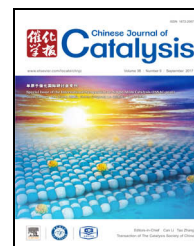


available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/chnjc](http://www.elsevier.com/locate/chnjc)

Perspective (Special Issue of the International Symposium on Single-Atom Catalysis (ISSAC-2016))

## Unravelling single atom catalysis: The surface science approach



Gareth S. Parkinson\*

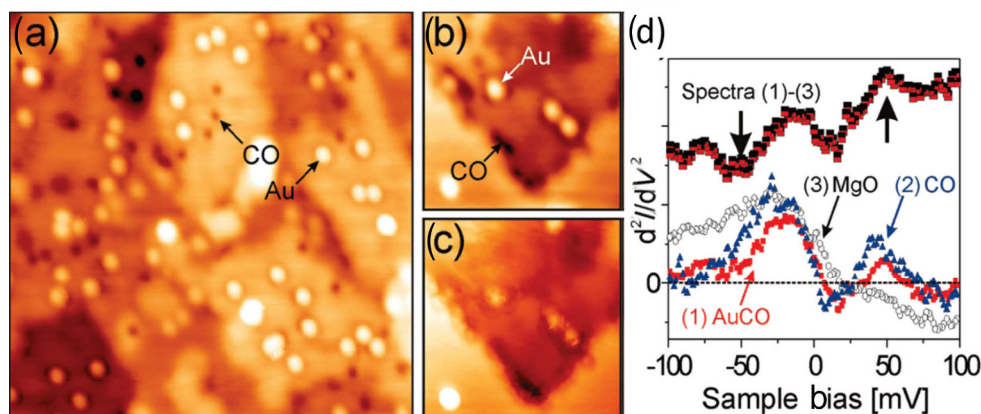
The rapidly emerging field of single-atom catalysis (SAC) aims to slash the precious metal loading in heterogeneous catalysts by replacing metal nanoparticles with so-called “single-atom” active sites [1]. While there are many reports of active SAC systems, the topic remains somewhat controversial because it is very difficult to characterize a system based on adsorbed single atoms, and to distinguish between these and subnano particles [2]. In practice, most groups use aberration-corrected transmission electron microscopy (TEM) to demonstrate the atomic dispersion, sometimes supplemented by X-ray absorption near edge structure (XANES), which can rule out significant metal–metal bonding [1]. The activity of the catalyst is then tested, and although some mechanistic information can be drawn by in-situ techniques such as infrared reflection absorption spectroscopy (IRAS), the catalytic mechanism is proposed largely on the basis of theoretical calculations. Such calculations are based on an idealised model of the system, in which both the support structure and active site geometry are assumed. Thus, a one-to-one correspondence between the experimental and theoretical results is difficult to prove.

Traditionally, surface science has provided mechanistic information to understand heterogeneous catalysis. The idea is to strip away the complexity of a real catalyst and study well-defined single-crystal samples in a highly-controlled ultrahigh vacuum (UHV) environment. This way, the adsorption of individual reactants can be studied in detail, and an understanding of the basic interactions can be built up. The downside of the approach is that the highly idealised model system may not be as representative of the real catalyst as one would like, but on the upside, the model systems do strongly resemble what is calculated with density functional theory (DFT). Crucially, the structure of the model catalyst can be precisely determined from experiment, which ensures that accompanying theoretical calculations are realistic. In principle, one can obtain hard numbers for important parameters such as the adsorption energies (from thermal desorption experiments) and vibrational frequencies (from IRAS experiments), which can be used to benchmark the theoretical approach.

As one of the few techniques capable of true atomic resolution, scanning tunneling microscopy (STM) is potentially ideal to study SAC. In STM, an atomically sharp metallic tip is

brought to within a few nm of a sample surface, and a bias from a few mV up to a few V is applied. Electrons tunnel into, or out of the sample depending on the applied bias, resulting in a tunneling current of the order  $nA$ . Since the tunneling current is exponentially dependent on the tip-sample distance, atomic-resolution images are obtained by scanning the tip over the surface and recording the tip movements necessary to maintain a constant tunneling current. There are a few important provisos, however, that must be fulfilled to perform a successful experiment. First, the support needs to be extremely flat (so that only the terminal atom of the tip interacts with the surface at any one time), which largely restricts the method to highly-oriented single crystal substrates. Second, the sample must be sufficiently conductive that a stable tunneling current can be established. The latter condition is problematic because many catalyst supports are semiconducting metal-oxides. Over the years, several strategies have been developed to circumvent the conductivity issue. Of course, some metal oxides are intrinsically conductive (e.g.  $Fe_3O_4$ ), while others can be rendered conductive by vacuum annealing (e.g. rutile  $TiO_2$ ). If this fails, materials can be extrinsically doped (e.g. Nb-doping of anatase  $TiO_2$  or  $SrTiO_3$ ). An alternative, and now common approach [3] is to grow the oxide support as an epitaxial thin film on a metallic substrate, which provides the requisite conductivity.

To apply the surface science approach to study SAC requires that metal adatoms are stable on a well-defined metal-oxide support. This is not straightforward because, just as in real catalysts, there is a strong thermodynamic driving force for isolated adatoms to agglomerate into metallic nanoparticles. One option is to prepare a clean, flat, conductive metal oxide surface in UHV, and then sublime metal atoms directly onto the support at low temperature. The Freund group at the Fritz Haber Institute in Berlin have specialized in such experiments in recent years, and Fig. 1 shows an example of their work on the Au/MgO(100)/Mo(100) system. Fig. 1(a) contains an STM image acquired after Au adatoms were sublimated onto two monolayers of MgO(100) at 5 K [4], and the system subsequently exposed to CO. The Au adatoms are imaged as bright protrusions, and CO molecules adsorbed at the MgO step edges are imaged as dark depressions (Fig. 1(a) and (b)). Adsorption of CO on an Au adatom causes it to appear “fuzzy”, because the



**Fig. 1.** (a) STM image ( $V_{\text{sample}} = +0.1$  V,  $I_{\text{tunnel}} = 3$  pA,  $20 \times 20$  nm<sup>2</sup>) of single Au atoms and CO molecules on MgO thin films acquired at 5 K. (b, c) High-resolution STM images of an identical surface region taken with (b) a metallic and (c) a CO-modified tip ( $V_{\text{sample}} = +0.1$  V,  $I_{\text{tunnel}} = 3$  pA,  $7.7 \times 7.7$  nm<sup>2</sup>). The fuzzy appearance of the Au species in (c) occurs because the CO of the adsorbed carbonyl interacts strongly with the tip. (d)  $d^2I/dV^2$  spectra taken on the bare MgO surface, a single CO molecule, and an Au-CO species (set-point: 75 mV, 10 pA). The upper curve is a difference spectrum between the Au-CO and bare MgO. The symmetric peak/dip structure at  $\pm 50$  mV is assigned to excitation of a frustrated CO rotational mode. Figure adapted with permission from Ref. [4]. Copyright 2010 American Chemical Society.

CO molecule interacts with the STM tip as it sweeps by on each scan line (Fig. 1(c)). Particularly interesting in this work is the use of inelastic electron tunneling spectroscopy (IETS) to study the vibrational properties of adsorbed species [5]. The  $d^2I/dV^2$  spectra acquired above the Au carbonyl (Fig. 1(d)) exhibit a symmetric peak-dip signature at  $\pm 50$  mV due to the excitation of the frustrated CO rotation. The blue shift of this rotational mode with respect to that observed on a clean Pt surface ( $\pm 35$  mV) is taken as evidence of the negative charge of these species, consistent with the idea that electrons tunnel from the underlying metal into the empty 6s level of the Au when the oxide is so thin. These results are remarkable as, in general, IETS is rarely performed on metal oxides due to the lack of final states in the band gap for the inelastically tunneling electrons.

In recent times, the CO-stretching frequency measured in IRAS has been used to differentiate between adatoms and nanoparticles [2]. The interpretation of such frequencies is somewhat controversial [6], and an important role for surface science is to provide definitive vibrational frequencies to identify different species. The above described system, Au/MgO(100), is an excellent example of what can be achieved, and illustrates how complex the situation can be [7,8]. For example, Au adatoms can be neutral, negatively charged, and positively charged depending on the adsorption site, and both neutral and negatively charged clusters can also exist. Moreover, the adsorption of a CO molecule on a neutral Au adatom on the terrace induces sufficient charge transfer from the substrate that this species appears even more red-shifted than the negatively Au charged species! Clearly, CO is not an innocent probe of the system, and care must be taken characterizing SAC on solely the basis of IRAS frequencies.

At this juncture I would like to highlight an exciting methodological development occurring in surface science today that can directly impact the characterisation of a model single-atom catalyst. The latest generation of low-temperature scanning-probe instruments combine non-contact atomic force microscopy (nc-AFM) and STM in one system. This removes the

limitation regarding conductive supports, but also offers unprecedented resolution [9] and additional functionalities. For example, Onoda et al. [10] demonstrated a method to directly determine the Pauling electronegativity of adsorbed adatoms on Si(111) by measuring the maximum attractive force directly above. It is easy to imagine similar experiments for metal atoms adsorbed on metal oxide supports, with the different charge state of atoms in different adsorption sites (regular terrace/oxygen vacancy etc.) of particular interest.

While much can be learned from experiments at cryogenic temperatures, the resulting surface is probably not representative of a single-atom catalyst. In general, adatoms are probably not bound at regular lattice sites at elevated temperatures, and will quickly diffuse to occupy more strongly binding defect sites. Early surface science studies identified surface oxygen vacancies as nucleation sites for metal nanoparticles [11], and the first surface science study to report catalytically-active single atoms (already in 2000 [12]) proposed acetylene cyclotrimerization to be catalysed by negatively charged Pd<sub>1</sub> species anchored at oxygen vacancies on MgO(100). It is important to note that some materials, e.g. the iron oxides [13], do not exhibit oxygen vacancies in the bulk when reduced, instead preferring to accommodate the non-stoichiometry with bulk Fe interstitials. As such, excess Fe is a more common surface defect than an oxygen vacancy.

Since SAC really came to the fore through the work of Flytzani-Stephanopoulos [14] and Zhang [1], surface scientists have begun to investigate the stability and reactivity of Pt<sub>1</sub> on ceria and iron-oxide supports. Neyman and coworkers [15] proposed that Pt<sup>2+</sup> cations could be stabilized within so-called Pt-O<sub>4</sub> nanopockets. Using a combination of STM, X-ray photoelectron spectroscopy (XPS) and DFT, Dvorak et al. [16] demonstrated that such nanopockets could exist at step edges on CeO<sub>2</sub>(111). Specifically, they found that Pt<sup>2+</sup> dominated for samples with a high step density (Fig. 2(g)–(i)), whereas flat, oxygen vacancy rich samples promoted the formation of metallic clusters on the terraces (Fig. 2(d)–(f)). Interestingly, alt-

Download English Version:

<https://daneshyari.com/en/article/6505829>

Download Persian Version:

<https://daneshyari.com/article/6505829>

[Daneshyari.com](https://daneshyari.com)