

Multi-scale modeling of the dissolution/growth dynamics of metallic copper clusters during synthesis or catalysis processes

DESCOUBES Marina,^A GERARD Helene;^B

A and B) Laboratoire de Chimie Théorique, Sorbonne Université, 4 place Jussieu, Paris, France.

marina.descoubes@sorbonne-universite.fr

Copper nanoparticles (Cu NPs) are well known and widely used for their catalytic and plasmonic properties. In both cases, the control of size and shape is essential for a good control of the physicochemical properties. Understanding the processes involved in the synthesis of these NPs is attractive as it could open the way to rational control. However, this is a complex task because many synthetic processes take place at high temperatures, which allow many competitive reactions to take place. In this context, the recent results published by Vrancken et al.¹ are interesting because they described a synthetic process that takes place close to room temperature. It is based on the thermal decomposition of an alkyl copper reagent leading to a Cu precursor, which then evolves towards the formation of Cu NPs after stabilization with thiolates. Whereas the stabilization step is extensively reported, the formation of Cu⁽⁰⁾ precursors is unusual in the context of Cu NPs synthesis. The decomposition reaction itself has been known for a long time, having been first described in 1970 by Whitesides et al.² It is proposed to take place in a two-step mechanism. A first copper alkyl (1_L-1_L) reacts by β -hydride elimination to form an alkene and a Cu-hydride intermediate (2_L) (Figure 1). A second copper alkyl then reacts with the intermediate copper hydride by reductive elimination to give an alkane and Cu⁽⁰⁾ (3_L-3_L) (Figure 1).

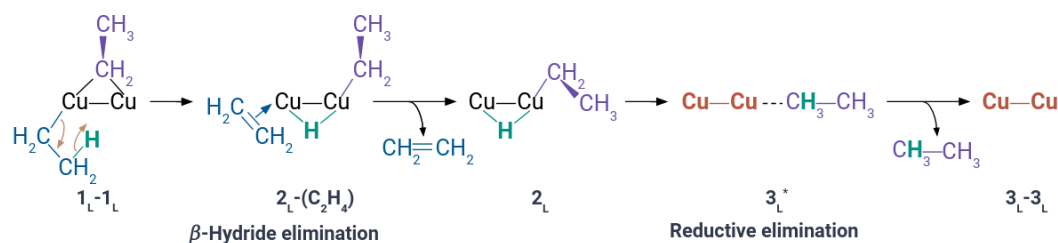


Figure 1 – Thermal decomposition mechanism made of a reaction of β -hydride elimination (left) and reaction of reductive elimination (right) where the green H is a hydride, red copper atoms are metallic copper atoms and L is a Lewis base, represented in this study by trimethylphosphine (PMe₃) or tetrahydrofuran (THF) (not represented here).

This mechanism highlights the formation and reactivity of the intermediate copper hydride (2_L), a chemical species of high added value for its many applications, particularly in the field of energy conversion. It is indeed proposed as a reaction intermediate in CO₂ conversion and methanol upgrading. Kinetic studies by Kochi et al.³ have shown that the reaction is accelerated by the introduction of metallic seeds in the reaction medium, among which Cu⁽⁰⁾ seeds, demonstrating an autocatalytic behavior. In particular, they propose the formation of multinuclear mixed valence Cu^(I)-Cu⁽⁰⁾ intermediates during the course of the reaction, which can act as catalytically active species. In addition, the reaction can occur with or without phosphine additives in the reaction medium, the role of which is not clearly understood.

In this presentation, we will examine the effects of adding metallic copper to the reaction medium, as well as the effects of ligands on the relative stability of the species involved.

Keywords: Copper catalysts, density functional calculations, reaction path, copper hydride

1 L. Ouyang, V. Noël, A. Courty, JM. Campagne, A. Ouali, E. Vrancken, "Copper Nanoparticles with a Tunable Size: Implications for Plasmonic Catalysis", ACS Applied Nano Materials, 5, (2), 2839-2847, 2022, doi: 10.1021/acsanm.2c00016

2 G. M. Whitesides, E.R. Stedronsky, C.P. Casey, J San Filippo Jr. "The Mechanism of Thermal Decomposition of n-Butyl(tri-n-butylphosphine)copper(I)." J. Am. Chem. Soc., 92, 1426-1427, 1970, doi: 10.1021/ja00708a067

3 Jay K. Kochi, K. Wada, M. Tamura, "Autocatalytic decomposition of alkylcopper(I) species. Electron spin resonance spectrum of binuclear copper(O) intermediates" J. Am. Chem. Soc., 92, 6656-6658, 1970, doi: 10.1021/ja00725a055