Title	Surface Synthesized Carbene networks for electrocatalysis

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Background and main research objectives

Electrocatalysis is expected to play a key role in the energy transition toward renewable sources and to be an active player in the struggle against climate changes, given its potential to establish a virtuous chemistry/energy cycle, enabling an effective utilization of CO_2 producing a variety of added value products.[1,2] Despite the promising results on the lab scale and large gamut of proof of concept studies, many factors still hinder the practical implementation of the electrocatalytic route to CO_2 reduction reaction (CO_2-RR), and among these scarce activity and selectivity of the electrocatalysts are the most critical. The limited activity and selectivity are intrinsically related to the many elementary steps associated with the CO_2-RR and the competition with the hydrogen evolution reaction, since water electrolytes are the most eligible media for practical applications and since it is highly desirable the introduction of hydrogen atoms in the final products (i.e. CH_3OH, CH_4, C_2H_4, etc.). Thence it is mandatory to address the problem of CO_2-RR at a very fundamental level, because only by the microscopic comprehension of the reaction mechanism, a rational design of new catalytic materials can be achieved. DFT calculations and experimental data have clearly demonstrated that the most promising route to achieve superior performances is based on bifunctional effects, that is the combination/interaction of multiple reaction steps, since it consents a control of selectivity by steering the reaction path along the obtainment of select products and it allows escaping scaling laws.[3,4,5] Normally, this approach is exploited with molecular catalysts by designing with great care the first, second, or even third coordination sphere around the catalytic sites. Unfortunately such molecular materials are extremely expensive, little durable and difficult to implement on practical electrode. A solution to this problems is the bottom-up preparation of tailored molecular networks on metal surfaces through the protocols of the so called on-surface synthesis.[6] In this way it is possible to carefully control the reactivity of metal surfaces either creating surface metallorganic species with very reactive metal cen-

tres as well as "special reaction pockets" where the metal surface exhibit a chemical activity through because of a variety of interactions with the molecular overlayer. Quite recently, carbenes have emerged as possible building blocks for the formation of covalent molecular layers on metal surface leading to the formation of metallorganic
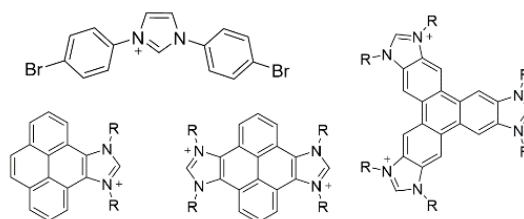

species [7,8] or reaction pockets able to control the selectivity of electrochemical reactions including the CO_2-RR [9,10].

Figure 1. Examples of carbene precursors to be used as building blocks for the on-surface synthesis of covalent molecular networks.

Methodology

In collaboration with the Applied Organometallic Chemistry group, we propose to design carbenes with special functional groups (aromatic rings, halogens, amines, carboxyls, see Fig.1) poised for both a highly controllable surface polymerisation through Ulmann coupling and a precise design of the chemical environment around the single metal centre and metal surfaces. The preparation of on-surface synthesized monolayers will be carried out under ultra high vacuum (UHV) conditions on Au(111) and Cu(111) single crystals, by a proper choice of the metal support, molecular precursor, cov-
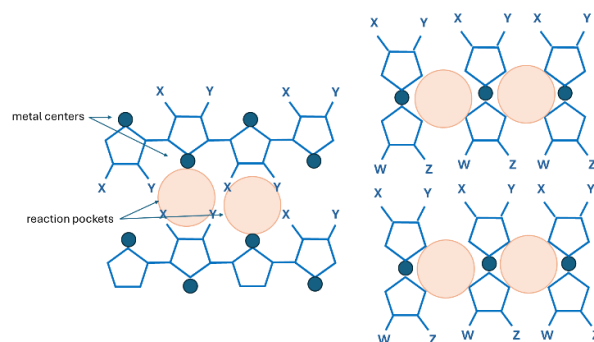

Figure 2 Examples of the possible connectivity of carbenes for the formation of molecular networks of surface metallorganic species bearing active centres and reaction pockets

erage, temperature etc. The chemical and structural properties of the resulting layers will be investigated by the techniques available at the INCAT group (XPS, UPS, UHV-STM, LEED, TPD). Their stability in electrochemical conditions will be tested *in operando* by electrochemical STM and *in situ* experiments by XPS. The preparation of surface carbene networks will be accelerated thanks to the collaboration with Prof. C. Baddeley of the St Andrew University, who has a long standing experience in the synthesis and characterization of carbene monolayer under UHV conditions, and investigation of their stability in electrochemical environment.[10] The most promising molecular networks (highly ordered, robust and stable in electrochemical conditions) will be tested as catalysts for the CO_2-RR using standard *ex situ* electrochemical methods (cyclic and linear sweep voltammetry, chronoamperometry, analysis of the reduction products by NMR and gas chromatography), and *in operando* by the noise-EC-STM method developed in the INCAT group [11].

Expected results:

By preparing systems with different *chemical composition* (nature of the metal centre/surface), and *tailored microenvironment* (first and second coordination around the catalytic centre, side groups in the molecular precursors), and systematic investigating their structure and catalytic activity, we expect to understand:

1. what are the stable/durable/active phases during electrochemical reactions
2. the role of the metal/covalent network interface, which is endowed with special electronic properties and the main place where co-adsorption of different species can take place and therefore representing the trigger
3. unravelling cooperative effects at different interfaces (metal surface/covalent framework, and in general the solid/electrolyte interface) and between different active sites (adjacent metal centres, reaction pockets, specific functional sides groups in the metal precursors and metal centres)

Given its unsurpassed spatial resolution (sub nm), the use of operando EC-STM will allow to identify with atomic scale precision all these "ensemble catalytic sites" and to evaluate directly and quantitatively their catalytic activity by the noise analysis method.[11] The gathered information can be used as a blueprint for the design of new catalysts for CO_2 valorisation.

References

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