 [18]. In that study, a combined IR and kinetic analysis of the in situ surface concentration of ethylidyne during ethylene hydrogenation was performed on a Pd/Al$_2$O$_3$ catalyst and the results uncovered that the formation and hydrogenation of ethylidyne was 2–3 orders of magnitude slower than that of ethylene. They also observed that the reaction rate was unchanged on a clean or ethylidyne pre-covered catalyst. This served as a critical observation in demonstrating that the reaction mechanism did not involve a proposed ethylidyne-ethylidene conversion as a reaction intermediate — rather, ethylidyne has been found to act purely as an inactive spectator.

It has been noted on several occasions in the literature that the application of the nomenclature of structure insensitivity is not without its detractors, and critique of this concept has appeared. In particular, two major questions have been posed: (i) without testing *all* particle sizes down to a single atom how can a reaction be unequivocally labeled as structure insensitive (especially when much smaller particles are predicted to behave differently [19]), and (ii) what are the local origins of this structure insensitivity on the metal catalyst. A common explanation for (ii) is that carbonaceous species (in particular the aforementioned ethylidyne) populate the surface and mask structural features that may be expressed on different surfaces and that potentially could underlie different reaction outcomes, i.e. the reaction would exhibit structural sensitivity if the surfaces were left naked. These two issues with classifying a reaction as structure insensitive have been pointed out in review articles spanning the course of almost thirty years [10,11,19,20].

This line of reasoning concerning the methodology of deciding whether a reaction catalyzed by a given metal is demanding (structure sensitive) follows the one outlined in [19], where it is proposed that: "*The best way to proceed is to choose a molecule reacting along two parallel paths and measure the <u>selectivity</u> defined as the rate of the two parallel reactions. If the two products come from different adsorbed states requiring different surface structures, a change of selectivity with dispersion or mode of preparation of the metal may be found. The most unequivocal case is when the specific activity for one of the parallel reactions changes from one catalyst to the next, while the specific activity for the other remains unchanged*". In the following we refer to the above as the: "*parallel reactions selectivity criterion*" (PRSC).

Real catalysis typically employs highly dispersed small particles supported on metal oxides or other high-surface-area substrates, whereas the results that were reviewed above were all obtained from investigations on extended single crystal metal surfaces. To bridge the so called