Cluster Structure and Reactions: Gaining Insights into Catalytic Processes

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Abstract To many researchers outside the field of cluster science it may come as a surprise that much can be learned of its relevance to catalysis, even restricting the discussion to ionized systems. This perspective is largely focused on catalytic oxidation reactions in which oxygen radical centers on transition metal oxides play a dominant role. The objective is to present how fundamental insights into reaction mechanisms can be gained through employing alternative approaches that complement rather than supersede more conventional methods in t he field of catalysis. In view of the well acknowledged role of defect centers in effecting reactivity, and the preponderance of recent papers presenting evidence of the importance of charged sites, the need/desire to conduct repetitive experiments is clear. Presented herein are approaches using clusters to accomplish this in order to unravel fundamental catalytic reaction mechanisms, and to use identified superatoms and the concepts of element mimics to tailor catalysts with desired functionality.

Keywords Heterogeneous catalysis · Catalysis · Gas-phase kinetics Elementary kinetics · Reaction intermediates · Superatoms

1 Introduction

Considering the global need for new sources of energy, enhanced methods of pollution abatement, advanced approaches to the production of fine chemicals, sensors for the detection of harmful materials, as well as new methods of evaluating medical and biological issues, it is clear that catalysis, which impacts all of these, is one of the most important subjects for scientific investigation [1]. In view of the large diversity of reactions and accompanying physical phenomena involved, unraveling the fundamentals of catalytic processes requires a wide range of studies [2]. Clearly no single approach is sufficient to elucidate all of the issues which arise in unraveling catalytic processes, and advances in the subject benefit from well devised investigations of many types [3–6].

One valuable approach employs the use of clusters whose chemistry can be used to follow the course of reactions influenced by various reactive centers/defect sites, and the present invited perspective focuses on past developments and future prospects in this area [2, 5, 7–10]. While acquiring reproducible defect sites for the purpose of elucidating their influence on the course of catalytic reactions is an arduous task, it is a relatively straight forward procedure to recreate and conduct repetitive studies on model clusters which mimic specific reaction centers. There is growing evidence that sites of differing charge density can greatly influence reactions and the effect of these is identifiable through a study of mass selected cluster ions [7–12]. Comparison of the reactivity of anionic and cationic clusters can therefore provide insight into the importance of an accumulation or deficiency of electron density on the reactivity of catalytic materials.

There is increasing interest in the field of nanocatalysis which can be easily modeled through the use of clusters, both in terms of the operative catalytic reaction mechanisms as well as the production of the catalysts themselves [2–4]. Moreover gas-phase cluster experiments allow the fundamental reactive behavior of catalytic materials to be studied in an environment that enables the influence of

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such factors as size, stoichiometry, as well as ionic charge state on cluster reactivity to be determined with atomic-level precision. For nanocatalysis this is particularly relevant since the reactive properties have been known to change dramatically with the addition or removal of even a single atom [7–12].

2 Elucidating Mechanisms of Catalytic Reactions

It is clearly a daunting task to design effective catalysts based solely on fundamental principles and, prior to the last few decades, much of the earlier successes in this endeavor depended on empirical tests employing materials of known effectiveness for promoting selective classes of reactions. The available methods began to change as progress was made in the field of surface science, first in the area of UHV and subsequently under more realistic reaction conditions [2, 3]. In recent years increasing focus has turned to basic studies with various modern techniques such as surface harmonic generation, scanning tunneling microscopy, ambient-pressure X-ray photoelectron spectroscopy, and X-ray absorption spectroscopies, for example [4]. One of the main problems has been identifying specific reaction sites as these frequently involve defects which are difficult to generate, characterize and reproduce.

In recent years cluster science has begun to make significant inroads into this area, making it possible to generate species that can emulate certain reaction centers. For example, in various studies we found that clusters of selected sizes can serve as surface sites, where their structure may have geometries akin to steps, ledges, or corners, with characteristic accompanying charge densities [7–10]. Certain cluster structures such as those shown for example in Fig. 1, can serve as model surface sites. These can be readily formed using standard methods from cluster science [13, 14].

During the course of conducting studies having particular focus on work related to cluster models of catalytic activity, we obtained findings which showed the dramatic effect that can arise upon making minor compositional changes in a cluster. The Castleman group has had a long standing interest in the application of cluster science for unraveling certain catalytic mechanisms such as oxygen transfer, employing specific clusters as model surface sites [8, 9]. One example is seen from a consideration of the dehydration reaction of 1,3-butadiene initiated by vanadium oxide clusters of particular stoichiometries; see Fig. 2. Among the many clusters of varying vanadium to oxygen ratios which have been studied, only $V_3O_7^+$ and $V_5O_{12}^+$ effected such a specific chemical transformation.
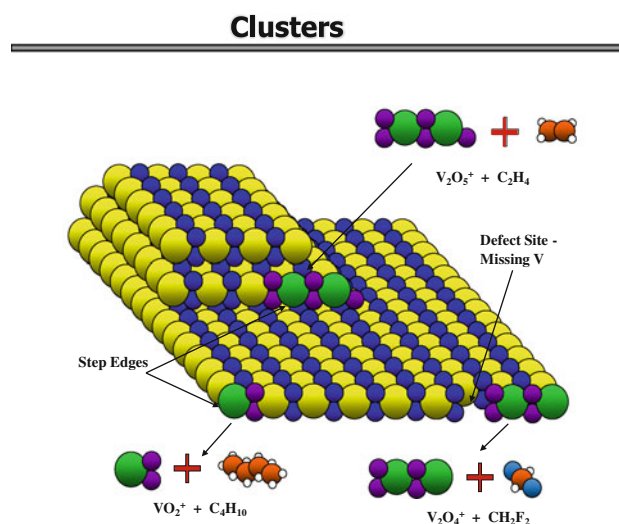

Fig. 1 Steps/ledges/corners: reactive centers mimicked by clusters (adapted from [10])
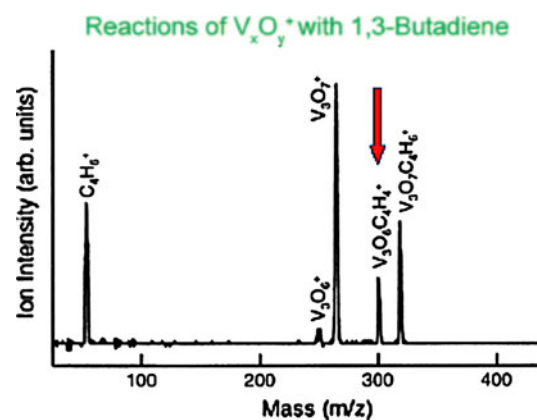

Fig. 2 Reaction of $V_xO_y^+$ clusters with 1,3 butadiene. Only $V_3O_7^+$ and $V_5O_{12}^+$ display a dehydration reactive channel [15]

One example of the success made in identifying mechanisms for oxygen transfer reactions involved the formation of acetaldehyde from ethylene interacting with vanadium oxides as the reaction sites. See Fig. 3. Significantly, among a wide range of clusters studied, only $V_2O_5^+$ and $V_4O_{10}^+$ were found to function in effecting this reactive transformation. This is particularly interesting as 2:5 is the metal to oxygen composition of bulk catalysts that yield a similar reaction product.

It is well accepted that cluster experiments provide insight into the influence of composition, geometry and size on reactive behavior. In combination with theory, the enhanced reactivity of these cluster species was traced to the presence of an oxygen centered radical on a metal atom, and its influence on the energy barrier [15, 16]. See the calculated reaction profile in Fig. 4.

Branching Ratios of $V_2O_{4-6}^+$, $V_3O_{6-8}^+$ and $V_4O_{9-11}^+$ with Ethylene
$(V_2O_5)_n^+ + C_2H_4 \rightarrow (V_2O_5)_{n-1}V_2O_4^+ + (C_2H_4O)$

$V_2O_{4-6}^+$ **$V_3O_{6-8}^+$** **$V_4O_{9-11}^+$**

Fig. 3 Branching ratios for reactions of vanadium oxide cluster cations with ethylene. Note that the formation of C_2H_4O occurs only for $V_2O_4^+$ and $V_4O_{10}^+$; *red squares* (adapted from [10])
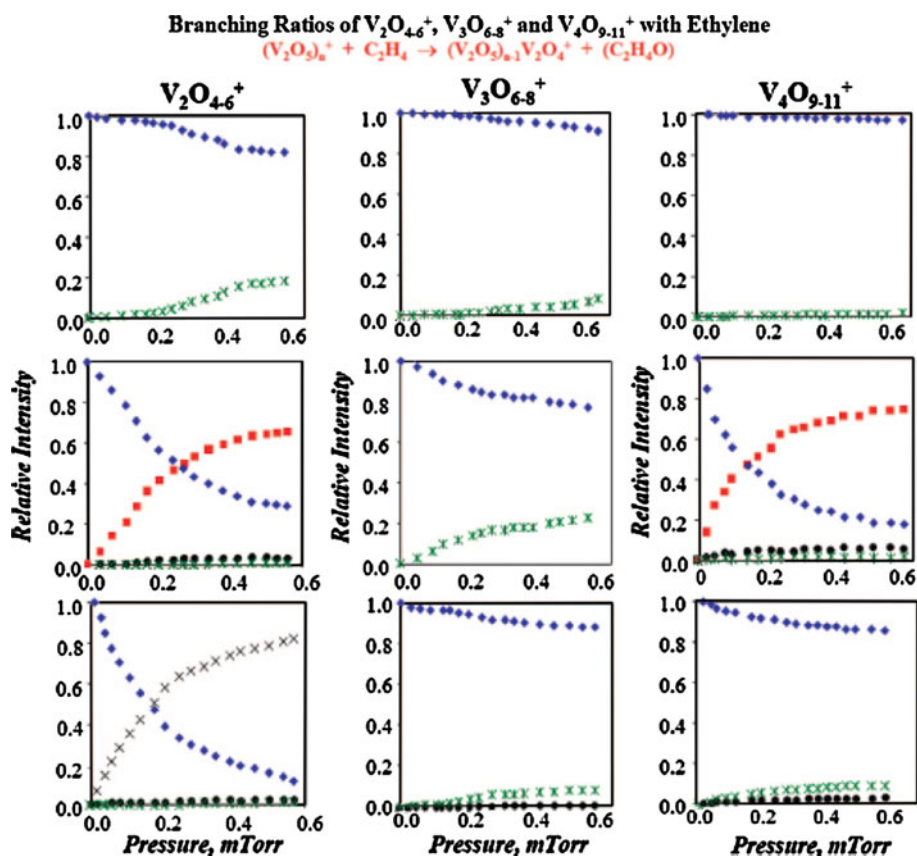
Oxidation of Ethylene by Vanadium Oxide

- Vanadium oxide catalyzes the selective oxidation of hydrocarbons on the industrial scale
  - In laboratory experiments, the clusters $(V_2O_5)_{1,2}^+$ selectively oxidize ethylene
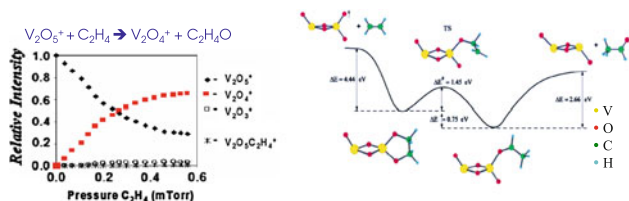 - Oxidation occurs by a **radical cation** mechanism

$V_2O_5^+ + C_2H_4 \rightarrow V_2O_4^+ + C_2H_4O$

Fig. 4 $V_xO_y^+$–C_2H_4 reaction profile involving a radical oxygen cation center (adapted from [17])
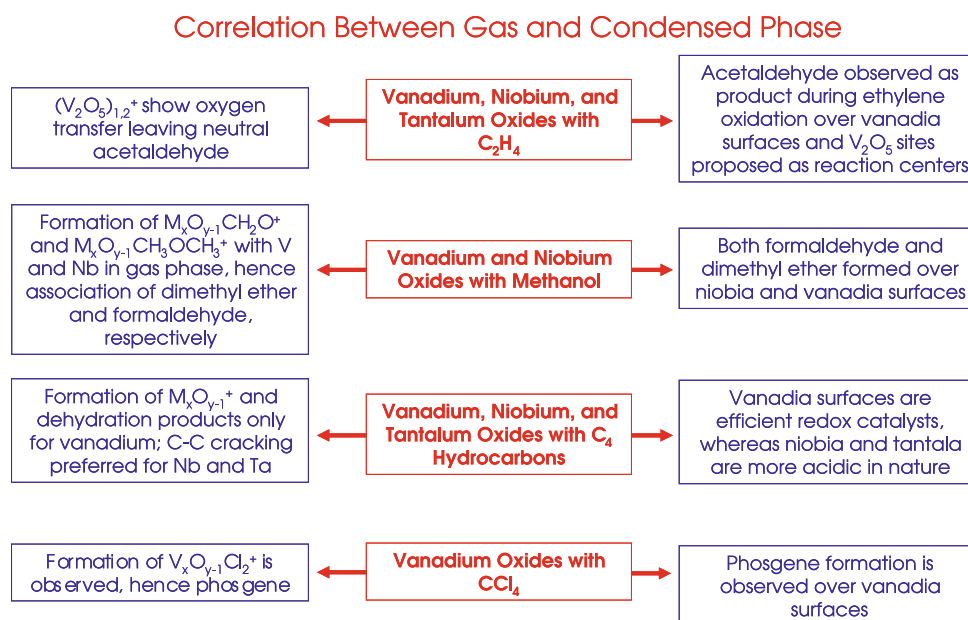
As mentioned above, one other issue that sometimes arises in comparing the findings of cluster studies with bulk catalytic investigations is the matter of cluster charge. Earlier debates raised issues such as questions whether charged clusters were suitable catalyst mimics; the large number of recently reported findings that charged centers play a role in the functioning of many classes of catalytic reactions have put these concerns to rest. In fact it is becoming increasingly realized that a large variety of heterogeneous catalysts function due to the presence of defects having large local charge-density centers [18–36]. And, in the context of our own findings, this issue was also settled in the course of comparing cluster reactions for a variety of classes of reactions with the findings of known catalysts. Although the rates of reactions involving isolated charge centers may differ from those of a bulk material, in many cases the reaction mechanisms are similar [15–17, 37–55].

Further evidence that cluster studies can provide insights into broad classes of reaction mechanisms is seen from examples shown in Fig 5. The finding of a similarity in chemical behavior of numerous clusters compared to those of various bulk catalysts, is striking.

That there is often some close correspondence between cluster reactions and bulk catalytic processes is not completely surprising. It is a relatively straight forward assumption to conceive of increasingly larger clusters asymptotically approaching properties corresponding to those of surfaces, albeit in the cluster case ones suspended in a gas. Depending on the reactive domain size, we can expect relatively small differences with cluster size and we expect the main differences to be reflected in the operative dynamical cross sections. Therefore similar mechanisms should obtain for reactions involving either large clusters or analogous surface sites, whereupon the study of large

Fig. 5 Similarities in chemical behavior between various clusters (Column 1) and bulk catalysts (Column 3)

Correlation Between Gas and Condensed Phase

$(V_2O_5)_{1,2}^+$ show oxygen transfer leaving neutral acetaldehyde	← Vanadium, Niobium, and Tantalum Oxides with C_2H_4 →	Acetaldehyde observed as product during ethylene oxidation over vanadia surfaces and V_2O_5 sites proposed as reaction centers
Formation of $M_xO_{y-1}CH_2O^+$ and $M_xO_{y-1}CH_3OCH_3^+$ with V and Nb in gas phase, hence association of dimethyl ether and formaldehyde, respectively	← Vanadium and Niobium Oxides with Methanol →	Both formaldehyde and dimethyl ether formed over niobia and vanadia surfaces
Formation of $M_xO_{y-1}^+$ and dehydration products only for vanadium; C-C cracking preferred for Nb and Ta	← Vanadium, Niobium, and Tantalum Oxides with C_4 Hydrocarbons →	Vanadia surfaces are efficient redox catalysts, whereas niobia and tantala are more acidic in nature
Formation of $V_xO_{y-1}Cl_2^+$ is observed, hence phosgene	← Vanadium Oxides with CCl_4 →	Phosgene formation is observed over vanadia surfaces

clusters should enable fundamental insights into the related chemistry of the oxides to be acquired.

As an extension of these ideas, we undertook an investigation of reactions of stoichiometric ZrO_2 cationic clusters, interacting with a variety of small molecules including CO, ethylene and acetylene [56]. The findings revealed the presence of an active site consisting of a radical oxygen center that can be transferred, thereupon readily oxidizing these species.

In contrast to the cationic species which were found to be highly active toward the oxidation of all three molecules, anionic clusters of indicated stoichiometry corresponding to $(Zr_xO_{2x+1})^-$ ($x = 1$–4) (that can be conceptionally formed by adding one oxygen atom with a full octet of valence electrons (O^{2-})) were also found to oxidize carbon monoxide, but only strongly associate acetylene rather than oxidize it, and weakly associate ethylene [57].

Theoretical investigations indicate that a critical hydrogen transfer step necessary for the oxidation of ethylene and acetylene at metal oxide clusters containing radical oxygen centers is energetically favorable for cationic clusters but unfavorable for the corresponding anionic species as found experimentally. The reason is traced to the nature of an interacting electrostatic potential of the cluster which reveals that in the case of cations, a favorable interaction with nucleophilic molecules takes place over the whole surface of the $(ZrO_2)_x^+$ ($x = 1$–4) clusters, while a restricted interaction of ethylene and acetylene with the less coordinated zirconium atom is involved in the case of the anionic $(Zr_xO_{2x+1})^-$ ($x = 1$–4) species. See Fig. 6. In the case of C_2H_2, for example, the association with $Zr_2O_5^-$ occurs in two configurations: at the oxygen radical center

and at the less coordinated zirconium atom. The initial encounter complex is about 2 eV more stable than the separated reactant. Also the oxygen radical is localized on one of the oxygen atoms on the opposite side of the cluster to where the acetylene associates. For reaction to occur, considerable rearrangement is required and a substantial barrier is involved in breaking the zirconium–carbon bond and migration of the oxygen atom. Therefore, in spite of the common presence of a radical oxygen center in species with specific anionic and cationic stoichiometries, the extent to which various classes of reactions are promoted is significantly influenced by charge state/local charge density.

That the reactions are catalytic in nature was determined for the $(Zr_xO_{2x})^+$ ($x = 1$–4) series of cationic clusters where it was shown that the reactant ion could be regenerated by reacting oxygen deficient clusters with a strong oxidizer. See Fig. 7.

This work demonstrates that not only cationic species, as shown in previous work, but also anionic clusters may
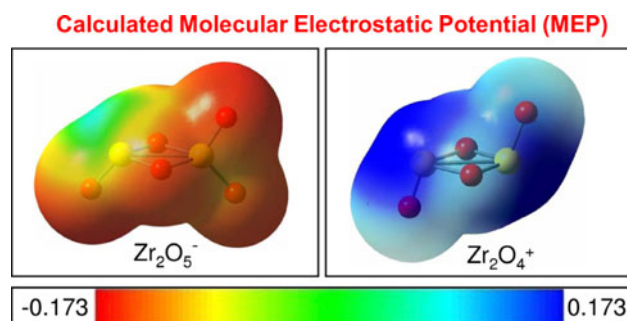
Calculated Molecular Electrostatic Potential (MEP)

-0.173		0.173

$Zr_2O_5^-$ $Zr_2O_4^+$

Fig. 6 Surface electrostatic potential [56]

Full Catalytic Cycle for Oxidation of CO, C₂H₄ and C₂H₂
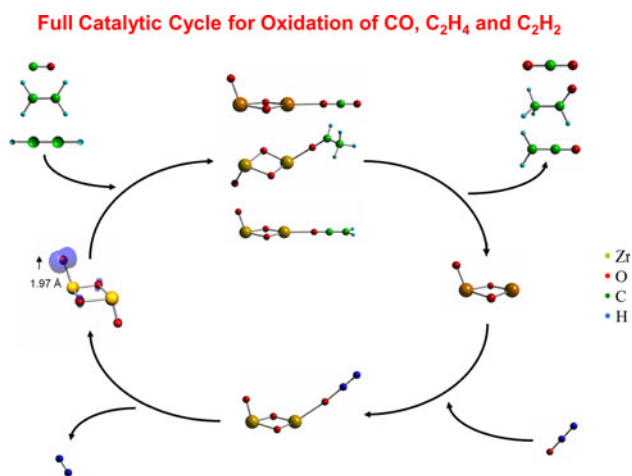

Fig. 7 Full catalytic cycle obtained for the reaction of $Zr_2O_4^+$ with CO, C₂H₄, and C₂H₂ and regeneration of the reacted cation with N₂O [57]

Peripheral Oxygen

- Eley-Rideal-like Mechanism

- CO attacks O forming complex (I)
  - CO weakly bound to O

- Charge transfers to CO forming complex (II)
  - CO strongly bound to O

- Two possible channels from complex (II)
  - Au-O bond rupture followed by Au-C bond formation, complex (III)
  - Rotation of CO out of molecular plane
- CO₂ departs transferring charge back to Au
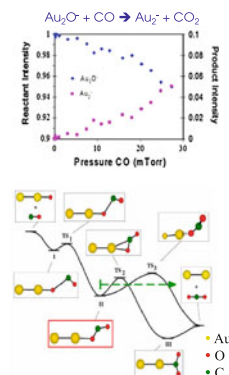
Is O₂ Dissociation Sufficient to Enable CO Oxidation?

- Energy of first transition state (TS1) is higher than the reactants
  - Due to electron withdrawing bridging O atom which makes charge transfer to CO unfavorable
  - Bottleneck for reaction

- No products observed experimentally for Au₃O₂⁻ + CO

- Dissociated O is not sufficient to enable CO oxidation in the presence of anionic gold
  - Energy barriers have to be surmountable

Fig. 8 Oxidation sites for gold–oxygen cluster systems [43]

promote multiple cycles of carbon monoxide oxidation, for example [56, 57]. The findings reveal the prospect of being able to tailor the characteristics of a catalyst via doping a system to control the charge density and hence reactivity.

Another example of the value of cluster studies in shedding light into mechanisms of individual reaction steps pertains to the role of small gold clusters in effecting the oxidation of CO. Prior to the experimental investigations of Haruta [58], gold was considered to be inert. In recent years, numerous experimental and theoretical studies have revealed the contrary, prompting extensive work to elucidate the mechanisms involved [59–67]. Important remaining questions included: Do small gold clusters contribute to the presence of O-atoms sufficient to promote oxidation of CO; and what is the influence of charge accumulation or deficiency on the reactivity? Forming small cationic and anionic clusters is quite facilely accomplished, whereupon such questions can be readily addressed. For example, as shown for anionic gold oxides in Fig. 8, clusters comprised of peripheral and bridging O sites, as well as the presence of molecular O₂ can be formed and investigated, answering the questions raised above as well as others. Cluster studies revealed that the formation of O atoms is necessary, though not sufficient as barriers to transfer can still impede the oxidation reaction.
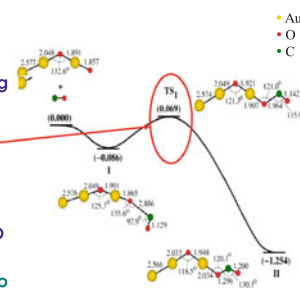
The results obtained provide further aspects of the insights that can be gained from cluster experiments [7–10].

3 An Approach to Designing Nanoscale Catalysts

Studying individual clusters of selected size provides the opportunity to investigate factors governing physical and chemical behavior such as size, composition, and charge state and electron density. With well designed studies, clusters can serve as tractable models for unraveling mechanisms of catalytic reactions on the one hand and yield information of value in designing nanocatalysts with specific reactivity and/or selectivity on the other. Our own work has brought out these aspects in investigations of numerous classes of reactions [7–10].

In addition to questions of selectivity, when applications are considered, concerns about costs of materials often arise. In this context fundamental studies which serve to identify mechanisms and hence, also point to possible substitute materials, play an important role in choice. Important are guiding principles to follow in designing an alternative material through the use of the concept of element mimics which we have pioneered. If the cluster functions as a viable substitute, "its chemistry" should bear some resemblance to that of the corresponding element. This raises the prospect that one approach would be to look for related electronic states, hence providing a way to quantify a concept we considered as an extension of Mulliken's unified atom [68, 69], subsequently termed a
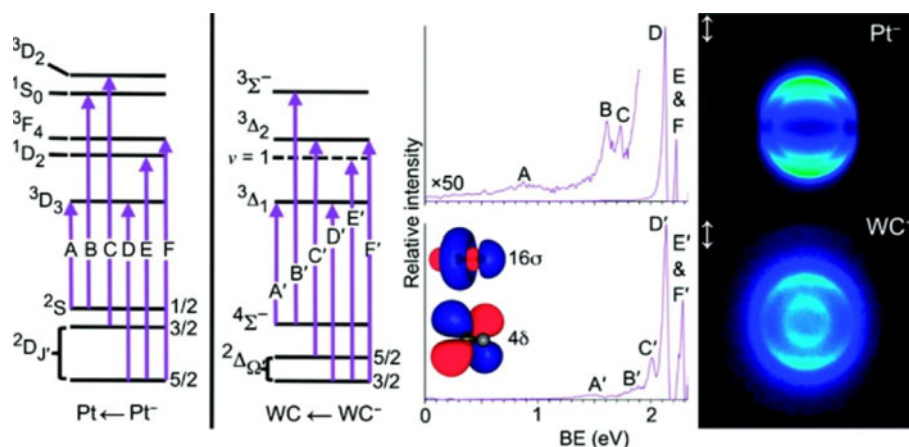
Fig. 9 Energy level diagrams, binding energy (BE) spectra, and raw photoelectron images for Pt^- and WC^- at a photon energy of 2.33 eV (532 nm). The *inset* to the Pt^- binding energy spectrum displays weaker intensity transitions from anion excited states. Isosurface plots of the highest occupied 16σ and 4δ molecular orbitals appear as *insets* to the WC^- binding energy spectrum. See details in [51]

Fig. 10 Energy level diagrams, binding energy (BE) spectra, and raw photoelectron images for Ni^- and TiO^- at a photon energy of 2.33 eV (532 nm). Surface plots of the highest occupied 9σ and 1δ molecular orbitals from ab initio calculations appear in the *inset* of the binding energy spectrum of TiO^-. Note their resemblance to the associated 3d and 4s atomic orbitals of Ni. See [51] for details
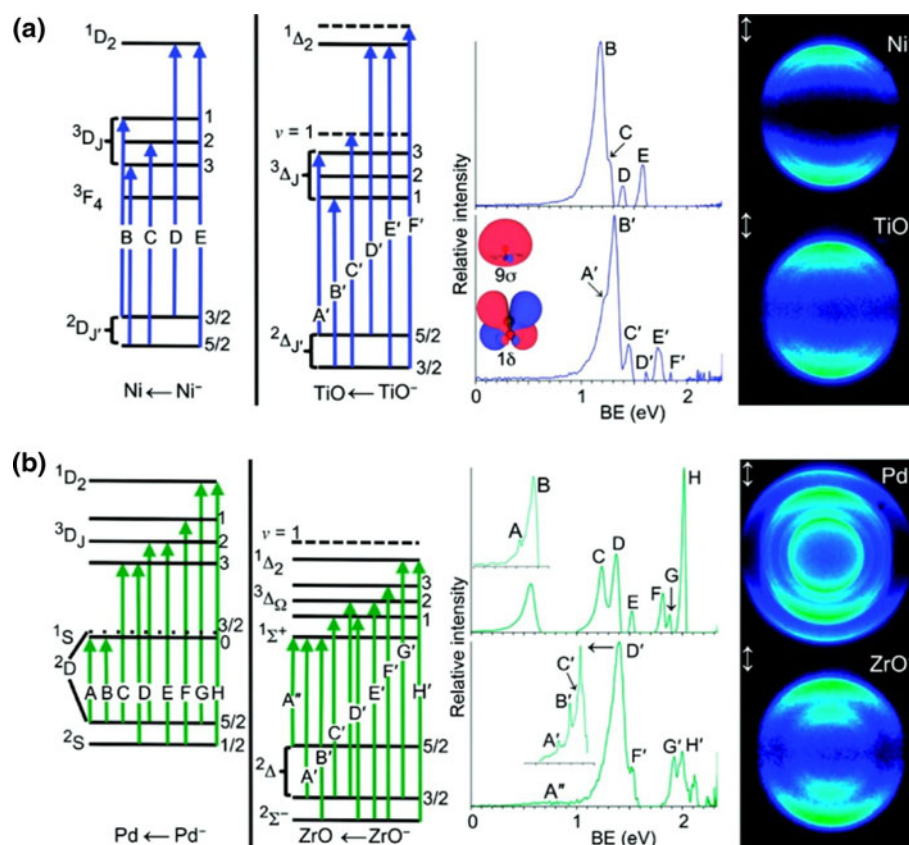

"superatom" in the case of clusters [70]. It was soon realized that element cluster mimics are not only of value in identifying reaction mechanisms, but in addition may provide a valuable tool to tailor the design of new nanoscale materials having selected properties [71].

It has been found that even species with differing compositions but having similar structural arrangements (hence displaying similar electronic character) can be quantitatively quite similar. This is seen from comparison of the nearly identical vertical detachment energies and electron affinities found for a series of large clusters

showing the prospect of being able to extend the concepts to larger (nanocatalytic) systems.

It is a known principle in chemistry that compounds having nearly the same electronic character will yield species with somewhat similar properties. However, "isoelectronic" implies similar structure as well as valence electrons [72]; lacking similar structural geometry, a term such as "isovalency" may be more appropriate. Hints that certain cluster compounds with similar electronic character to various elements might display similar chemistry to an element was suggested by early studies of Boudart and

Fig. 11 Energy level diagrams, BE spectra, and raw photoelectron images for Pd$^-$ and ZrO$^-$ at a photon energy of 2.33 eV (532 nm). The *insets* to the BE spectra display higher-resolution reconstruction slices of the indicated energy regions. Peak C′ and the $^3\Delta_1 \leftarrow {}^2\Sigma^-$ component of D′ appear as unresolved shoulders to more intense transitions. See [51]. The lower diagrams are the branching ratios for the two systems, showing similar reactivities for Pd and ZrO [76]
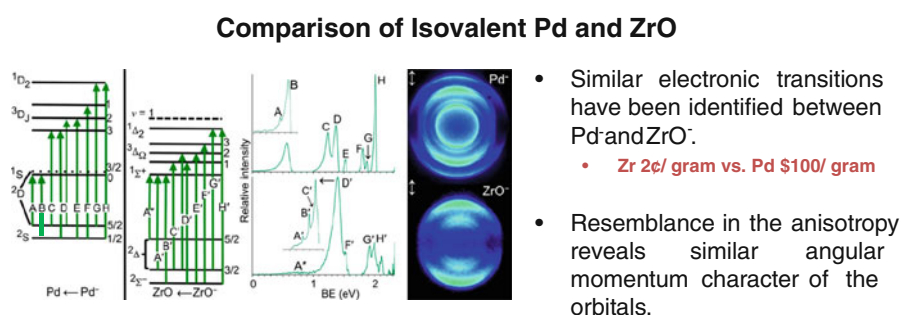
Comparison of Isovalent Pd and ZrO

- Similar electronic transitions have been identified between Pd$^-$ and ZrO$^-$.
  - Zr 2¢/ gram vs. Pd $100/ gram
- Resemblance in the anisotropy reveals similar angular momentum character of the orbitals.

Reaction of Pd$^+$ and ZrO$^+$ with Ethane
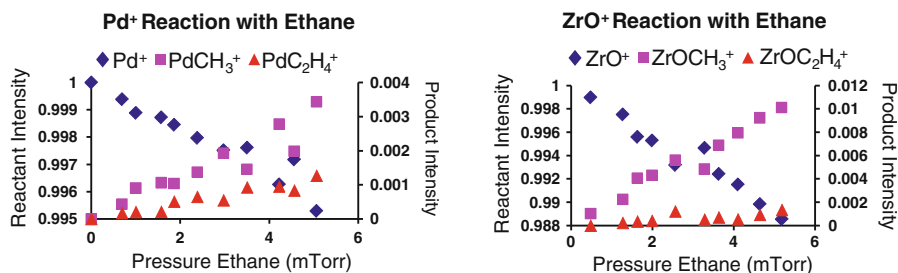
co-workers [73] who, during the early 70s, reported that WC and platinum, which have somewhat similar electronic configurations, could both display some similar catalytic behavior. Considerations were based on the expected similar vertical electron detachment energies of WC and Pt, and their electron affinity values, a fact that we experimentally established via photoelectron measurements [74].

Due to the more restrictive selection rules involved in evaluating electronic transitions via absorption spectroscopy, photoelectron spectroscopy results were considered more appropriate for evaluating the validity of various superatoms as element mimics. Employing the technique of velocity map imaging enabled us to quantify the electronically excited state characteristics of cluster element mimics, including their anisotropies which provide information on the symmetry of the orbitals from which the electrons are ejected. Extending these quantitative measurements to a variety of systems led us to similar findings of other promising element mimics [75, 76].

Although not fully rigorous, a first step in comparing the expected similarity of potential catalyst materials in terms of element mimic characteristics is to consider their electronic states. Here we give consideration to three systems where electronic states are the bases chosen.

First we consider platinum and tungsten carbide, species which have the same valence [74]. An energy level diagram for the systems is given for the two species along with images determined for the anisotropy parameters employing a velocity map imaging technique. See Fig. 9.

The images corresponding to the electron emissions from various orbitals are displayed. Evident is the fact that WC does reveal electronic transitions closely akin to those of Pt,
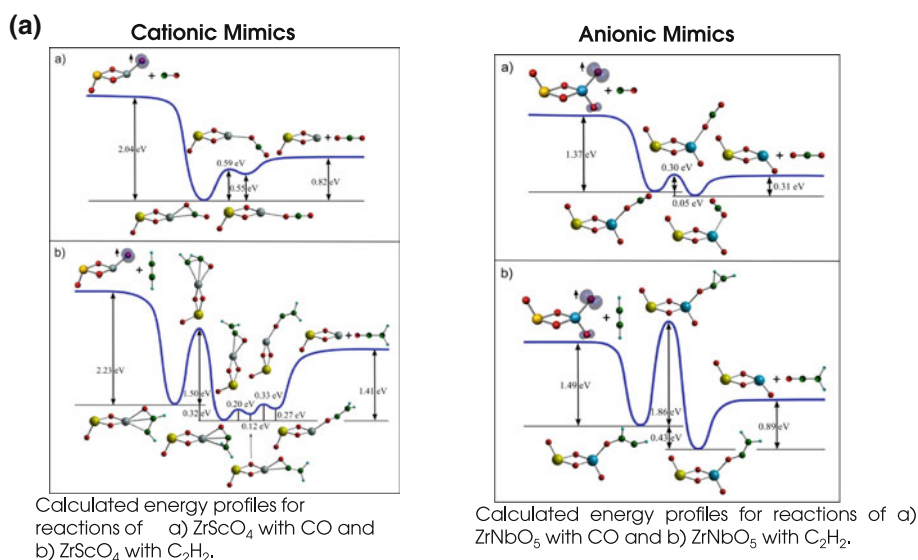
accounting for the fact that WC reveals similar surface catalytic behavior [28]. Although the spectra are not quantitatively identical, the similarities of the electronic excited states as well as the anisotropy parameters (β) are evident. Evidence that this is not a mere coincidence in the Pt/WC case is apparent by comparing spectra for other isovalent pairs such as TiO$^-$, which reveals remarkable similarity [75] to that of Ni$^-$, and similarly, ZrO$^-$ compares well with Pd$^-$. Examples are shown in Figs. 10 and 11.

Even though mimics having similar electronic states as various elements have been found, a question regarding the similarity or equivalence of their reactive/catalytic behavior arises. To shed light on this possible issue, we commenced detailed study of a number of small organic molecules interacting with various cluster ions of equivalent valence. In this context particular attention was given to reactions of some palladium cation-clusters with small organic molecules such as ethane and propane, finding nearly identical behavior for chemical reactions of Pd and the mimic ZrO, even for species of a differing ($+1$ vs. -1) charge state. See Fig. 11 which reveals C–C bond scission and hydrogen abstraction. This unexpected, but promising behavior does still require further investigation for other systems. Nevertheless, the promise is also upheld so far by our recent results found for reactions of ZrO$_2{}^+$ yielding products analogous to those acquired with PdO$^+$.

4 Devising New Catalyst Materials

In this perspective we have shown that under carefully chosen conditions, the study of cluster properties and

Fig. 12 a Mixed metal neutral cluster mimic charged cluster reactions [53]. **b** The prospect of tailoring catalyst effectiveness via doping/mimicking charge state effects. Altering characteristics of catalytic materials via doping materials with elements of differing electron density to mimic charge effects (adapted from [53])

(a)

Cationic Mimics

Anionic Mimics

Calculated energy profiles for reactions of a) $ZrScO_4$ with CO and b) $ZrScO_4$ with C_2H_2.

Calculated energy profiles for reactions of a) $ZrNbO_5$ with CO and b) $ZrNbO_5$ with C_2H_2.

(b)

Generation of Radical Centers in Binary Neutral Metal Oxide Clusters for Catalytic Oxidation Reactions
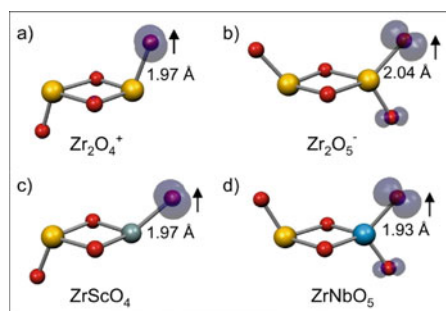
Calculated lowest energy structures for a) $Zr_2O_4^+$ b) $Zr_2O_5^-$ c) $ZrScO_4$ and d) $ZrNbO_5$. The radical oxygen centers are indicated by an arrow. The gray isosurface indicates the localized spin density.

reactions can enable further understanding of the fundamentals of selected catalytic mechanisms at the molecular level. Additionally insights into potential superatom element mimics can be deduced from measurements of electronic states, suggesting the prospect that materials with desired functionality might be designed and constructed employing appropriate building blocks. Although materials formed via cluster assembly are usually composed of varying numbers of assemblies of the building blocks, and it is important that the individual clusters that provide the desired functionality do not coalesce; designing an approach to effectively impede this is currently one of the major challenges in the superatom field.

One can raise the issue of why there may be an advantage in materials formed via the assembly of element mimics rather than employing ones simply produced using the elements themselves. The key reason is that through an assembly process, it may be possible to acquire materials with more than a single functionality, for example, detection followed by destruction. Indeed, the prime objective of the studies presented here is to acquire the ability to tailor the chemical nature of superatom cluster building blocks for devising new nanoscale materials with desired selectivity. If one can attain the ability to form a material with certain chosen chemical characteristics that perform differently when perturbed, a wide variety of new avenues would be opened up. In some cases another potential motivation derives from cost considerations of mimics versus elements.

Until recently the jellium shell model has provided the main basis for conceiving the design of new superatoms.

This has been overridden by the semi-quantitative concepts allowed by determinations of orbital symmetry and related asymmetry parameters identified through studies of velocity map imaging. Focusing on compositional effects, and particularly on the role of support materials is becoming a subject of increasing interest.

A recent example of how local compositional variations can substantially alter catalytic characteristics is seen from calculations of the generation of oxygen radical centers in binary metal oxide clusters [77]. The energetics and associated barriers in catalytic oxidation reactions have been shown to be readily altered in reactions of zirconium oxides with C_2H_2 and CO through partial substitution of Sc to acquire charge depletion or Nb for change density enhancement. See Fig. 12.

The fields of cluster science and nanoscale science have in some respects grown up separately. The former nearly always involved a study of species formed from the bottom up, while in the beginning nanoscale materials most often had birth arising from the subdivision of bulk materials. Nevertheless it is becoming increasingly obvious that the two have much in common and that cluster science enables considerable new insight into the fundamental properties and behavior of matter of small size. Cluster science offers many advantages in that as they grow, they approach the properties of a surface, and ones can often be produced that model various surface sites and defects; they are reproducible in character which is frequently not the case for bulk catalysts. Small clusters are amenable to theoretical treatment, allowing comparison with experimental findings for more in depth interpretation of properties; the influence of charge density can be determined since clusters can usually be produced in any of the three states: cations, anions and neutrals. Considering the many recent findings in the field reveals that catalytic defect centers most often have either excess or in some cases depleted charge density. Hence studies of charged clusters are especially relevant.

A regime of particular interest is one where each atom counts, giving rise to materials (including catalysts) with differing properties and reactivity. The most exciting prospect is one in which material properties can be tailored to display valuable catalytic properties. Adopting selected combinations of elements to produce complex molecules and assemblies, that produce both compounds which mimic individual elements and also give rise to species of multifunctionality, offers uncountable new prospects. Contributing to the further development of this emerging area of science provides an exciting intellectual challenge and one where gas phase cluster research offers new insights and alternate approaches.

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