Applying modulation excitation spectroscopy to characterize the active species in homogeneous copper catalysts

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Recently, the Cu(I)-catalyzed alkyne-azide cycloaddition (CuAAC) was reported independently by Morten Meldal and K. Barry Sharpless[1],[2]. The CuAAC can be performed under mild reaction conditions using multiple Cu sources and also permits large variations in substrate scope. As a result, CuAAC is applied in many different fields in chemistry, ranging from material[3] to life sciences[4]. Despite its wide applicability, the mechanism of the CuAAC reaction is still under debate[5]. Very recent kinetic and computational studies suggest the participation of dinuclear Cu complexes in the catalytic cycle (Scheme 1)[6],[7].

In this study we aim to gain insight into the active site of homogeneous Copper catalysts, using modulation excitation spectroscopy (MES). MES has already been successfully applied to study heterogeneous catalysts[8], but the methodology has not been extended to homogeneous catalysts. We explore the feasibility of the MES methodology applied to homogeneous catalysts. The approach relies on the perturbation of the steady state equilibrium via a periodic change in an external stimulus (i.e. temperature or concentration). The measured response is mathematically filtered with the excitation frequency. As a result, only the signal of the species responding to the stimulus is observed; this allows to distinguish between active and spectator species[9]. We have designed novel catalysts based on iminophosphorane ligands. The ligand acts as internal base, making it possible to perform the reaction without additional base. The reaction is again second order in copper concentration, suggesting a reaction mechanism involving two copper atoms. Time resolved 1H-NMR and 31-P NMR show the presence of Cu-bound phosphorane and Cu-bound alkyne species. In the first modulation excitation experiment the alkyne concentration is periodically modulated with respect to a constant Cu complex concentration. A similar experiment was performed to periodically modulate the azide concentration with respect to a constant concentration of both Cu complex and alkyne to probe the catalytic cycle. The experimental results are further supported and the XANES spectra analysed by a computational study in which we have modelled the catalytic cycle and corresponding intermediate species with DFT. The results will be presented in this contribution.


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