Spectroscopic and structural characterization of molecular organic frameworks for heterogeneous catalysis

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Aiming at more sustainable chemical processes, the development of efficient catalysts plays a major role. In that context, the development of single-atom catalysts has a huge potential since they can bridge the gap between homogeneous and heterogeneous catalysis due to very good performance, better catalyst separation and handling as well as maximum metal utilization [1]. Single-atom catalysts based on carbon-nitrogen polymers with low metal loadings have shown applicability for several catalytic systems. For example, Ir-complexes bound to Covalent Triazine Frameworks show great activity and selectivity in the catalytic decomposition of formic acid [2], which is considered a potential hydrogen storage material. Interestingly, and contrary to common expectations a reductive treatment at elevated temperatures led to an increased catalytic performance.

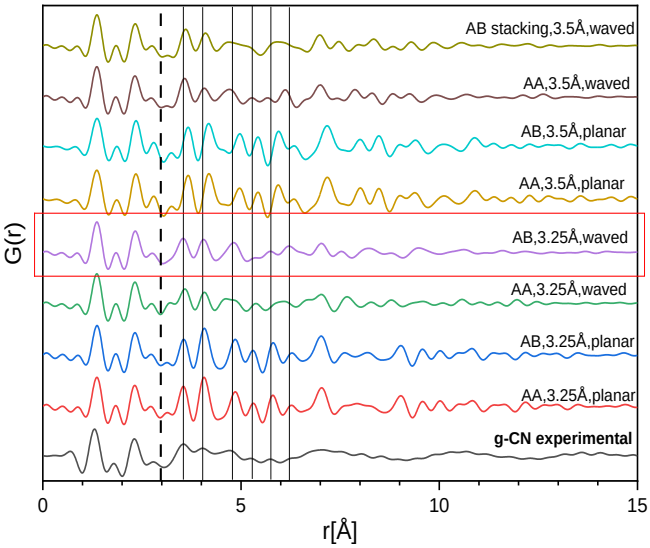

Fig. 1 Comparison of experimental X-Ray PDF of g-CN with calculated PDFs based on DFT calculations.

A transfer of this procedure to other supports and metals shall be analyzed. Graphitic carbon nitrides (g-NC) where 1wt. % Pd was immobilized is at the center of this research. A detailed local structure analysis shall give rise to structure-property relationships in such systems. However, the characterization comes with some challenges due to the amorphous nature of the catalysts. The evaluation of possibilities and limits of different characterization methods to characterize the polymeric support material and the as-synthesized catalyst is aimed. Fig. 1 shows the comparison of the experimental g- CN pair distribution function (PDF) analysis with different calculated PDFs based on periodic density functional theory (DFT) calculations of different g-CN models with varying interplanar distances and stacking sequences. It was found that the model which was calculated to be the most stable matched the experimental data best. Furthermore, *ex* and *in situ* synchrotron X-ray total scattering and photoelectron spectroscopy measurements have been conducted.

[1] Soorholtz, Mario, et al. "Local platinum environments in a solid analogue of the molecular Periana catalyst." *ACS Catalysis* 6.4 (2016): 2332-2340.

[2] Bavykina, A. V., et al. "Efficient production of hydrogen from formic acid using a Covalent Triazine Framework supported molecular catalyst." *ChemSusChem* 8.5 (2015): 809-812

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