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Electrocatalysis of the nitrite reduction : a mechanistic study

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Summary

The core topic of this thesis is the electrocatalysis of nitrite reduction, a reaction of paramount importance from both a fundamental and an applied point of view; specifically, nitrite is released from the reduction of nitrate in groundwater, and these two polluting anions both pose a threat to human health. Therefore, their levels must be carefully monitored and efficient removal methods must be developed. Electrochemical water remediation is a promising technique, provided that selectivity to harmless (N_2) or industrially valuable products (NH_2OH) is achieved. The determination of the factors influencing reaction selectivity represented one of the main motivations of this thesis, which has addressed nitrite reduction with an eye to the elucidation of mechanistic details underlying the preferential formation of certain reaction products at a specific electrocatalyst. Our approach has relied on several experimental techniques, ranging from basic electrochemical methods (such as cyclic voltammetry with stationary and rotating ring-disk electrodes –RRDE) to advanced methods combining electrochemistry and *in situ* determination of intermediates or reaction products. In particular, spectroelectrochemical techniques (external reflection FTIRS) have allowed us to image the species residing at the electrode surface, and *online* mass spectrometry (OLEMS) has enabled us to detect volatile reaction products. A wide selection of catalytic materials has been screened, including bio-inspired moieties (hemin) and many polycrystalline transition-metal electrodes. Additionally, Pt single-crystals have been used as model surfaces to investigate the structure sensitivity of nitrite reduction.

The opening chapter of the thesis (Chapter 2), inspired by our review on the electrochemical nitrogen cycle (Chapter 1), readdresses nitrite reduction at polycrystalline Pt electrodes as a function of the electrolyte pH. In fact, the

conjugate acid of NO_2^- , HNO_2 (the predominant species below $\text{pH} = 3.3$) undergoes an acid-catalyzed decomposition mainly to NO , which readily adsorbs at most noble metals. Chapter 2 reports on the decomposition of nitrous acid, showing that it follows a second-order kinetics and that it can be quenched by an increase in pH . Secondly, the presence of dissolved NO determines the formation of N_2O (detected with the OLEMS setup) in a broad potential window. When the potential is lowered and approaches the region of hydrogen evolution, NO_{ads} is removed and HNO_2 is directly converted to NH_3OH^+ (detected with RRDE) in a diffusion-controlled reaction. These findings, highlighting the importance of homogeneous-phase reactions, support our subsequent investigation of other electrocatalysts for nitrite reduction (Chapters 6-8). The dual selectivity to volatile and soluble products as a function of potential also characterizes the reduction of HNO_2 on other polycrystalline transition metal electrodes. Rh, in particular, features a higher affinity to nitrogen-containing molecules which, on one hand, explains the poisoning effect subsequent to NO adsorption but, on the other hand, facilitates the complete hydrogenation of HNO_2 to NH_4^+ . The metal- NO interaction is the crucial parameter for the evaluation of the performance of catalysts as different as noble/coinage metals (Chapter 7) and hemin immobilized at a graphite electrode (Chapter 8). An intermediate affinity to NO characterizes the most active noble metals, which are also the least prone to poisoning (Pd, Pt). Moving to the right of the Periodic Table, coinage metals (Cu, Ag, Au) are penalized by their weaker metal- NO interaction; contrarily, Ir is easily poisoned due to its intrinsic ability to dissociate NO . Our findings follow what is known in heterogeneous catalysis as the “Sabatier Principle”. The binding of NO to the catalytic centre is also the key parameter to discuss the performance of hemin. This isolated prosthetic group, deprived of any protein scaffolding, is unable to bind nitrite; consequently, it can only react with NO available from HNO_2 decomposition, and so its reactivity is restricted to acidic pH values, where NH_3OH^+ is the final product.

The second main line of research stems from the detailed investigation of nitrite reduction in alkaline media on Pt electrodes (Chapters 3-5). Although this metal is not as active as Rh, Pt is extremely interesting because, as we show in Chapter 3, Pt single-crystals feature highly different voltammetric profiles during nitrite reduction, which is therefore a structure-sensitive reaction. Intriguingly, Pt(100) displays an unexpected peak which, thanks to the OLEMS setup, we can ascribe to the direct nitrite reduction to N_2 . This is the first report ever of such a high

selectivity to N_2 at a monometallic surface. The detailed elucidation of the mechanism is dealt with in Chapter 4, along with the investigation of the effect of the introduction of controlled defects (“steps”) in the Pt(100) surface. This research, performed in collaboration with Prof. Feliu’s group at Alicante, highlights the importance of a proper pretreatment of the (100) surface, minimizing defects. Steps of any symmetry, in fact, dramatically impair the selectivity of the nitrite conversion to N_2 . Spectroelectrochemical experiments demonstrate that this reaction is caused by the recombination of two surface species, both originating from nitrite (NO_{ads} and $\text{NH}_{2,\text{ads}}$), which fleetingly coexist at a specific potential. This recombination mechanism can be described as a “selective catalytic reduction” and seem to be a universal pathway to N_2 , being operative in practical catalysts (NO_x abatement in car exhausts) and in microorganisms (“anammox” bacteria). Finally, we exploit the structure-sensitivity of nitrite reduction in alkaline media as an ancillary novel characterization tool for preferentially oriented nanoparticles prepared with an innovative surfactant-free method (“cathodic corrosion”). A preferential (100) orientation can be achieved by this method and the N_2 formation at high-quality (100) facets is described in Chapter 5. The indications from nitrite reduction are in agreement with other reactions or processes specific to Pt(100) domains, such as Ge irreversible adsorption, ammonia oxidation and dimethylether (DME) oxidation.

In conclusion, this thesis paves the way for several future research lines: many issues still need unraveling. To begin with, (100) surfaces of other transition metals should be tested for direct nitrite conversion to N_2 . Despite the lower activity of Pt(111) surfaces, a fundamental investigation of nitrite reduction in alkaline media on stepped (111) crystals could also be informative. More importantly, the pathway for N_2 formation unveiled in Chapters 3 and 4 has so far only been verified for a very specific model surface, Pt(100), while we must ideally design an electrocatalyst more suitable for practical use (for instance a bifunctional or bimetallic nanoparticle-based catalyst) which is still able to stabilize NH_2 and NO simultaneously, thus achieving N_2 formation. The development of a new class of materials performing “electrochemical selective-catalytic reductions” (that is, the aqueous-phase analogous of the catalytic process which removes nitrogen oxides from diesel engine exhaust gases) would represent a veritable breakthrough towards the control of the accumulation of Nr in wastewater as NO_3^- and NO_2^- . However, the quest for cheaper materials than Pt(100) is only the first challenge

towards the application of this N_2 -forming strategy in wastewater remediation technology. Limitations concerning the reactants must also be overcome; the pathway discussed in Chapters 3 and 4 is operative in the presence of NO_2^- , while the most ubiquitous pollutant of groundwater is NO_3^- , which can only be reduced by Pt (with an acceptable activity) in acidic media. The actual composition of wastewaters represents another formidable obstacle, since the simultaneous presence of different electroactive species, giving rise to a complex mixture, brings to the fore the issue of selectivity *from the point of view of the reactants*. In fact, one should ideally achieve the selectivity of natural systems, which, as discussed in Chapter 8, can specifically select one reactant among the several components of the cellular environment. Given these limitations, the N_2 -generating pathway discovered in this thesis is currently only suitable for the treatment of very simple wastewater streams. For example, the electrochemical reduction of nitrites in water could be applied to destroy this pollutant, or lower its concentration below the admissible levels, as a one-step treatment of alkaline wastewater containing nitrite as the main pollutant. Some low-level nuclear wastes (alkaline solutions laden with nitrites and nitrates) are very similar to the simple electrolytes used in this thesis.