

## One or two electron redox: mechanism study in homogeneous catalysis

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Homogeneous catalysis is an actively studied research field, which major topic, C-H activation has addressed huge amount of attention during the past few decades. A lot of progress has been made, while at the same time, great challenges is also in front of scientists. Mechanism study in homogeneous system, thus, is one of the biggest challenge in this field, due to the complexity and lack of effective methods to study the real active catalysis species.

Scientists used to use NMR (nuclear magnetic resonance), in-situ IR (infrared spectroscopy), MS (mass spectroscopy), et, al. to study the organic species in homogenous catalysis reactions. While, with the development of organometallic chemistry, very few techniques are targeting to study the metal catalysts in solution with in-situ or operando methods. Thanks to the development of synchrotron techniques, XAFS (X-ray absorption fine structure) is a powerful technique to study the metal catalysts in a real homogeneous catalysis system. Especially, the quick-XAFS under cryogenic measurement condition provides a very important method to bring people with a new tool to see and rethink the homogeneous catalysis mechanism.

Based on XAFS, we studied several homogeneous system: 1. Gilman reagent preparation. XAFS revealed that copper salts, eg.  $\text{Cu(II)Cl}_2$ ,  $\text{Cu(II)Br}_2$ , reacts with  $n\text{-BuLi}$ , forms  $\text{R}_2\text{CuLi}$  reagent, while  $\text{Cu(I)Cl}$  and  $\text{Cu(I)Br}$  need an extra  $\text{LiX}$  salts to assist the formation of  $\text{R}_2\text{CuLi}$ , otherwise, it will form  $\text{Cu(0)}$  instead of Gilman reagent.  $[\text{Cu(I)X}_2]^-$  is a crucial intermediate in this transformation.<sup>[1]</sup> 2. Oxidative induced mechanism.  $\text{Cu}^{2+}$  reacts with alkoxy anion<sup>[2]</sup>, sulfinic acids<sup>[3]</sup> and nitrogen containing compounds, in which, one electron redox was observed from XAFS and EPR. New chemical bond and compounds was formed in these kinds of

organic transformations. 3. C-H bond activation<sup>[4]</sup> and reductive elimination<sup>[5]</sup> step study by XAFS. We studied the reductive elimination step in Glaser-Hay reaction catalyzed by copper. With the help of cryogenic quick-XAFS, we trapped an active Cu(II)-phenylacetylide species in solution.

In conclusion, XAFS provides an effective technique studying the mechanism of transition metal catalyzed homogeneous catalysis reaction.

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