Templated synthesis of single-site electrocatalysts with microporous materials

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Metal single atoms in nitrogen doped carbon materials (M-NC) have attracted plenty of attention during the last decades in the field of electrocatalysis for oxygen reduction and carbon dioxide conversion amongst others. In the cathode of proton exchange membrane fuel cells Fe-NC are the most promising solution to scarce and expensive Platinum-group-metal catalysts,[1] and in the cathode of CO_2 conversion electrolysers, Fe and Ni-NC are predicted to be as active as Au or Ag.[2,3] However, their controlled synthesis and stability for practical applications remains challenging due to the high temperature pyrolysis step that results on Fe aggregation and formation of oxides and carbides. Decoupling high temperature pyrolysis and the Fe coordination, can circumvent the disadvantages of the high temperature pyrolysis,[4] nevertheless, the metal utilization within these materials remains very low owing to the lack of scaffolds that combine adequate micro- and mesoporosity.

We and others have recently shown that the pyrolysis of organic building blocks (such as adenine or 2,4,6-Triaminopyrimidine amongst others[5]) with the porogen $MgCl_2.6H_2O$ leads to highly porous N-doped carbons (~3300 m^2 g^{-1}) that expose efficiently the Fe-NC active sites (>50% electrochemical utilization),[6,7] resulting in state-of-the-art fuel cell and CO_2 reduction performance.[3,8] The high Mg^{2+} content needed in such syntheses, however, leads to low reaction yields and metal loadings. We are now addressing such drawbacks by employing microporous covalent and molecular materials in combination with Mg^{2+} as reactants. The intrinsic microporosity of covalent organic polymers or zeolitic imidazolate frameworks allows the utilization of lower Mg^{2+} contents while maintaining higher reaction yields and catalytic activity in the oxygen reduction reaction. Furthermore, the presence of residual Mg sites within Fe-NC frameworks helps boosting the stability of the catalysts, which can perform oxygen reduction for more than 20,000 cycles and a kinetic mass activity >3 A g^{-1} at 0.8$V_{vs\ RHE}$ in acidic electrolyte.

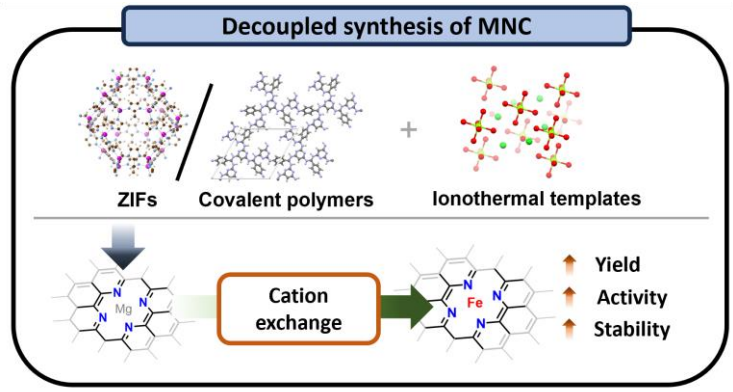

Figure 1. templated synthesis of single-site electrocatalysts with microporous materials.

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