**Relazione Scientifica sui Risultati dell'Attività di Ricerca durante una Visita nell' ambito del Programma STM del CNR**

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Area della Ricerca del CNR – Pisa

**Dipartimento di afferenza:**

Scienze Fisiche e Tecnologie della Materia

**Titolo del programma:**

Nanoporous Metals – Structural and Catalytic Properties via Computational Simulations

**Istituzione ospitante:**

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**Obiettivi:**

The aim of this STM visit is to unveil the relationship between structure and catalytic function and the origin of enhanced catalytic performance in nanoporous platinum via advanced computational simulations. The final goal is to design platinum systems with optimal catalytic activity for applications in low-temperature hydrogen fuel cells for sustainable and energy-efficient electrical power. Impact on the general theme of nanoporous metals and their science and technology is also aimed at.

## Report

Nanoporous metals have attracted an explosive interest in the last 10 years [1-11]. These materials are usually obtained by electrochemical leaching an alloy of the target metal with a more electropositive element. The final outcome is a metallic nanostructure in a meta-stable state whose framework exhibits continuously connected cavities (pores) with nanoscale dimensions (typical pore diameter between 1 and 5 nm) and reaching up to the surface. These peculiar structural features endow nanoporous metals with unique properties leading to applications in catalysis [1-6,12], sensors [7,10], and opto-electronic devices [8,11], with several other possibilities currently being investigated. Applications in the field of catalysis remain the most appealing, as nanoporous metal catalysts promise to solve such fundamental scientific and societal problems as fuel cell [6] and water splitting [13]. In this

respect, the atomistic and electronic structure of the nanoporous surfaces clearly play a crucial role, and rigorous information on these topics is strongly needed to rationalize experimental findings and orient the synthesis toward improved materials with enhanced activity and selectivity.

Despite an intense experimental effort, in fact, basic fundamental questions still remain on these systems concerning: (i) their exact geometric features (e.g., coordination environment of surface atoms, electronic surface structure rearrangements); and (ii) the relationships between these features and the corresponding catalytic properties. Experiment has provided only limited insight into the answers to these questions, as characterization techniques are limited by the complexity of nanoporous structures, exhibiting different length scales and with inner surfaces (most difficult to characterize experimentally) playing an important role [9]. Development in this field is hindered by the present lack of fundamental knowledge and understanding on structural and response properties, leaving a trial-and-error approach (expensive in terms of human resources, of possibly limited thoroughness and transferability) as the only viable possibility to advance research.

The goal of this visit is to achieve this knowledge and understanding via first-principles-based theory and reactive dynamics simulations, aimed at steering experiments in synthesis and optimization. Due to the intrinsic and technical complexities of the problem, previous simulations on nanoporous metals [14,15] have been limited to solving diffusion equations and kinetic Monte Carlo models of rates, which furnish information only on the mesoscale features of these materials [16] ignoring the atomistic details of the nanoporous surfaces needed for materials optimization. Atomistic models derived from these studies [17] suffer from constraints implicit in spinodal decomposition and the assumption of a bi-continuous structure. Other methods to create atomistic models of nanofoams [18] are subject to the uncontrollable effect of generating a random distributions while ignoring the underlying bonding network plus additional constraints associated with artificially enforced periodic boundary conditions. A link of such structural models with catalytic properties has been proposed for nanoporous gold [19] but could be based on only very general features such as the presence of stepped or vicinal surfaces, or the residual presence of the electropositive element component [20]. However, under the harsh operating conditions of an electrochemical cell such descriptions are doubtful. Moreover the paucity of predicted steps is not consistent with the experimentally determined massive number of active sites. Finally, the electropositive component is often nearly absent from the final nanoporous structures. For example as discussed below [6] the Ni-Pt nanoporous systems leads to improved catalysis despite the observation that no Ni remains near the surface! Current theoretical modeling has thus not been able to provide a consistent rationale to explain the experimental data on these complex phenomena.

The project work of this STM has consisted of the following steps:

*Step 1:* Prepare Ni-Pt nanoparticle models of realistic size and shape and in a range of compositions (starting with crystalline-like particles of the order of 5-10 nm diameter with random alloy chemical ordering as initial configurations) using the Pt/Ni ReaxFF developed by the Caltech group.

*Step 2:* Simulate the Ni de-alloying process (i.e. leaching) via dynamical simulations leading to the extraction of the electropositive element (Ni).

*Step 3:* Analyze the resulting structures in terms of number of internal and external surface sites, their local coordination environment (radial distribution functions) and the corresponding stress and strain fields, the bulk and surface entropy and free-energy, and the porosity percolation characteristics of the overall nanostructure, as a function of the particle initial size and composition.

*Step 4:* Investigate the catalytic properties of the system via density-functional theory (DFT) modeling of surface sites – in the DFT simulations appropriate treatable models of the nanoporous active surfaces are derived.

*Step 5:* Correlate the catalytic activity to the geometric and electronic state of surface atoms including the previously derived analysis of local coordination environment and the corresponding stress and strain fields – compare/contrast with non-porous systems (standard Pt nanoparticles or extended surfaces) and with available experimental information.

Let us then describe the main results obtained through this work.

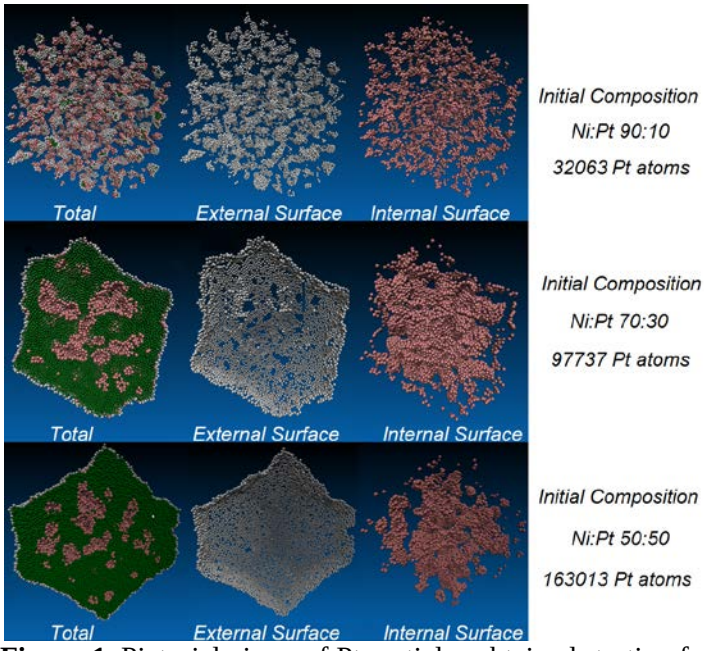


**Figure 1.** Pictorial views of Pt particles obtained starting from truncated-octahedral Ni-Pt nanoparticles about 10 nm in diameter with different initial compositions (ranging from 50:50 to 70:30 to 90:10 ratio in Ni:Pt) and

de-alloying and equilibrating them at 70 °C. “Total” is the entire particle, “External surface” shows only the external surface of the particle, “Internal surface” shows only the internal nanopores of the particle. Atoms on the external surface of the particle in white, atoms on the surfaces of the internal nanopores of the particle in pink, and inner (core) atoms in green. For clarity, only a cross-section (half) of the particle is shown.

Figure 1 shows pictorially the results of our investigation conducted on truncated-octahedral Ni-Pt nanoparticles about 10 nm in diameter (about 326000 atoms in total) with various initial compositions (ranging from 50:50 to 70:30 to 90:10 ratio in Ni:Pt). Configurations obtained after de-alloying and equilibrating the particles at the temperature of catalytic experiments (70 °C) are shown. “Total” is the whole particle, with atoms on the external surface of the particle in white, atoms on the surfaces of the internal nanopores of the particle in pink, and inner (core) atoms in green. For clarity, only a cross-section (half) of the particle is shown. “External surface” shows a view of only the Pt atoms on the external surface of the particle, while “Internal surface” shows a view of only the Pt atoms on the surfaces of the internal nanopores of the particle. Some statistical information has been obtained by considering different (4) seeds for each composition for the generation of the initial randomly alloyed configuration.

Even a simple visual analysis of Figure 1 (confirmed by more sophisticated structure recognition algorithms) shows that when the initial composition is too rich in Ni (i.e., Ni:Pt = 90:10) the final particle comes out fragmented into tiny clusters with no pores, whereas if the initial composition is too low in Ni (i.e., Ni:Pt 50:50) cavities exist within the particle but they tend to “close up” without reaching the surface. Already at compositions around 80:20 significant fractures rather than percolating nanopores start being observed within the interior of the nanoparticles which point to a mechanical instability [27] and thus a breaking of the nanoparticles into smaller pieces. On the other hand we find that an initial composition around Ni:Pt = 70:30 is nearly optimal for creating nanopores that percolate through the particle, reaching the surface. The percent of total surface sites (internal and external, which provide roughly equal contributions) for initial composition Ni:Pt = 70:30 is about 24-25% whereas it is around 15% for an initial composition Ni:Pt = 50:50, of which only ~9% are estimated to be accessible to reactant molecules because of pore constriction reasons.

These results are in excellent agreement with experiments [6], which show that the de-alloyed particles exhibit a surface area roughly doubled with respect to standard Pt particles of similar size and a peak in catalytic activity for an initial Ni:Pt composition around 70:30.

We also observe that for a particle with Ni:Pt = 70:30 initial composition but a smaller size (about 7 nm in diameter, not shown) the percent of surface sites is around 20%, i.e., is smaller than for the larger 10nm-diameter particle. This counterintuitive result (the percent of surface atoms should inversely

correlate with particle size) suggests that there is an optimal initial nanoparticle size as well as an optimal initial composition, thus rationalizing experimental results in nanoparticle size optimization [24].

Also interesting are the preliminary results concerning the atomic stresses of the surface atoms. Figure 2(a-c) compares the atomic stresses in a particle obtained after de-alloying a Ni-Pt particle with initial composition Ni:Pt = 70:30 (97737 final Pt atoms) with those of a regular truncated-octahedral pure Pt particle of a comparable size (98281 Pt atoms).

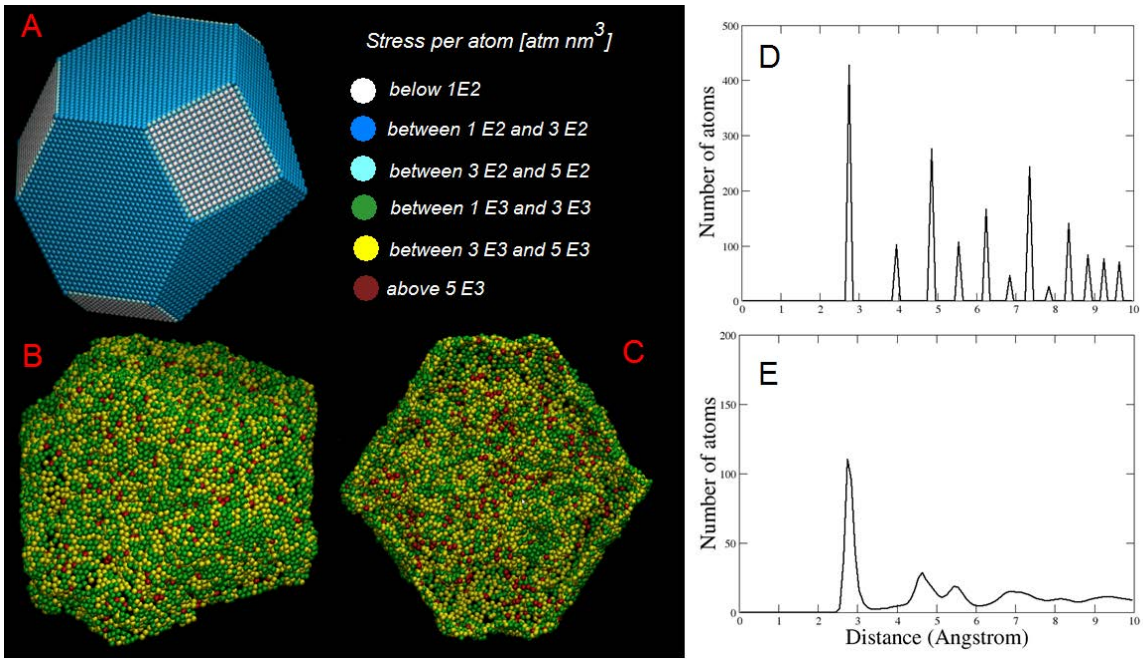


**Figure 2.** Atomic stresses at the surface of Pt particles: (a) a truncated-octahedral Pt particle of 98281 atoms; (b-c) two views (rear view in b, cross-section view in c with only internal and external surface atoms shown) of a Ni-Pt 70:30 de-alloyed particle (97737 final Pt atoms). Atoms are colored according to the value of their atomic stress as detailed in the legend. Radial distribution functions of Pt particles: (d) truncated-octahedral Pt particle of 98281 atoms; (e) Ni-Pt 70:30 de-alloyed particle of 97737 final Pt atoms.

Figure 2(a-c) shows that the atomic stresses on the surface atoms of the truncated octahedron are at least an order of magnitude smaller than those on the surface atoms of the nanoporous particle, supporting our hypothesis that complex bonding patterns that lead to strain at the surface play an important role in these materials. This is also confirmed by a comparison of the radial distribution functions of the two particles in Figure 2(d,e): the regular pattern of neighbors in the truncated-octahedron Figure 2(d) is blurred and shifted in the nanoporous particle Figure 2(e), with a lengthening of first-neighbor distances (the first peak in the RDF), the disappearance of the second neighbor peak at $\sqrt{2}$ distance, and a contraction and a broadening of third and fourth neighbor distances. It thus seems that the atomistic structure of nanoporous platinum is related to the amorphous

configurations found in nanoparticles [28] or kinetic-arrested arrangements in metallic glasses [29], so that the previous knowledge on the correlation between local topology and atomic-level stresses in the latter systems [30] may carry over to deepen the analysis of structure-property relationships in nanoporous particles. This analysis points out to a qualitative difference between the surface of regular and nanoporous systems which can be the origin of the difference in catalytic activity found experimentally, and this has been pursued further in the present project and combined with DFT simulations of catalytic properties as discussed below.

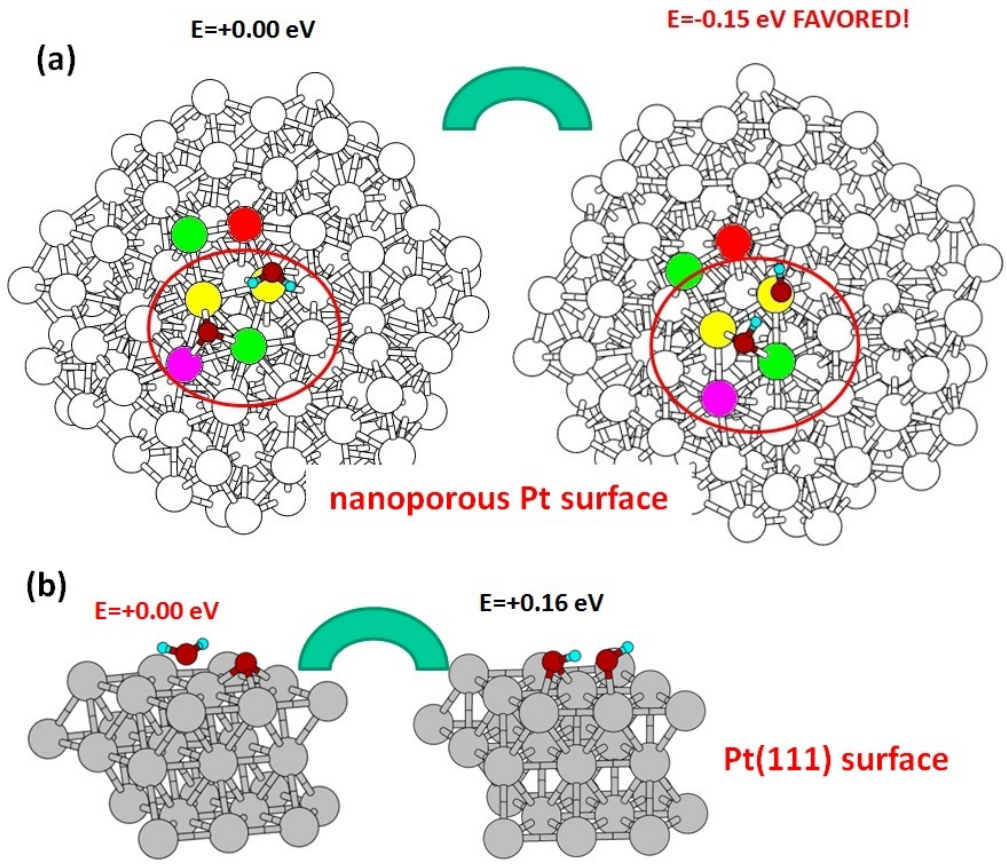


**Figure 3.** Energetics of the ORR rate determing step (rds) at the surface of Pt particles: (a) a portion of a Ni:Pt 70:30 de-alloyed nanoporous particle; (b) the Pt(111) surface. The color coding is as follows: O atoms in red, H atoms in light blue. In (a) Pt atoms not directly interacting with O atoms are colored in white, whereas Pt atoms interacting with O atoms are colored according to the value of their atomic stress (green = low stress, yellow = intermediate stress, magenta = high stress). In (b) Pt atoms are colored in dark gray.

The starting point of our analysis is previous work by the Caltech group [31] proving that the rate determining step (rds) of the ORR on the fcc Pt(111) surface in aqueous medium is the “oxygen

hydration" or the "inverse hydroxyl disproportionation" step, see Figure 3(b). This process corresponds to the formula:

$$O_{ads} + H2O_{ads} \rightarrow 2\ OH_{ads} \quad (1)$$

In other words, an oxygen atom adsorbed on the Pt(111) surface reacts with a water molecule also in contact with the same surface to give two adsorbed hydroxyl species (in this sense it corresponds in the reverse direction to a disproportionation of two hydroxyls into an oxygen atom and a water molecule). This process is energetically uphill by 0.11-0.16 eV in the absence of a solvent, leading to a reaction energy barrier of 0.23-0.28 eV, which further increases to around 0.5 eV when solvation effects of the acqueos medium are included. It is now our goal to understand what happens in passing from the regular Pt(111) system to the surface of the nanoporous particles. To this purpose, we have considered several sites on different particles produced by our protocol and depicted in Figure1, selecting those sites which most closely resemble a Pt(111) surface with its regular tessellation of equilateral triangles. We then created finite models of a size affordable for calculations at a first-principles (DFT) level by centering on a given site and including all Pt atoms within a sphere with radius such that the resulting cluster model did not contain more than 200 Pt atoms. Finally, the oxygen hydration step has been investigated on these cluster models, simultaneously testing its accuracy by comparison with results obtained with a smaller truncation radius.

In Figure 3(a), we report the results of an energetic analysis on a prototypical site on one of the Ni:Pt 70:30 particles, and we compare these with results obtained on the regular Pt(111) surface. It can be immediately be appreciated that the ORR rds, which is uphill on Pt(111), becomes energetically favored on the nanoporous surface. A very important observation is that we have verified that this change in the reaction energetics occurs on all the eight (8) sites selected on the 70:30 particle.

How does this change in the reaction energetics translate into a change in reaction rate ? In Figure 4 we report the energy profile of the oxygen hydration step on a given site of a nanoporous surface obtained via a nudged-elastic-band (NEB) calculation. This picture shows that the change in reaction enthalpy to negative values on nanoporous Pt is accompanied by a reduction in the reaction energy barrier from about 0.23-0.28 eV on Pt(111) to 0.05-0.10 eV on the nanoporous surface (solvent effects are not included here for simplicity, but can be taken as being additive). Again, this is confirmed in all the cases that we have considered for increasing our statistics.

This *proves* that nanoporous Pt particles obtained via dealloying Ni:Pt particles around 70:30 compositions must exhibit an increased ORR catalytic activity, in perfect agreement with experimental observations.

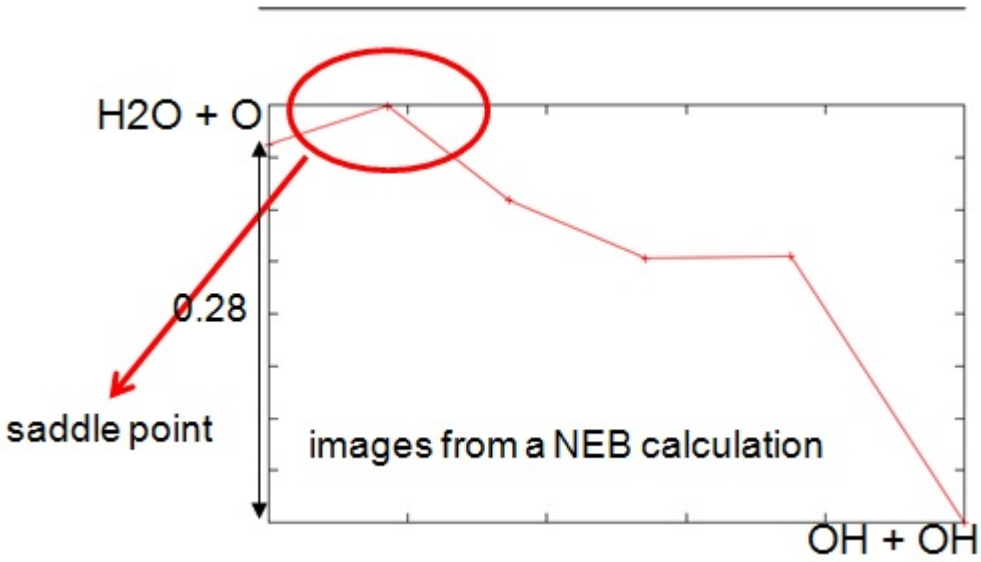


**Figure 4.** Energy profile of the ORR rate determing step (rds) on a specific site of a Ni:Pt 70:30 de-alloyed nanoporous particle.

What is the reason of this phenomenon ? The origins of this enhanced activity lie in the peculiar atomistic structure of the nanoporous surfaces and ultimately to its relationships to lowering of reaction energy barriers in the crucial inverse hydroxyl disproportionation step. First, the nanoporous character of the system obviously entails the presence of large surface areas. It can be estimated from a geometrical analysis of the 70:30 particles shown in Figure 1 that the catalytically active surface area is amplified 4-5 times with respect to crystalline particles, and is considerably increased even with respect to roughened pure Pt aggregates: roughly doubled, again in perfect agreement with experimental data [6]. Clearly, this increase is not obtained when the initial composition in Ni is too low (say – 50:50) so that the internal pores are less numerous, and one finds strictures as they connect to the external surface so that they are not accessible to reactants (percolation). As Figures 3 and 4 prove, this however is *not* the only reason. The fact is that the nanoporous surfaces obtained from our protocol are not rough, but rather are smooth, at least up to an initial Ni:Pt composition of 70:30, and for the most part exhibit a triangulated surface arrangement reminiscent of a regular Pt(111) surface. What makes a difference is then the subsurface layer, which is not in fcc stacking but exhibits a reduced coordination so that finally each surface Pt

atoms is surrounded by 7-8 – rather than 9 as on Pt(111) – first neighbors. It is important to note that Pt(100) has been shown to be much less catalytically active with respect to Pt(111) even though it presents a reduced coordination number of 8 with respect to 9, and this is due to the fact that reactants interacts too strongly with Pt(100) and are thus trapped into lower energy minima from which it is more difficult to escape. In contrast, on the nanoporous surfaces the dilemma of how to decrease the coordination number and increase the bond strain without roughening and disrupting the Pt-Pt bond network, which corresponds to enhancing the catalytic activity, is solved. Such smooth surface arrangements can also be shown to be robust to the harsh operating conditions of electrochemical ORR, at variance with the original Ni-Pt particles which contain subsurface electropositive Ni species which are at best metastable in reaction conditions and are thus effectively leached in real-world catalysts, leading to the nanoporous configurations environment. Clearly (and a more detailed analysis of our results confirm this), at some point the initial composition is so poor in Pt (i.e., for compositions over Ni:Pt 70:30) that these smooth surfaces cannot be obtained any more, the bonding network is disrupted, and the catalytic activity decrease, once more in perfect agreement with experimental data and actually providing *for the first time* a consistent explanation of the puzzle of a *maximum* catalytic activity for initial Ni_Pt 70:30 compositions.

Before concluding, it is worthwhile pointing out that the present research has many possible and promising developments. The widespread and overarching interest on nanoporous metals in general and on metal/oxide hybrid nanostructures justifies extending our work along two different lines: (1) study Al-Ni nanoparticles in which Al is the electropositive (electrochemically leached) component, and compare with Ni-Pt to explore drawing possible general principles and concepts in nanoporous metal structures; (2) simulate the de-alloying process in Ni-Pt nanoparticles using Reactive Molecular Dynamics (also developed by the Caltech team), assuming that a partial concentration of the electropositive element (Ni) remains at the surface but in oxidized form (NiO), thus producing hybrid nanoporous-metal(Pt)/oxide-nanoparticle(NiO) systems, and investigate their structural, mechanical and catalytic properties, and structure-property relationships.

These two possibilities are particularly important to broaden the results of the present investigation and achieve a full understanding of the behavior of both traditional nanoporous metals (Raney Nickel, obtained by leaching Al-Ni alloys, being the prototype and first historical example [32]) and the current research on novel systems different from Pt (such as nanoporous Au, obtained by leaching Ag-Au or Au-Fe-Ti alloys [2,20,33].

We emphasize that further development of the proposed work would also produce as side-products the tools to address significant scientific and computational problems in several other fields. For example:

1) Understanding the kinetic factors in de-alloying processes;

2) Determination of the surface free-energy and stress fields with atomistic details;

3) Prediction of mass transport processes through nanoporous structures;

4) Understanding the interplay between local and global structural features;

5) Understanding the effect of electronic surface structure reorganization in determining the catalytic response of Pt nanosystems;

which will be briefly touched upon and expanded below.

1) Kinetic factors in the de-alloying process are often neglected in the scientific literature on nanoporous metals, hindering rationalization of the experimental observations. For example, the difference between Ni-Pt and Co-Pt de-alloyed systems is usually attributed to electronic effects, overlooking the fact that both Ni and Co are only marginally present in the final porous nanostructures. It is much more sensible to speculate (and this should be specifically investigated) that this difference stems from the difference in Co-Pt and Ni-Pt bond strengths which leads to different kinetics of de-alloying. If this speculation will be confirmed by the computational results, it will direct future investigations to even more complicated (e.g., ternary) systems as viable candidates to achieve the optimal balance between barriers of atomic switching to obtain kinetic arrest in metastable yet well-organized bond networks. Moreover, our work would contribute improved fundamental understanding of structural dynamics in alloy nanoparticles, a very recent and promising research topic.

2) Atomistic information on the surface free-energy and stress fields in nanoporous systems is severely lacking. The reasons for this lie in the missing connection between local coordination environment and mesoscopic framework, i.e., in the lack of information on how the mesoscopic stress fields described by continuum theories are realized in non-standard configurations rather than in configurations only slightly perturbed with respect to crystalline lattices as assumed e.g. in quasi-continuum modeling. Our work would thus contribute to fundamental knowledge on off-lattice nanostructured systems.

3) The prediction of mass transport and diffusion processes through nanoporous structures is a topic of great interest in current nanoscience and nanotechnology with links to such challenging and important problems as mass transport in nano-confined systems. Here we would focus on the water/metal

interface which is of great interest e.g. in the field of electrochemistry, and expect to achieve an improved understanding of these phenomena.

4) Topics 2) and 3) rely on and should ultimately lead to a deeper understanding of the interplay between local and global structural features in nanostructured systems. This interplay is at the heart of multi-scale materials modeling in the crucial passage from the atomistic to the micrometric length scale. The proposed study is thus of general significance and has bearings with one of the central issues in current computational research in materials science, representing a significant test case from both scientific and technological points of view. The proposed research would both take advantage of recent progress and also contribute to further developments.

5) Despite numerous studies, a general understanding of the factors determining catalytic activity and selectivity of platinum-based structures has not been achieved. This is likely due to the complexity of the phenomenon, exhibiting a multi-dimensional phase space (i.e., several different factors playing an important role) with both geometric (topology of local coordination environment, atomic bond strains and stresses) and electronic (bond saturation, relative position of s and d states) effects affecting the final behavior. Our work, contributing to expand the range of sampled structural and electronic possibilities, would thus enrich the empirical structure/property database, and then if successful would shed further light on the origins of such a varied phenomenology.

These topics could be the basis of future STM visits.

In summary, the results obtained in the present STM represent a breakthrough in the field of H2 fuel cells as they clearly single out for the first time the main factors at the basis of the exceptional ORR catalytic activity of nanoporous platinum. These factors are traced back to the unique atomistic structure of these systems and to its relationships to lowering of reaction energy barriers in the crucial inverse hydroxyl disproportionation step. The presence of large surface areas (roughly doubled with respect to even roughened Pt pure aggregates, but amplified 4-5 times with respect to crystalline particles) exhibiting a smooth, triangulated surface arrangement coupled to a reduced coordination subsurface stacking constitute a nearly optimal catalyst. Further improvements can be reached by operating on (i) the fine details of the structure, in which the surface structural arrangement singled out as the most favorable to ORR should be maximized; (ii) the experimental conditions, on which novel ideas arosen from the present research and not reported as still unpublished are also currently being tested. The main

future challenge as indicated by our analysis is a more precise and predicted modeling of the kinetics of de-alloying which will enable one to achieve objectives (i) and (ii).

To conclude, we thank the STM program of Italian CNR for having made this visit possible. We aim at publishing the corresponding results, even in this preliminary but already revealing status, on high-impact scientific journals. Besides, they have already been the basis of a presentation at a previous conferences (FisMat2013, Milano, September 2013) and are planned to be such of two ones in 2014 as invited contributions.

We are confident that this is only the first result of a fruitful collaboration between CNR-Pisa theoretical chemistry group and the largest and one of most prestigious theoretical chemistry group in the world (Caltech has been ranked 1st in 2012 in Times Higher Education World University Rankings in both fields: “Engineering and Technology”, score: 94,4, and “Physical Sciences”, score: 93,4, see www.timeshighereducation.co.uk/world-university-rankings/2012-13/world-ranking; Prof. W. A. Goddard has more than 900 publications on peer-reviewed journals and a H-index of 103).

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