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Account

# A Career in Catalysis: Gianfranco Pacchioni

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**ABSTRACT:** This Account traces the scientific journey of Gianfranco Pacchioni, a pioneer in the theoretical understanding of catalysis and materials chemistry. From his early contributions to the study of metal clusters and organometallic compounds to his groundbreaking work on surface defects and single-atom catalysis, Gianfranco has profoundly shaped our understanding of the electronic structure and reactivity of catalytic materials. A defining feature of his career has been his ability to translate chemical complexity into comprehensive and powerful theoretical models, often anticipating experimental findings and guiding the design of catalytic systems. His work on defect engineering, oxide-supported metal clusters, and ultrathin films has laid foundational principles in surface science. At the same time, his more recent contributions have elevated the field of single-atom catalysis through a unique blend of coordination chemistry, solid-state physics, and computational rigor. Gianfranco's legacy extends beyond his scientific output: he has fostered international collaborations, mentored generations of researchers, and played a pivotal role in shaping the landscape of theoretical chemistry in Italy and beyond.

**KEYWORDS:** *density functional theory, theoretical chemistry, oxide surfaces, point defects, metal clusters, single-atom catalysts*



## 1. INTRODUCTION

Passion for science, innate curiosity, intuition, and a deep scientific knowledge have guided Gianfranco Pacchioni's journey in catalysis. A pioneer in applying first-principles calculations to heterogeneous catalysis, he has combined scientific rigor with an exceptional ability to translate complexity into simplicity, distilling intricate processes into relatively simple models. This approach has been instrumental in advancing the field, providing fundamental insights, and shaping our understanding of surface processes and catalytic phenomena. Gianfranco was born in Milan, Italy, in 1954. He studied chemistry at the University of Milan and graduated in 1979. During this period, he was fascinated by the chemistry of clusters,[1−5] an area of research in which Milan was a center of excellence. After his studies, Gianfranco decided to pursue a Ph.D. and receive further training in physical chemistry. Gianfranco got an offer from Jaroslav Koutecky and moved to Berlin,[6−9] studying ways to combine the effective core potential (ECP) method with the multireference configuration interaction (MRCI) approach developed by Bunker and Peyerimhoff,[10] to allow correlation effects to be considered when describing materials and chemical processes.[11] During this period, he came into contact with several young researchers from the Academy of Sciences of East Germany, including future leaders such as Helmut Haberland, Joachim Sauer, and Angela Merkel. His time in Berlin was intellectually transformative and personally enriching, shaping his scientific vision and instilling a deep appreciation for international collaboration and rigorous theoretical work. These experiences remain a source of inspiration for Gianfranco, who frequently shares stories from this period with early career colleagues, encouraging them to embrace scientific mobility, interdisciplinary research, and the vital connection between theoretical insight and experimental validation.

After getting his Ph.D. in 1984, Gianfranco moved back to Milan as an Assistant Professor at the University of Milan, working on metal clusters and molecular complexes, and taking inspiration from the seminal works on metal−carbonyl compounds done by Renato Ugo and Paolo Chini, professors at the same university and pioneers in organometallic chemistry.[12−18] The scientific environment in Milan at the time was extremely stimulating, marked by a strong tradition in inorganic and organometallic chemistry and a vibrant intellectual community. The results by Renato Ugo were instrumental for the work on surface organometallic chemistry by Jean-Marie Basset a few years later.[19−21] In 1987,

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Gianfranco decided to expand his research interests to the properties of immobilized clusters on surfaces, fascinated by the structure of support-immobilized metals in traditional heterogeneous catalysts, and started visiting the group of Paul Bagus, a pioneer in the field of wave function methods,[22−24] at IBM in Almaden, California regularly, until 1993. In that period, Gianfranco met Francesc Illas, a keyperson in Gianfranco's life, as they became intimate collaborators and close friends.[25−27] Gianfranco and Francesc, with their research groups based in Milan and Barcelona, respectively, exchanged a wide number of students and collaborators over the years, a factor which became of great importance for the Italian-Spanish community in computational catalysis. Their collaboration resulted in about 50 publications with over 3000 citations. The period at IBM in Almaden was also key for Gianfranco because it was his first contact with the theory of solids,[28−30] something that has fueled Gianfranco until nowadays. Following this, Gianfranco dedicated his research in the 1990s to the theory of surfaces of inorganic oxides, first by using Hartree−Fock-based (HF-based) approaches, and later by using density functional theory (DFT). The latter was possible also due to the fruitful collaboration with Notker Rösch at the Technical University of Munich, Germany.[31−33] These years represent a turning point in Gianfranco's career, as he was among the first to demonstrate the power of DFT, particularly using hybrid functionals such as B3LYP, in describing the structural and electronic properties of inorganic solids, including insulating and semiconducting materials.[31−35] In 1997, he left the University of Milan and moved to the newly established University of Milan-Bicocca, as an Associate Professor (1997) and then Full Professor (2000) of Inorganic Chemistry at the Department of Materials Science. Since then, Gianfranco has continued to transfer the importance of general and inorganic chemistry to materials science students.

The first decade of the new millennium was constellated by several milestones in his career, such as his highly cited work on the theory of defects in inorganic materials. Beginning with covalent and ionic insulating oxides such as $SiO_2$ and MgO,[36,37] his research later expanded to semiconducting oxides such as $TiO_2$.[38−40] Central to this progress was his close collaboration with the electron paramagnetic resonance (EPR) group in Turin, led by Elio Giamello, that resulted in 47 published papers with over 5200 citations. This collaboration exemplifies a core aspect of Gianfranco's career: his meticulous attention to bridging experimental observables—such as those from EPR measurements with theoretical insights. Major examples in this field are his contributions to understanding the structure of oxygen vacancies in insulating oxides,[41] or the role of nitrogen doping in $TiO_2$ and its impact on photocatalysis.[42] At the same time, Gianfranco started investigating the nature of metal clusters on oxides and ultrathin oxide films grown on metals, collaborating with Hajo Freund at the Fritz Haber Institute in Berlin. Their partnership led to 53 publications with over 3700 citations and continued until 2020s. Gianfranco contributed to solving several open questions regarding the chemistry of metal clusters on oxides, charge transfer across thin films on surfaces, and materials' interfaces.[43,44]

The past few years in Gianfranco's career have been dedicated to the emerging field of single-atom catalysis, which are materials where transition metal atoms are atomically dispersed on a solid support.[45−49] In a way, the understanding of the structure and reactivity of isolated metal atoms has been a *leitmotif* in Gianfranco's career,[31,50,51] before the name "single-atom catalyst" was coined in 2011.[52] With his work, Gianfranco showed the importance of considering in the modeling approach the similarity between single-atom catalysts and organometallic compounds.

A characteristic of Gianfranco's research was his curiosity-driven approach to science, leading to a genuine interest in understanding chemical phenomena and explaining experimental puzzles. This aspect was always intertwined with his desire to transmit his knowledge, know-how, and passion to young students and collaborators. Overall, the main milestones of Gianfranco's scientific activity can be summarized with four bullet points, having always the purpose of working with useful models, in the sense that all models are wrong, but some are useful:

i) He contributed to unravelling the importance of point defects in catalytic materials.
ii) He contributed to discovering the unique properties and catalytic activity of two-dimensional (2D) oxides.
iii) He contributed to showing the power of DFT and hybrid functionals to treat solids.
iv) His work on the catalysis of anchored metal atoms and clusters anticipated the emergence of single-atom catalysis.

Besides his contributions to surface science and catalysis research, Gianfranco's passion for science has driven him to work tirelessly in two additional directions. Since the foundation of his University, he has played a key role in strengthening the scientific directions of the institute, holding several leading positions over the past three decades, including Director of the Department of Materials Science, Director of PhD school in Nanotechnology, and Vice-Rector for Research. Similarly, he has significantly contributed to advancing the field of theoretical and computational chemistry in Italy, serving as the first President of the Theory and Computational Division of the Italian Chemical Society. Last but not least, Gianfranco has always believed that one of the scientist's duties is to engage with the general public and promote scientific culture (Figure 1). His natural talent for writing has led him to author

**Figure 1.** A live action: Gianfranco delivering a passionate and rigorous talk on the critical interplay between theoretical modeling and experimental validation in chemical sciences.

several bestselling books,[53−55] focusing on the role of scientists, the present and future directions of science, and the transformative impact of materials science on society.

## 2. FROM ORGANOMETALLIC CHEMISTRY TO HETEROGENEOUS CATALYSIS AND SURFACE SCIENCE

**2.1. Metal Clusters and Their Chemistry.** In the 1980s, Gianfranco made seminal advances in theoretical and computational chemistry, focusing on small clusters, metal


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surfaces, and molecular interactions. His work covered a broad range of topics, from the nature of bonding in metal clusters to the electronic structure of transition metal compounds and how molecules interact with metal surfaces. Using computational techniques such as ab initio Hartree−Fock calculations, configuration interaction, and pseudopotential approaches, he helped define key principles that determine the stability and reactivity of these systems. From the beginning, his research was marked by a strong link between theory and experiment: many of his predictions, based on computational models, anticipated experimental results and guided the design of new catalysts and functional materials.

One of the central themes of Gianfranco's work was the study of metal clusters, particularly those formed by alkali and alkaline earth metals. He analyzed lithium, magnesium, calcium, aluminum, and germanium clusters,[7−9,56] uncovering trends in their electronic structures, stability, and bonding characteristics. His studies on $Li_4$, $Li_6$, $Li_7$, and $Li_{13}$ clusters,[56−58] for example, showed that 5-fold symmetric structures were often more stable than bulk-like crystalline arrangements.[56] These findings provided theoretical support for subsequent experimental studies on nanostructure growth and the formation of metal nanoparticles.[59] Another significant contribution was his work on alkaline earth metal clusters, particularly those of beryllium, magnesium, and calcium.[60] He demonstrated that beryllium clusters exhibit strong *sp* hybridization, whereas this effect is largely absent in magnesium and calcium. This difference explains why Be clusters form compact tetrahedral structures, while Mg and Ca clusters favor more open geometries.

Alongside his work on metal clusters, he also investigated the electronic structures of small carbon, silicon, and germanium clusters.[9,61] While these elements share similar valence electron configurations, he found that their clusters behave very differently. Unlike carbon clusters, which often adopt linear structures,[61] silicon and germanium clusters tend to form compact, nondiamond-like geometries.[9] This distinction helped explain the transition from molecular to bulk properties and the differences in macroscopic material behavior. These findings had direct implications for astrochemistry and spectroscopy,[62,63] as carbon clusters play a crucial role in interstellar chemistry.

His studies on transition metal clusters, especially those of palladium and rhodium,[64,65] further expanded the understanding of metal−ligand interactions. By analyzing Rh-CO and Pd-CO complexes,[64,65] he confirmed the dominant role of $\pi$-backdonation in metal−CO bonding, reinforcing a key concept in organometallic chemistry. This research deepened our understanding of how transition metals interact with ligands, with direct implications for catalysis and surface chemistry. Gianfranco's work also extended to the chemisorption of CO on other transition metal surfaces.[66] Using cluster models to approximate the metal surface, he examined how CO vibrational frequencies shifted upon adsorption. His findings showed that while $\pi$-backdonation from the metal to CO initially reduces the C−O stretching frequency, repulsive effects at shorter bond distances cause it to increase again. This analysis provided theoretical support for experimental vibrational spectroscopy data and demonstrated the interplay of electronic and electrostatic interactions in chemisorption. A more detailed decomposition of the interaction energy revealed that $\sigma$-donation from CO to Pd's partially filled 4d$\sigma$−5sp hybrid orbitals also played a crucial role, making metal-CO bonding more complex than previously assumed.[67] An intriguing discovery was made when he investigated how bond distances and vibrational frequencies responded to uniform fields. His analysis of CO adsorption on Pd(100) showed that field-induced vibrational shifts were primarily driven by electrostatic interactions rather than charge transfer, challenging some earlier assumptions about field effects in surface chemistry. While teaching, Gianfranco always remarks on the importance of the CO molecule as a probe species to unravel the properties of surfaces, Figure 2, with the iconic phrase "*CO on MgO is the hydrogen molecule of surface science*".

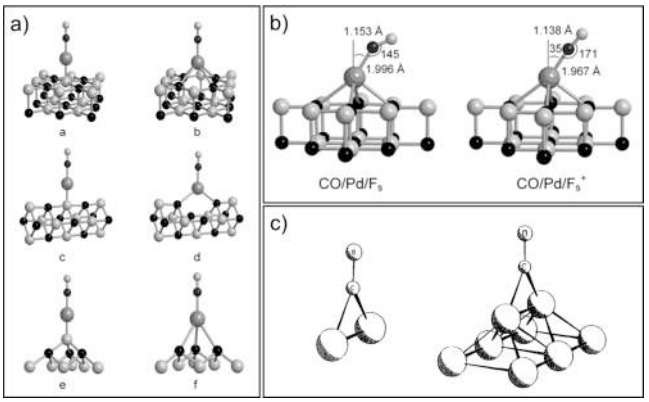


**Figure 2.** CO adsorption on Pd atoms and clusters anchored on defect sites of the MgO(100) surface. Panels (a) and (b) were taken with permission from the ref 67. Copyright 2001 American Chemical Society. Panel (c) was reproduced with permission from ref 71. Copyright 1990 American Institute of Physics.

Among his most influential studies from this period was his work on halogen bonding to the Ag(111) surface.[68] Using ab initio Hartree−Fock wave functions, he examined the nature of these interactions and concluded that the bonding was highly ionic, with halogen ionicity close to −1. In this study, he introduced new approaches to quantifying bond ionicity, such as charge transfer analysis using projection operators, dipole moment analysis as a function of distance, the influence of external electric fields on bond lengths, and the breakdown of interaction energy into electrostatic and polarization components. These insights provided a clearer picture of how charge transfer and polarization affect adsorption on metal surfaces and remain relevant in surface science research.

Beyond catalysis and chemisorption, Gianfranco contributed significantly to the theoretical design of new functional materials in these years. His research on the coordination of histidine in copper(II) complexes provided valuable insights into bonding modes relevant to bioinorganic catalysis and enzymatic activity.[69] Using circular dichroism spectroscopy and magnetic parameter analysis, he examined how metal ions interact with ligands, helping to explain selectivity and catalytic efficiency in bioinorganic systems.[70] The impact of the work extended to biologically and industrially important systems, reinforcing the predictive power of computational chemistry in understanding complex molecular behavior.

**2.2. From Metal to Oxidic Clusters.** The transition from metallic to oxidic clusters represented an important expansion of Gianfranco's career in the structural and electronic properties of nanoscale materials. While metal clusters exhibit delocalized electron behavior and metallic bonding, the introduction of oxygen leads to the formation of metal−


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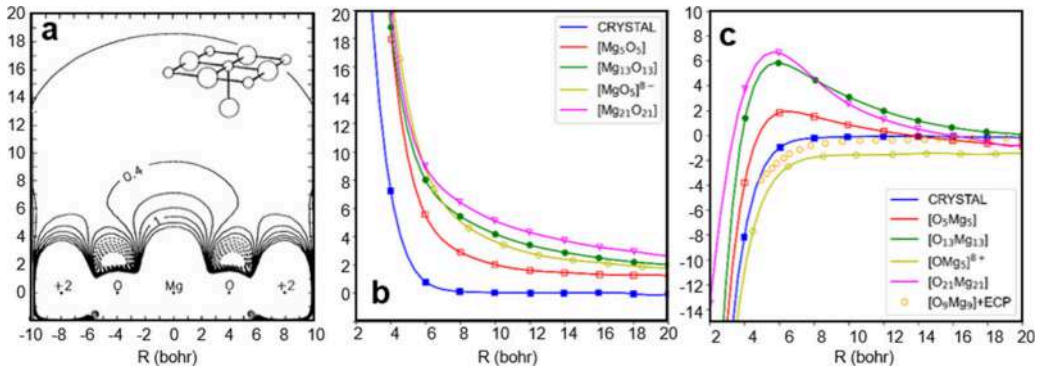


**Figure 3.** (a) Two-dimensional plot of the electrostatic potential (EP) at an $Mg^{2+}$ site of the MgO(l00) surface; the contours are drawn in intervals of 0.2 eV each. (b) One-dimensional plot of the EP at an $Mg^{2+}$ ion. (c) One-dimensional plot of the EP at an $O^{2-}$ ion. The results are based on the Hartree−Fock methods, and distances are in bohr, and EP in eV. Adapted with permission from refs 72 and 73. Copyright 1996 Wiley and Copyright 1997 Wiley.

oxygen bonds, increased ionicity, and changes in coordination geometry. Thus, Gianfranco became fascinated with the possibility of understanding oxides. The molecular cluster approach is based on the fact that many chemical phenomena, such as interactions with a catalytic site or the structural and electronic characterization of a defect, involve species localized on the surface. The substrate can therefore be described using a cluster consisting of a finite number of atoms or ions cut from the surface to reproduce the site of interest. However, using a cluster cut directly from the surface introduces nonphysical states at the edges, as it fails to account for the exchange repulsion between the ions or edge atoms and the exterior of the cluster, as well as the absence of long-range electrostatic contributions from the infinite surface.

Different embedding techniques were proposed at that time to address these drawbacks. The simplest scheme was based on the use of an embedding of a set of point charges (PCs), placed at the lattice positions of the atoms in the surrounding to resemble the external potential thus reproducing the Madelung potential at the site of interest.[72,73] The value of the charges could be selected either based on chemical considerations, for example, in the case of MgO, considering its high ionicity, where the charges are generally chosen to be equal to the formal charge of the ions +2 and −2, or by referring to the Mulliken population analysis, as in the case of semicovalent systems such as $TiO_2$.

The use of PCs leads to several issues. First, the interruption of charge flow at the edge of the cluster was not compensated in any way, for example, between the ions (either positive or negative) in the magnesium oxide lattice. Second, the absence of Pauli repulsion between the electrons of the edge ions and the point charges causes unphysical polarization and excessively high magnitudes of the ion-edge cluster interactions. This is particularly problematic in the case of anions, as they are more spatially extended and more polarized. As a result, the wave function of the cluster extends beyond its actual dimensions. For MgO (and ionic crystals), Gianfranco reduced this issue by replacing the +2 formal ionic charges of the neighboring edge cations with simple effective core potentials (ECPs), which do not have the wave functions associated with them (see Figure 3).[72] This approach helped better represent the finite size of the edge cations outside the cluster and introduced a crude description of the exchange repulsion between the electrons in the oxide anions and these cations, which is captured by the ECP.

In Gianfranco's work, the choice of cluster shape and size (number of undercoordinated ions, stoichiometry, charge) together with the type of embedding (PCs or PCs+ECP) were evaluated by considering the electrostatic potential (EP) at the central ions of the clusters describing the $O^{2-}$ and $Mg^{2+}$ sites and compared with the same property computed with the periodic code CRYSTAL,[74] and by employing a three-layer slab of MgO (Figure 3). This kind of analysis underlined that the potential generated by the periodic slab converges significantly faster than that obtained from clusters and a large variability in the potential derived from the clusters not directly related to their size. In general, nonstoichiometric clusters tend to perform worse than stoichiometric ones, especially at larger distances and the use of ECP+PC embedding appears to improve the convergence of potential values.[72,73]

Even though the cluster approach was theoretically less satisfactory than the periodic approach since it involves an arbitrary surface cut and no theorem guarantees that the calculated properties could converge to those from the periodic method with the increasing cluster size, in the early 1990s this technique demonstrated notable advantages. It offered a simpler alternative to methods modeling the full complexity of surfaces, allowing for the inclusion of both dynamic and static electronic correlation and enabling the study of chemical bonding and electronic structure through the intuitive language of molecular chemistry. Gianfranco made this advance by employing standard computational codes for molecular calculations. Therefore, despite its limitations, the approach proved valuable for investigating local properties, point defects, interactions with adsorbates and supported metals, including single atoms and small clusters, as it effectively captured key phenomena in these systems.[75−79]

**2.3. Catalysis from Single Metal Atom and Small Clusters.** The idea that isolated metal atoms could act as active catalytic centers was a radical departure from conventional thinking in the 1990s when catalysis was still largely associated with extended surfaces or metallic clusters, as shown in the previous paragraphs. Gianfranco was among the first to be captivated by this emerging concept, recognizing early on − and thanks to work in surface science − its potential to redefine our understanding of active sites in heterogeneous catalysis. Particularly, he was intrigued by the possibility of reducing catalysis to its most elementary unit, the single atom.


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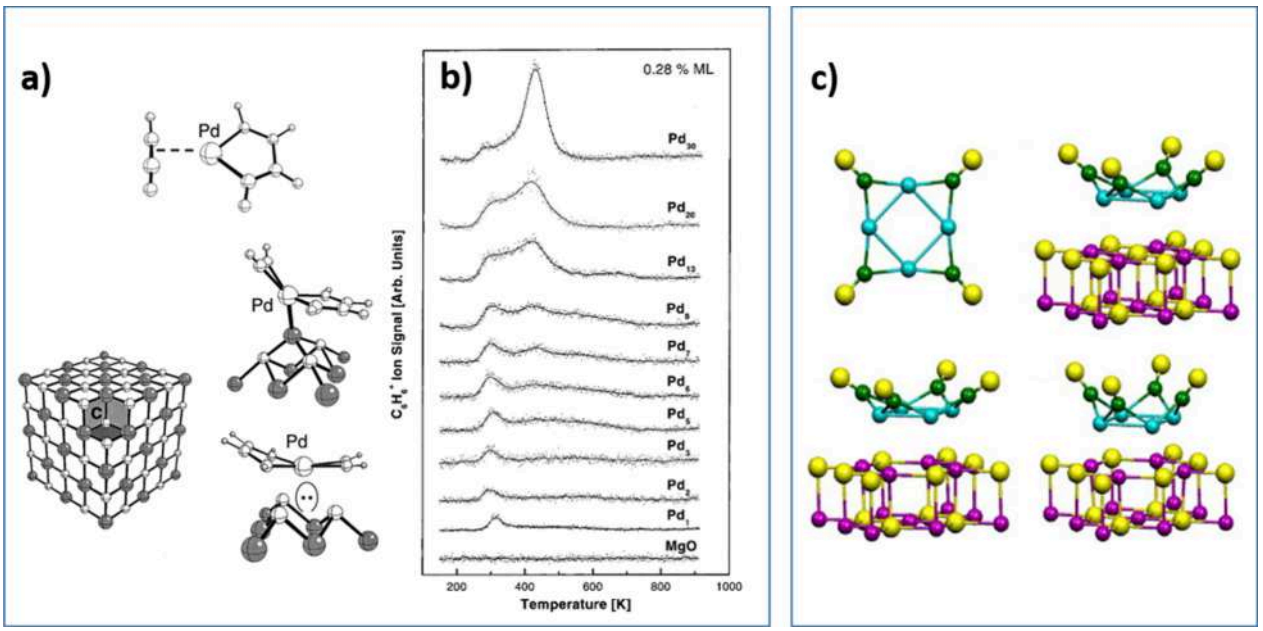


**Figure 4.** (a) Optimized structures of the complexes: $Pd(C_4H_4)(C_2H_2)$, $MgO\text{-}O_{3c}\text{-}Pd(C_4H_4)(C_2H_2)$, and $MgO\text{-}F_{3c}\text{-}Pd(C_4H_4)(C_2H_2)$. The two defect-sites are represented in a cube of MgO for illustration. (b) Catalytic $C_6H_6$ formation for different Pd cluster sizes obtained from temperature-programmed reaction experiments. The bottom spectrum shows that for clean MgO(100) films no benzene is formed. Cluster coverage is 0.28% of a monolayer for all cluster sizes, where one monolayer corresponds to $2.25 \times 10^{15}$ atoms/cm$^2$. (c) Structure of $Ni_4(CO)_4$ with CO in bridge positions (top), and unsupported cluster and cluster supported on a regular MgO(100) terrace cluster supported on a neutral $F_s$ center, and cluster supported on a charged $F_s^+$ center (bottom). Adapted with permission from refs 51 and 84. Copyright 2000 American Chemical Society and Copyright 2005 Elsevier.

One early and emblematic example is the use of palladium single atoms for the cyclotrimerization of acetylene,[80] where Gianfranco demonstrated that even a single Pd atom is sufficient to efficiently catalyze this transformation. The cyclotrimerization of acetylene to benzene on palladium single crystals had already been widely studied,[81] with Pd(111) being the most catalytically active surface. In particular, it has been shown that the reaction can proceed through the formation of a stable $C_4H_4$ intermediate that can add a third acetylene molecule, ultimately forming benzene. However, temperature-programmed reaction (TPR) spectra collected by Ueli Heiz's group revealed that, while larger Pd clusters enhance benzene production,[80] even a single Pd atom can effectively catalyze this transformation. Intrigued by this experiment, Gianfranco uncovered the subtle interplay between the isolated palladium atom and its oxidic support, revealing how specific surface defects enable the single Pd atom to become catalytically active.[51,82] Specifically, the electronic structure of Pd changes when supported on an oxide due to the support electron-donating capability. The oxide surface, in fact, acts much like a ligand in coordination chemistry, supplying additional electron density that strengthens the Pd atom capacity to back-donate charge to the adsorbed hydrocarbon. When the support contains no defects, the isolated Pd atom lacks the ability to add and activate three acetylene molecules, an essential step in the reaction. In this case, the isolated Pd atoms remain unaffected by the regular oxide anions of MgO(001) terraces, as their basicity is too low to significantly enhance electron density on the metal. A different scenario arises at low-coordinated oxide anions, such as defect sites found at edge ($MgO\text{-}O_{4c}$) and corner sites ($MgO\text{-}O_{3c}$). Because these sites experience a lower Madelung potential, their anion basicity is substantially higher, leading to increased charge donation to the metal atom, which can then make them catalytically active. Moreover, oxygen vacancies, which contain two electrons confined in the cavity left by a missing oxygen atom, exhibit strong basicity and enhance the catalytic efficiency of adsorbed Pd atoms in a way similar to low-coordinated oxide anions (Figure 4a,b).

This groundbreaking work served as the foundation for a long series of follow-up studies on metals supported on both pristine and defective oxide surfaces.[82] These studies demonstrated how variations in the substrate nature influence the electronic structure, magnetic behavior, and catalytic performance of the supported metal species, providing deeper insight into fundamental structure−property relationships and their relevance for material engineering (Figure 4c).[31,34,82−85] Many of these follow-up works were carried out in collaboration with Notker Rösch, using the scalar relativistic program ParaGauss[86] developed within the Rösch group at the Technical University of Munich, Germany.

**2.4. Defects in Solids.** As shown in the previous paragraph, defects are important in catalysis and often play a crucial role in determining the bulk properties of solids, influencing optical absorption and emission, the mechanical and electrical characteristics, as well as the reactivity.[87] Even at concentrations as low as $10^{16}$ cm$^{-3}$, defects can have a dominant impact on both physical and chemical properties of inorganic materials. A well-known example is the formation of color centers (or *F*-centers, from the German word *Farbe*, meaning "color") in ionic halides,[88,89] where an electron trapped in an anion vacancy gives a normally colorless solid a deep blue hue.

Anion vacancies, in particular those in oxide materials, are a particularly important class of defects, highly relevant in catalysis. Gianfranco made seminal contributions in ration-


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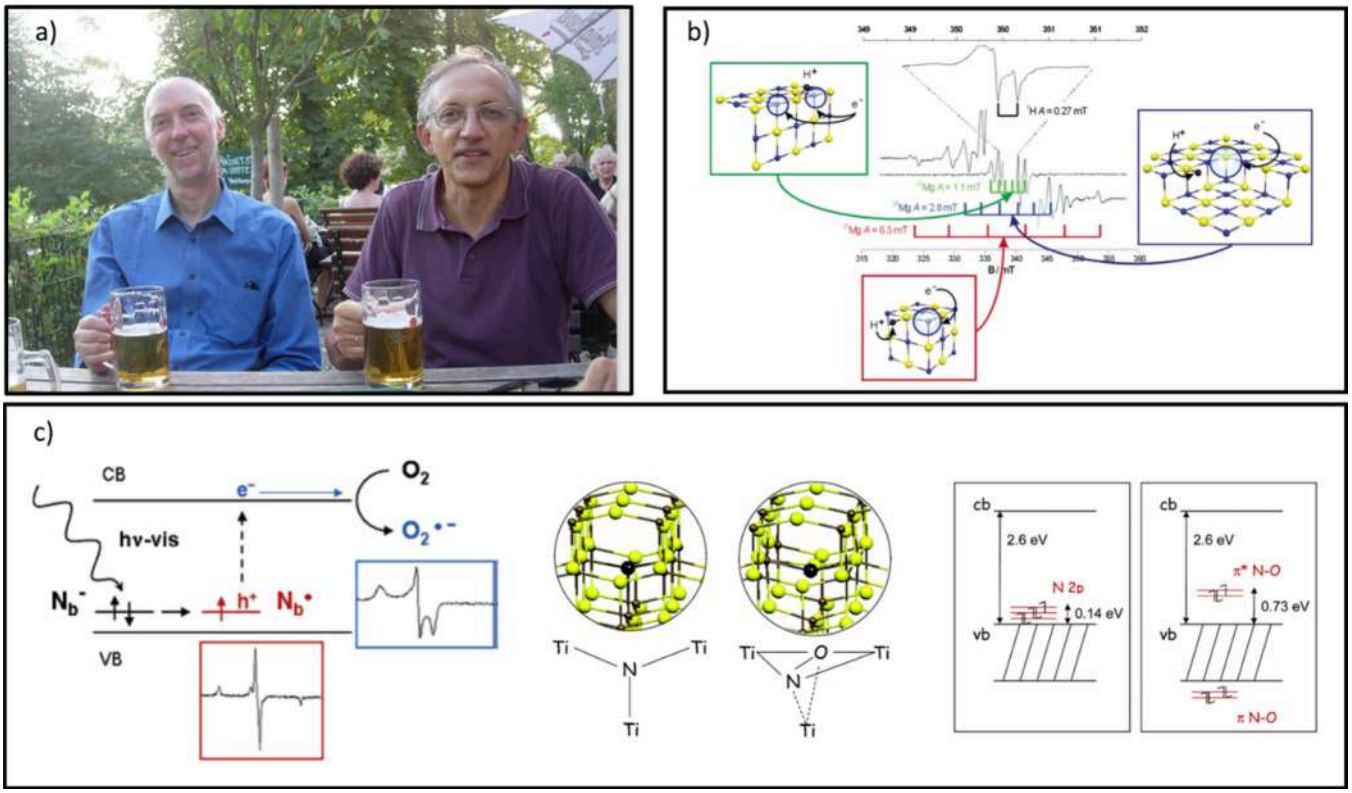


**Figure 5.** (a) Gianfranco Pacchioni and Elio Giamello in Berlin, year 2009 (courtesy of Elio Giamello). (b) Electron trapping sites on MgO (reprinted with permission from ref 98. Copyright 2006 American Chemical Society. (c) Mechanism of photoinduced electron transfer in N-doped sample and atomistic models and related electronic band structure for substitutional and interstitial N-doped anatase $TiO_2$. Adapted with permission from refs 39 and 40. Copyright 2005 American Chemical Society and Copyright 2006 American Chemical Society.

alizing their nature in systems like $SiO_2$ and MgO.[41] These two materials represent two cases of oxides with pronounced covalent and dominant ionic character, respectively. By comparing them, Gianfranco was able to draw general guidelines about the nature of these point defects in oxide materials. Importantly, oxygen vacancies in oxides can be either neutral or positively charged. In this last case the defect is paramagnetic and EPR studies − in particular hyperfine coupling constants − provide key information about their structure. This was recognized by Gianfranco in his work on $SiO_2$ defects, where the comparison between experimental and computed $^{29}Si$ and $^{17}O$ hyperfine constant was instrumental in order to obtain the correct structure of the defect and correctly use DFT methods in this context. This was highlighted in a seminal paper published in the year 2000 in collaboration with John Weil, one of the most influential EPR researchers worldwide. The work, titled "*Theoretical description of hole localization in a quartz Al center: The importance of exact electron exchange*"[90] solved a controversy between experiment and theory, concerning the structure of the $[AlO_4]^0$ defect center in irradiated quartz. The $[AlO_4]^0$ defect consists of an unpaired electron in a localized orbital on one of the four nearest O atoms to the Al impurity. Analysis of the hyperfine coupling parameters for $^{27}Al$, $^{29}Si$, and $^{17}O$ by Weil[91] provided clear experimental evidence for the localized nature of the unpaired electron up to at least 35 K. The derived model consisted of an Al atom substituting for a four-coordinated Si cation with an unpaired electron located in a nonbonding O orbital or, in different terms, a localized hole center. This model was challenged by theoretical papers based on supercell calculations with proper inclusion of boundary conditions and DFT that predicted a fully delocalized nature of the defect at 0 K.[92−94] The validity of the experimental data could not be questioned and the computation of the hyperfine interactions for different model defects with localized or delocalized structure clearly validated the original experimental model, bringing into evidence the importance of the treatment of exchange in DFT and the well-known problem of the self-interaction correction. Also in this case, Gianfranco's methodological approach emphasized the importance of reliable experimental data in validating theoretical models, stressing that great care is needed when DFT is used to describe the localization or delocalization of excess electrons and holes in inorganic solids, which are a key element in efficient redox catalysts.

The hyperfine interaction as a key observable for the correct determination of defect structures emerged again a few years later in the study of surface vacancy defects on MgO, in close collaboration with Elio Giamello from the University of Turin (Figure 5a). By the late 1990s, growing interest emerged within the surface chemistry and surface science communities regarding the role of point defects at the surfaces of metal oxides and in particular on the nature of oxygen vacancies on the surface of MgO. These defects were increasingly recognized for their influence on the chemical and catalytic properties of supported metal oxides. Giamello and his group were using EPR to study the electron trapping properties of polycrystalline MgO surfaces. In short, the white MgO powder, after UV irradiation in the presence of molecular hydrogen turned into a deep blue color and displayed a distinct EPR


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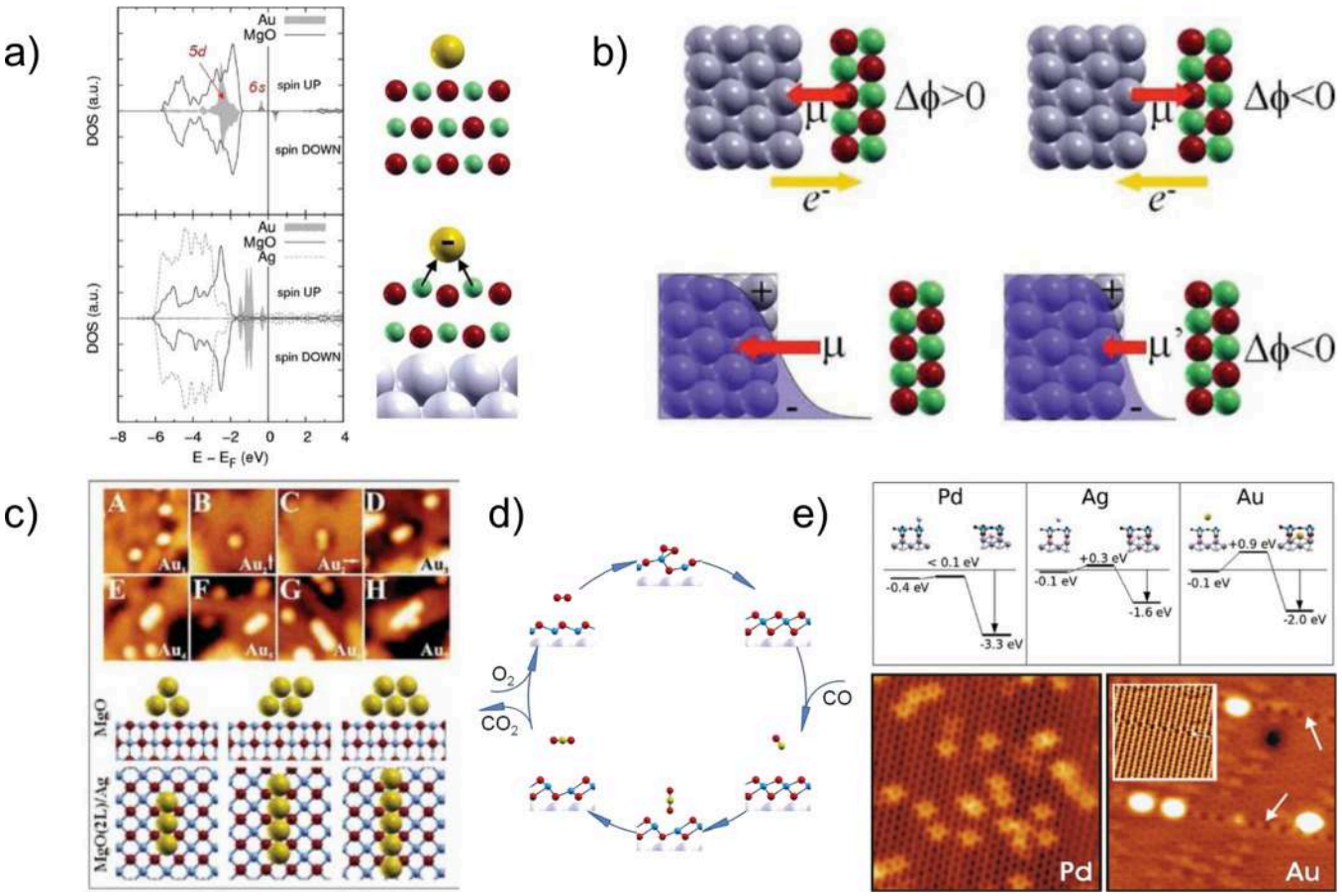


**Figure 6.** Properties of 2D oxide films on metal substrates. (a) Density of states (DOS) and adsorption geometries for $Au_1$ on MgO(100) and MgO/Ag(100). (b) Two major contributions to the change in work function Φ induced by an ultrathin dielectric layer on a metal: charge transfer at the interface and compressive electrostatic effect. (c) STM topographic (top) and DFT calculated (bottom) Au linear clusters on MgO/Ag(100), Adapted from ref 110. Copyright 2008 American Physical Society. (d) CO oxidation mechanism FeO/Pt(111) involving the formation of the active $FeO_2$/Pt(111) phase starting from FeO/Pt(111). (e) Energy profiles for Pd, Ag, and Au insertion into the silica film (top) and STM images for Pd and Au. Adapted with permission from refs 118 and 119. Copyright 2008 Wiley and Copyright 2009 Elsevier. All panels are reproduced with permission from ref 104. Copyright 2011 American Chemical Society.

spectrum, characterized by small $^{1}H$ and $^{25}Mg$ hyperfine interactions. These experimental evidences were in very good agreement with those reported for trapped electrons in bulk anion vacancies of ionic solids (*F* centers) and the most natural explanation was the formation of similar centers at the surface of the oxide, indicated as $F_s^+$ centers, where "s" stands for surface and the + charge indicates the paramagnetic defect.[95] However, the high cost for the oxygen vacancy formation, with respect to the rather mild experimental conditions and the issue of charge compensation, were the driving force to look for alternative models. These were first proposed by Gianfranco to be morphological surface defects such as step edges and reverse corner sites,[96] which do not belong to the class of "oxygen vacancies". However, the final solution to the puzzle once again was revealed by the measurement of hyperfine interactions. The observation of large Mg hyperfine coupling constants in high-resolution EPR experiments provided evidence for a large spin density localization at single Mg ions.[97] This new piece of experimental evidence immediately triggered Gianfranco's curiosity and led to the discovery that low coordinated $Mg^{2+}O^{2-}$ surface sites act as electron traps stabilizing excess electrons in the form of $[(H^+)(e^-)]$ proton−electron pairs (Figure 5b).[98] This discovery reshaped the understanding of electron trapping, highlighting the role of naturally occurring surface defects in stabilizing excess electrons. Of course, while excess electron-trapping sites on polycrystalline MgO are not due to oxygen vacancies, such vacancies still play a crucial role in surface chemistry and catalysis in particular when reducible oxides such as $TiO_2$ are involved, as described in an important feature paper in collaboration with Annabella Selloni.[99] This marked the second major highlight of the collaboration between Gianfranco and Elio Giamello. In a series of follow-up influential papers,[100−102] they provided critical insights into the origin of the photoactivity of nitrogen-doped $TiO_2$, dispelling misconceptions about impurity doping and its role in photocatalysis under visible light. Finally, by combining *in situ* photoinduced EPR spectroscopy to monitor the photochemistry of N-doped $TiO_2$ with DFT calculations, they identified the nature of the highly debated photoactive species responsible for harnessing visible photons in photocatalytic reactions (Figure 5c). Their findings demonstrated that the photoactivity arises from intraband gap states associated with $NO_x$ centers, where interstitial nitrogen atoms are bound to oxygen lattice ions.


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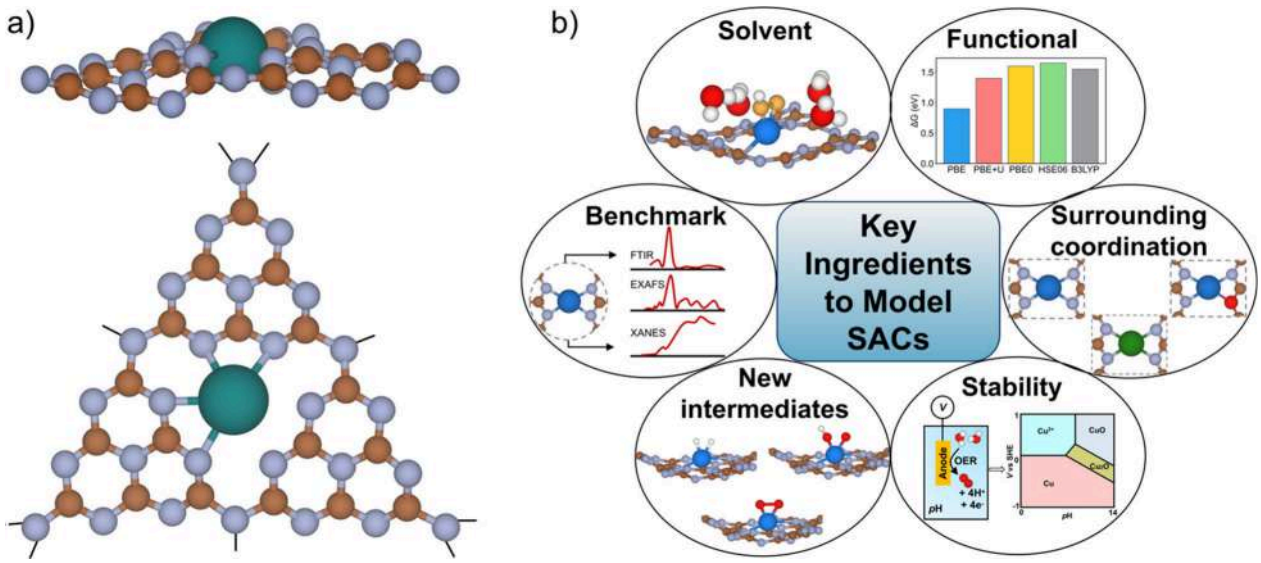


**Figure 7.** (a) Side and top view of a palladium single-atom supported on the heptazine pore of carbon nitride and (b) key ingredients to model single-atom catalyst.

## 3. CHEMISTRY AT THE INTERFACE

**3.1. Catalysis on Oxide Ultrathin Films on Metals.** In early 2000, the emergence of nanotechnology stimulated an interest in low-dimensional materials. A team of Italian researchers, led by Gianfranco, which included experimentalists (Sergio Valeri and Gaetano Granozzi) and theoreticians (Cesare Pisani and Alessandro Fortunelli), teamed up to investigate the properties of oxide ultrathin films deposited on metal surfaces. In a seminal work, Gianfranco and collaborators compared the adsorption properties of two metal atoms with different electron affinities, Au and Pd, on the MgO(100) surface and on MgO films supported on Mo(100).[103] They found that while Pd atoms had very similar adsorption properties and remained neutral on MgO(100) and MgO/Mo(100), Au atoms would become negatively charged on the thin films as demonstrated by the double occupation of the 6s states (Figure 6a), whereas they are neutral on the oxide surface.[37] Further analysis highlighted that the charge transfer from the metal/oxide interface to the adsorbed atom is more favorable for thinner films and further stabilized by a polaronic distortion of the oxide around the adatom (Figure 6a).[104] A considerable reduction of the work function, induced by a compressive effect of the insulating film on the metal electronic tails (Figure 6b), contributes to promoting the electron transfer to species with high electron affinity via electron tunneling through the thin insulating film.[105,106]

The Au atoms charging was proved experimentally by STM for MgO/Ag(100) by Hajo Freund and co-workers in a follow-up collaborative work.[36,107] This contribution also started a fruitful collaboration between Gianfranco's and Hajo's groups, which continued for many years. Combining Gianfranco's group DFT calculations with Hajo's group STM measurements on well-defined ultrathin films, they demonstrated that the charge transfer was not only possible for isolated atoms but also for metal clusters, where interestingly also the shape of the cluster is affected by the charge transfer. For example, an $Au_{20}$ cluster, which prefers a 3D shape on MgO(100), takes a flat shape wetting the oxide surface on a MgO/Mo(100) ultrathin film,[108] due to the charge transfer from the metal substrate. The effect was then confirmed experimentally by STM,[109] where Au clusters were found to have a 2D shape on MgO(3L)/Ag(100) in contrast to the 3D shape observed on MgO(8L)/Ag(100). Similarly, smaller Au clusters form linear shapes on ultrathin MgO films on Ag(100) (Figure 6c).[110]

Besides metal clusters, also molecules were predicted to become negatively charged on the supported oxide film.[111,112] Remarkably, $O_2$ molecules are activated on the oxide ultrathin film, where it was predicted by DFT calculations to form a superoxo $O_2^-$ paramagnetic species on MgO/Mo(100). This effect was confirmed by low temperature EPR spectroscopy.[113] These examples demonstrated the opportunity of tuning the structural and electronic properties of metal clusters and molecules on 2D oxides on metals with important implications in catalysis. Such oxides layers can form on the surface of metallic nanoparticles used in catalysis when supported on reducible oxides, such as $CeO_2$, undergoing the so-called "strong metal surface interaction" (SMSI), which is known to have a role on the catalytic properties of the nanoparticle under operating conditions.

An example of ultrathin oxide film enhancing the catalytic activity of a metal is the monolayer FeO(111)/Pt(111), another system investigated in depth by Gianfranco and Hajo's groups. While at low $O_2$ pressures ($<10^{-3}$ mbar) FeO/Pt(111) films are essentially inert for CO oxidation, at higher pressures, thanks to the structural flexibility of the monolayer, the film reconstructs and forms a new phase of $FeO_2$ stoichiometry. This oxygen-rich film was found to be catalytically more active than Pt, and to oxidize CO to $CO_2$ (Figure 6d).[114]

Another important class of oxide thin films are porous materials, and Gianfranco contributed to this field by studying the properties of 2D silica monolayers ($SiO_{2.5}$/Mo(112)), bilayers ($SiO_2$/Ru(0001)), and their amorphous structures. The peculiarity of these films is that their surfaces are inert, but their porous structure allow for the size-selective diffusion of metal atoms and small molecules into the nanopores beneath the surface modifying the chemical properties of the film (Figure 6e).[115] The collaboration between Gianfranco's and Hajo's groups revealed essential also on this topic to unravel the characteristics of the pores and the adatoms that allowed penetration through the porous films.[116,117] As an example, Pd


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ACS Catal. 2025, 15, 10271−10285

atoms diffuse through the silica rings to the Mo surface, perturbing the electronic structure of the film locally as detected by STM (Figure 6e). Conversely, due to the larger size Au atoms are not able to penetrate through the silica film and aggregate along line defect (Figure 6e).

**3.2. Approaching Single-Atom Catalysis.** Single-atom catalysts are now emerging as a promising class of catalysts in which individual metal atoms are dispersed on solid supports, such as metal oxides, metal surfaces, carbon-based materials, or zeolites.[120−128] SACs merge the positive aspects of both homogeneous and heterogeneous catalysts.[129−131] Besides, they maximize the exposure of active metal sites and reduce the amount of used metal during the synthesis, enhancing catalytic efficiency, two aspects of paramount importance for making more sustainable chemical processes.[132] The term "single-atom catalysts" appeared in 2011 in a seminal paper from Tao Zhang et al.[133] and widely afterward.[51,134−136] However, the concept of catalytically active single metal atoms was anticipated by Gianfranco through seminal surface science studies, as shown in Section 2.3, where the cyclotrimerization of acetylene on MgO-supported $Pt_1$ species has already been discussed.

Since then, Gianfranco has been deeply intrigued by the unique reactivity of single-atom catalysts, and in recent years, his research has consistently advanced the field. He has investigated the nature of single-atom catalysts supported on oxide materials in collaboration with Phillip Christopher,[137−139] and single-atom catalysts supported on carbon-based carriers with In-Hwan Lee and some of us.[140−144] The shift from oxide to carbon-based materials, which came later in his career after decades of work on oxides, reflects Gianfranco's ability to adapt and address emerging challenges in the catalysis field. Oxide-supported SACs pose modeling and characterization challenges due to their complex electronic structure, dynamic surface interactions, and strong metal−support effects. In contrast, carbon-based supports offer unique opportunities for tailoring coordination environments yet demand a distinct understanding of metal−carbon interactions and defect chemistry. This shift was also necessary because, while oxide-based SACs have been extensively studied and validated through decades of surface science studies, carbon-based SACs have only recently become accessible,[126,128] and today the majority of SACs are prepared on nitrogen-doped carbon carriers (Figure 7a).

Over the past years, Gianfranco has integrated coordination chemistry concepts into heterogeneous catalysis, and focused on a variety of important reactions, from organic synthesis to hydrogen and oxygen evolution reactions (HER and OER), as well as $CO_2$ conversion. For example, Gianfranco and co-workers showed that the reactivity of hydrogen with SACs involves the formation of adducts involving the molecular adsorption of the molecule,[145] in analogy with well-known Kubas−Crabree dihydrogen and dihydride complexes,[146−150] with relevant implications to the catalytic activity in hydrogen-related reactions, such hydrogen evolution or hydrogenations. Furthermore, this work was extended to other chemical species and reactions, and Gianfranco showed that a similar result is obtained for the oxygen evolution/reductions reaction, where oxygen complexes can form,[151] in analogy with organometallic chemistry, where the iron-peroxo adduct of the heme-group is the workhorse.[152−154] Gianfranco also demonstrated how rich is the chemistry of SACs, showing that oxygen evolution/reduction should involve the formation of unconventional intermediates, with respect to classical heterogeneous catalysis (metal surfaces).[155] This complex reactivity applies also to single-atom alloys (SAAs), metallic systems formed by metal impurities in a metallic matrix.[156] He was also recently intrigued by the use of SACs in complex reactions of key relevance for the fine chemical and pharmaceutical sector, and, jointly with experimental groups, he has investigated the active phase, catalytic pathway, and performance of SACs supported on N-doped graphene and carbon nitride in hydrogenations, oxidations, Ullmann-type C−O coupling reactions, cyclo-addition reactions, and light-driven C−X coupling.[157−161]

Beyond reactivity studies, Gianfranco also presented fundamental advances on the understanding of the structure of SACs,[162] through the description of the electronic structure using accurate functionals and the correct setup.[163,164] In these studies, Gianfranco and his co-workers analyzed the role of the functional in describing the HER and OER on 16 transition metal (TM) atoms embedded in N-doped graphene. Their findings suggested that using PBE appears acceptable for 4*d* and 5*d* metals, while for 3*d* metals, the PBE+U or PBE0 approaches are recommended, particularly for magnetic ground states.[163,164]

Since the active site in SACs is a metal atom, its performance is influenced by factors such as the local coordination, the support, and the type of metal. Gianfranco conducted several studies to examine the impact of these variables.[165−168] His findings have suggested that the surrounding environment plays a crucial role in determining the catalytic activity of specific reactions. In some cases, altering just one atom coordinated to the metal site can lead to different catalytic behavior. For these reasons, in many of his recent keynote lectures, he has stressed to the scientific community the critical importance of accurately defining and controlling the local environment of single metal atoms, not only through advanced characterization techniques, but also via rigorous theoretical modeling. In particular, he has highlighted the need for precise DFT calculations that reflect the actual coordination structures observed experimentally. Without such alignment, predictions of activity, selectivity, and reaction pathways may be misleading.

Gianfranco has also recently studied the stability of SACs under electrochemical conditions (e.g., pH and voltage).[169] His approach involved constructing a thermodynamic cycle and integrating experimental data with density functional theory (DFT) calculations. Specifically, he used Pourbaix diagrams to examine SAC stability in both reductive and oxidative environments, identifying those that are prone to dissolution or transformation into other chemical species under varying pH and applied voltage.[169] Last but not least, four important aspects that Gianfranco has investigated in SACs are the search for scaling relationships to describe the OER,[170] the role of the solvent,[171] the influence of the entropy of adsorbed species on the reactivity of SACs,[172] and the importance of the oxidation state of the active site for a more accurate description of catalytic performance.

Overall, Gianfranco's recent work has been instrumental in advancing the fundamental understanding of SACs (Figure 7b). His efforts have consistently emphasized two key principles: (i) the necessity of embracing structural and electronic complexity when modeling SACs to achieve meaningful and reliable predictions, and (ii) the critical importance of validating theoretical models through rigorous experimental data. To sum up, we can confidently say that his


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research has laid the groundwork for the rational design of next-generation single-atom catalysts with enhanced activity, selectivity, and stability.

## CONCLUSIONS

Gianfranco Pacchioni's career exemplifies the intellectual rigor, interdisciplinary insight, and scientific integrity that drive fundamental advances in science. His early interest in metal clusters evolved into a long journey to elucidate atomic-scale mechanisms underlying surface reactivity. Through groundbreaking contributions to the understanding of oxide surfaces, point defects, and single-atom catalysis, he has reshaped theoretical approaches in heterogeneous catalysis, demonstrating that reactivity is governed not only by the chemical identity of active sites but also by their local structural and electronic environments. His work has established critical links between molecular coordination chemistry and extended solid-state systems, offering a unified framework for interpreting catalytic function.

Equally influential is the scientific ethos Gianfranco has fostered, marked by collaborative spirit, dedication to mentorship, and a deep commitment to public engagement. He has advanced not only the frontiers of surface science but also the methodology by which catalysis is studied and communicated. As the field transitions toward more complex, multiscale, and data-integrated models, his clarity of thought and conceptual depth continue to provide essential guidance.

Gianfranco's legacy extends far beyond his publications. It resides in the global community of scientists he has mentored and inspired, in the methodologies he refined, and in the enduring impact of his ideas. For us privileged to work with him, his example remains a source of inspiration, urging us to pursue science with precision, creativity, and purpose.

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### Author Contributions

The manuscript was written with contributions from all the authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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