Controlling the speciation and reactivity of carbon-supported gold nanostructures in catalyzed acetylene hydrochlorination

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Carbon-supported gold nanostructures have the potential to ultimately replace the highly toxic mercuric chloride-based catalyst in acetylene hydrochlorination, a key technology for the manufacture of polyvinyl chloride [1]. However, the wide implementation of gold catalysts is still hindered by their limited durability under practically relevant reaction conditions. To enable the rational design of stable gold nanostructures it is essential to find the most active site among the variety of candidates that have been identified to date, including nanoparticles, clusters, and recently also single atoms [2]. Here, we unravel the activity hierarchy with a systematic evaluation of the Au dispersion and oxidation state as descriptors for gold-based catalysts in acetylene hydrochlorination, using a platform of supported gold nanostructures at a fixed metal loading, ranging from single atoms of tunable oxidation state to metallic nanoparticles. Our approach takes advantage of the fundamentally different behaviour of gold atoms hosted on activated carbon (AC) in comparison to polyaniline-derived N-doped carbon (NC). While on AC particle aggregation occurs progressively above 473 K, on NC gold single atoms exhibit outstanding thermal stability under reaction conditions and during thermal treatment up to 1073 K, as confirmed by aberration corrected transmission electron microscopy, high-angle annular dark-field scanning transmission electron microscopy, and extended X-ray absorption fine structure spectroscopy. With an integrated approach combining steady-state experiments, density functional theory, and transient mechanistic studies, using the temporal analysis of products, we show and rationalize the superior performance of atomically dispersed Au(I)Cl species irrespective of the choice of carrier. In relation to the structure of the active site and the corresponding reaction mechanism, we discuss perspectives for the development of highly active and stable hydrochlorination catalysts [3].

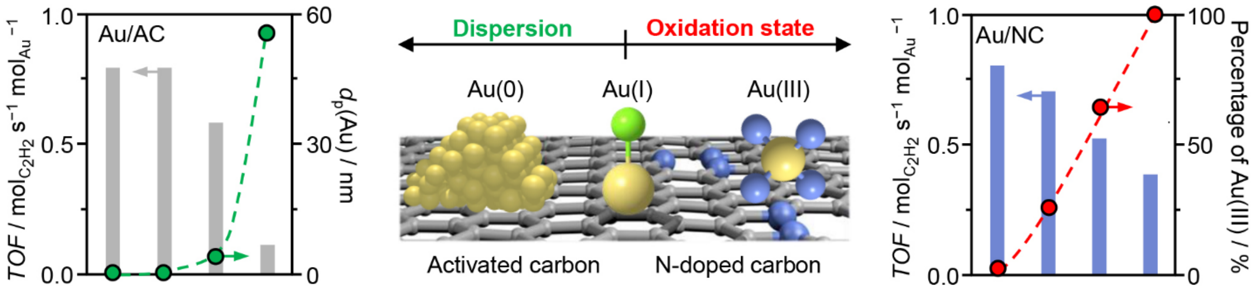

Figure 1 The gold particle size (d_p) and oxidation state determine the catalytic performance of gold-based catalysts in acetylene hydrochlorination, expressed as the turnover frequency (*TOF*).

[1] R. Lin, A. P. Amrute, J. Pérez-Ramírez, *Chem. Rev.* **2017**, 117, 4182.
[2] G. Malta, S. J. Freakley, S. A. Kondrat, G. J. Hutchings, *Chem. Commun.*, **2017**, 53, 11733.
[3] S.K. Kaiser, R. Lin, S. Mitchell, E. Fako, F. Krumeich, R. Hauert, O.V. Safonova, V.A. Kondratenko, E.V. Kondratenko, S.M. Collins, P.A. Midgley, N. López, J. Pérez-Ramírez, *Chem. Sci.* **2019**, 10, 359-369.