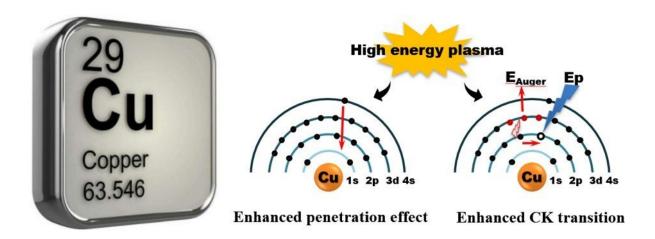


'Frozen' copper behaves as noble metal in catalysis: study

December 21 2018



Unique electron configuration of the 29th element Cu was excited by high energy plasma, resulting in the variation of its chemical property. Credit: SUN Jian and YU Jiafeng

As a non-noble metal, copper oxidizes more easily to a positive valence (Cu+ or Cu2+) than same-family elements Au or Ag. In general, this chemical property is mainly determined by electron structure. Can we change the chemical properties of an element by regulating its electron structure? Can Cu act as a noble metal in catalytic reactions?

A team led by Dr. Sun Jian of the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS) gives a positive answer. The team's recently published paper in *Science Advances* shows



that the electron structure of Cu can be changed, assisted by high energy plasma, making Cu exhibit significantly different catalytic behaviors than normal Cu in selective <u>hydrogenation</u> reactions.

The dimethyl oxalate (DMO) hydrogenation reaction, a typical multistep catalytic reaction producing methyl glycolate (MG), ethylene glycol or ethanol, was selected as a probe reaction for copper. In this reaction, the common product over supported Cu/SiO₂ catalysts is one of the latter two owing to the inevitable co-existence of Cu+ and CuO for deep hydrogenation.

The sputtered (SP) Cu, which is bombarded by high energy argon plasma, can be "frozen" at zero valence when exposed to oxidation or reaction atmosphere at a very wide range of temperature, presenting noble-metal-like behaviors.

In DMO hydrogenation, a high selectivity (87%) towards the preliminary hydrogenation product, MG, a high-value chemical, was observed. The molecule level free energy surface in various reaction pathways by DFT calculation also verifies that "frozen" Cu0 is crucial for preliminary hydrogenation.





Freezing Cu as a noble metal like catalyst with oxidization-resistance property



facilitates the controlling of selective hydrogenation. This behavior is similar to a warrior with a solid armor resisting the attack on the battlefield. Credit: SUN Jian and YU Jiafeng

More information: "Freezing copper as a noble metal–like catalyst for preliminary hydrogenation" *Science Advances* (2018). DOI: 10.1126/sciadv.aau3275, advances.sciencemag.org/content/4/12/eaau3275

Provided by Chinese Academy of Sciences

Citation: 'Frozen' copper behaves as noble metal in catalysis: study (2018, December 21) retrieved 26 April 2024 from <u>https://phys.org/news/2018-12-frozen-copper-noble-metal-catalysis.html</u>

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