

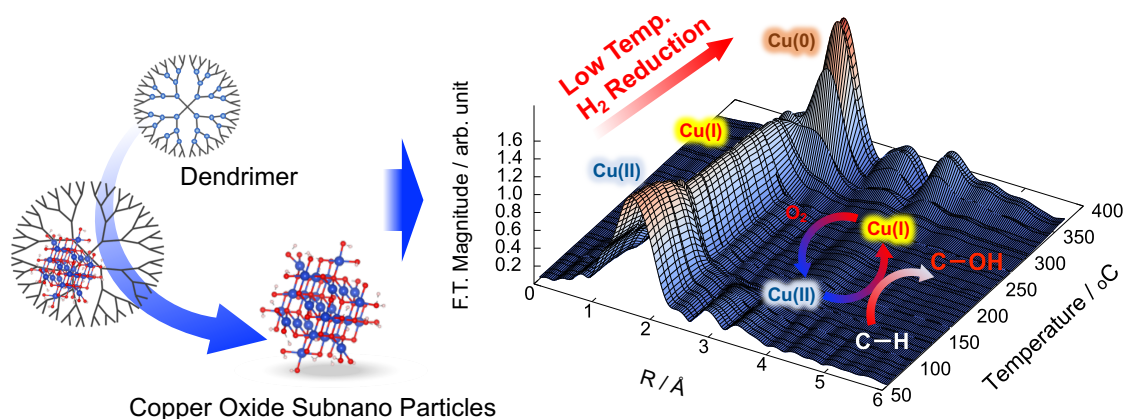
## Low-Temperature Reduction of Subnano Copper Oxides for Catalytic Hydrocarbon Oxidations

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**Keywords:** Subnanoparticles; Copper Oxide; Dendrimer; Catalytic Oxidation; Hydrocarbon

Metal oxide subnanoparticles have been attracted attention as remarkable active species in the catalytic property due to the large surface area and the irregular electronic polarization. Especially, the metal oxide subnanoparticles are expected as new active catalysts for hydrocarbon oxidations, which is one of the challenging issue in industrial chemistry. However, it is difficult to synthesize size-selected metal oxide subnanoparticles with conventional methods. Dendritic poly(phenylazomethine)s (DPA G4) exhibit an electronic gradient property from the core to terminal sites via the  $\pi$ -conjugated branched systems, which are suitable for the synthesis of subnano copper oxide particles in atomic-level precision.<sup>1)</sup> In recent work, we reported smallest size subnanoparticle ( $\text{Cu}_{12}\text{O}_x$ ) achieved a large number of TON (= 3597) for 5 h, which was enhanced by particle size effect<sup>2)</sup>. In this work, we fabricate them by using the dendritic template and revealed their reactivity for basic redox reactions.

The STEM observation of the atom-specific copper oxide subnanoparticles shows that the particle sizes were maintained in c.a. 1.0 nm with narrower size distribution. The redox properties of the particles was revealed using *in-situ* X-ray absorption spectroscopy (XAFS), and copper oxide subnanoparticles shows steeply reduction of Cu(II) into Cu(I) at lower temperature than bulk or nanoparticle of copper oxides. This significant stabilization of Cu(I) state was only discovered in a subnano region.



1) K. Yamamoto, T. Imaoka, *Acc. Chem. Res.* **2014**, 47, 1127. 2) K. Sonobe, M. Tanabe, K. Yamamoto, *ACS Nano* **2020**, 14, 1804