

Commentary

Utilizing synchrotron-based SVUV-PIMS technique to capture (CHO)Cu₁^{*} species in dimethyl oxalate hydrogenation

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Abstract: Utilizing synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) to capture intermediates has significantly enhanced the understanding of catalytic reactions. This commentary introduced the structure of SVUV-PIMS and then revisited an excellent work in science that utilized SVUV-PIMS to elucidate the mechanisms of dimethyl oxalate (DMO) hydrogenation into ethylene glycol over copper nanoparticles (Cu NPs) supported on dealuminated Beta zeolite (Beta-deAl). The observation of key intermediates, particularly (CHO)Cu₁^{*} species, using SVUV-PIMS provided real-time, in-situ insights into the dynamic behavior of Cu NPs in DMO hydrogenation. The findings highlighted the formation of a silanol nest and the presence of metallic Cu and Cu₂O phases following methanol treatment. This treatment helped maintain a small nanoparticle size, resulting in high EG yields and prolonged catalyst stability. Additionally, their catalyst addressed common issues, such as silica leaching, which often compromises the durability of CuSiO₂-based catalysts. By re-examining their work, this commentary underscores the transformative potential of SVUV-PIMS in catalysis research, and the operando adaptation of intermediates in reactions is invaluable for developing more efficient and durable catalysts.

Keywords: SVUV-PIMS; dimethyl oxalate hydrogenation; copper nanoparticles; dealuminated Beta zeolite; intermediates; catalyst stability

In recent years, there has been a growing focus on “soft” photoionization (PI) as a promising ionization method that could potentially become a standard and universal technique across various research fields. A key tool in this context is ultraviolet-photoionization mass spectrometry (PIMS) with a tunable synchrotron vacuum ultraviolet (SVUV) light source, which offers quasi-continuous light with excellent energy resolution and high photon flux. This makes SVUV light an ideal option for “soft” PI applications in diverse areas, such as combustion chemistry and molecular imaging. Tunable SVUV light, characterized by its adjustable wavelength and high photon flux, provides researchers with a versatile and powerful tool for conducting “soft” PI experiments. The excellent energy resolution of SVUV light enables precise control over the ionization process, allowing for detailed investigations of molecular structures, reaction pathways, and chemical dynamics [1–3]. There are two SVUV-PIMS facilities in the world. One is the Advanced Light Source (ALS) located at the Lawrence Berkeley National Laboratory in the USA, which mainly uses ion desorption to focus exclusively on premixed flame studies. The other one is the Hefei Advanced Light Source Facility (HALF) at the National Synchrotron Radiation Laboratory (NSRL) in China, which is equipped with laser desorption. In particular, the subsequent work done by three beamlines in the HALF has greatly extended the

application of SVUV-PIMS by a series of reactors, such as a plug-flow reactor and a jet-stirred reactor [4]. In addition, due to its wide tunability and superior energy resolution, SVUV-PIMS can minimize fragmentation interference, differentiate isomers, and detect free radicals. The detailed structure of representative SVUV-PIMS machines in China and the USA is shown in **Figure 1**.

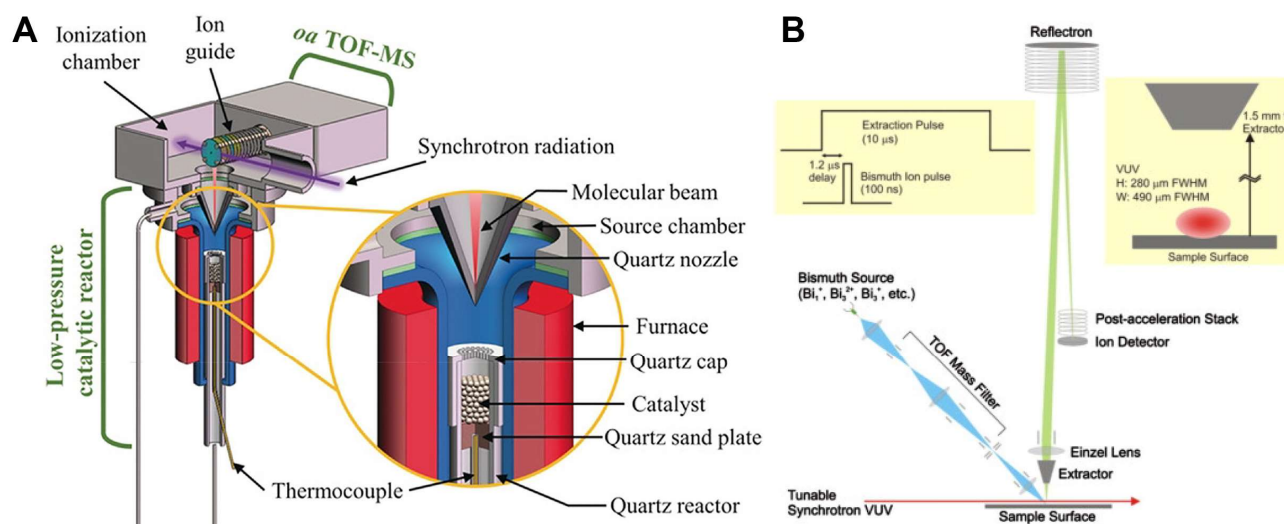


Figure 1. Structure of synchrotron vacuum ultraviolet photoionization mass spectrometry: **(A)** with laser desorption at NSRL and **(B)** with ion desorption at ALS (reproduced with permission from Takahashi et al. [5] and Wen et al. [6], copyright ACS 2009, Wiley 2020).

A recently published paper in the Science journal entitled “Dealuminated Beta Zeolite Reverses Ostwald Ripening for Durable Copper Nanoparticle Catalysts” explored the innovative use of dealuminated Beta zeolite (Beta-deAl) as a support for copper nanoparticles (Cu NPs) to improve their stability and performance in catalytic processes [7]. Ostwald ripening is a phenomenon where larger particles grow at the expense of mobile active metals [8]. Copper nanoparticles are widely used in industry but tend to sinter into larger particles under operational conditions, which degrades their catalytic efficiency. By incorporating dealuminated Beta zeolite, the researchers were able to reverse Ostwald ripening, resulting in more durable copper nanoparticle catalysts with improved stability and efficiency. The study employed various advanced characterization techniques to investigate the catalyst structure and mechanisms involved in the hydrogenation process. Among these techniques, SVUV-PIMS emerged as a particularly promising method for studying volatile intermediates during the reaction. SVUV-PIMS allowed for real-time and in-situ monitoring of surface species and reactions on catalyst materials, providing detailed insights into the dynamic behavior of copper nanoparticles supported on dealuminated Beta zeolite.

Figure 2(A) demonstrates the phenomenon of reverse Ostwald ripening and the formation of a silanol nest following the removal of tetraordinated Al sites from the Beta zeolite framework. In **Figure 2(B)**, the XRD pattern of the catalyst after methanol treatment revealed the presence of metallic Cu and Cu₂O phases. The methanol treatment gradually reduced the diffraction patterns over time until they disappeared, indicating the elimination of large particles. The X-ray absorption near-edge structure (XANES) spectrum (**Figure 2(C)**) of fresh Cu/SiO₂ suggested a multivalent

composition of Cu^0 and Cu^+ consistent with Cu/SiO_2 with $\text{Cu}^{\delta+}\text{-O-SiO}_x$ interaction. After methanol treatment, the Cu/SiO_2 became more metallic due to Cu nanoparticles sintering, destroying the interaction with silica. Extended X-ray absorption fine structure (EXAFS) analysis (**Figure 2(D)**) showed an increased coordination number (CN) of the Cu-Cu shell and the absence of Cu-O or Cu-O-Cu signals post-methanol treatment. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (**Figure 2(E)**) of $\text{Cu}/\text{Beta-deAl}$ revealed a nanoparticle size of approximately 2.2 nm on the Beta-deAl support, with no bulk Cu particles detected. The SVUV-PIMS monitoring process (**Figure 2(F)**) detected Cu species in methanol vapors, indicating the presence of Cu_1 -related intermediates during the migration. The hydrogenation of DMO using $\text{Cu}/\text{Beta-deAl-18\%}$ catalyst achieved an ethylene glycol (EG) yield of 90.8% at 200 °C under a liquid hourly space velocity (LHSV) of 0.6 h^{-1} and a yield of 90.1% at 230 °C with an LHSV of 3.6 h^{-1} at ambient pressure (**Figure 2(G)**). This catalyst remained stable in continuous reaction for 200 h, maintaining a Cu NP size of $4.0 \pm 1.0 \text{ nm}$ (**Figure 2(H)**).

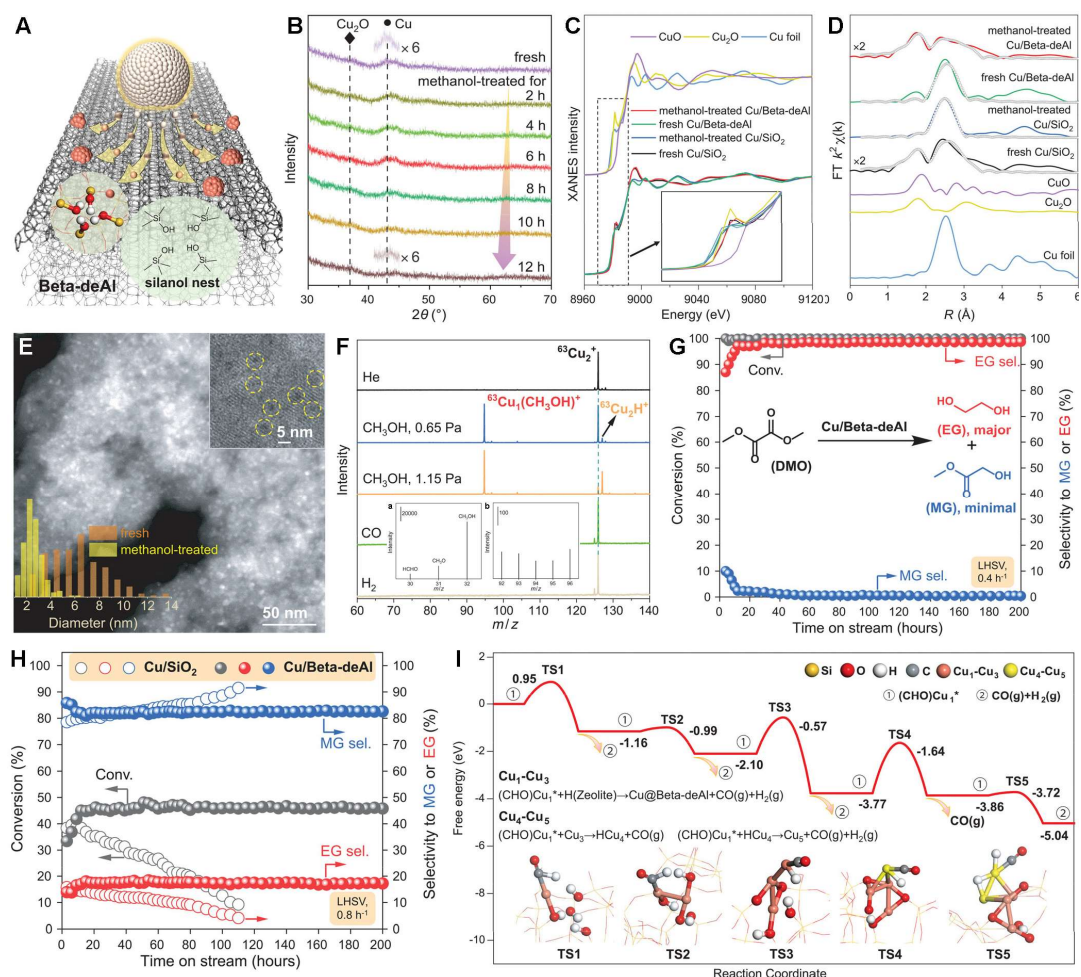


Figure 2. (A) State-of-art for reverse Ostwald ripening of Cu NPs on Beta-deAl support. (B) In-situ XRD patterns characterizing change of Cu NPs on Cu/Beta-deAl during methanol treatment at 200 °C. (C) Normalized Cu K-edge XANES spectra. (D) Fourier-transformed (FT) magnitudes of experimental Cu K-edge EXAFS spectra. (E) HAADF-STEM images of Cu/Beta-deAl. (F) Time-of-flight mass spectra for reactions (inset: SVUV-PIMS spectra). (G) Durability of Cu/Beta-deAl catalyst. (H) Effect of methanol treatment on performances of catalyst. (I) Energy profile during nucleation process (reproduced with permission from Liu et al. [7], copyright 2024 AAAS).

Apart from Cu sintering, another durability challenge for general CuSiO₂-based catalysts is silica leaching, where tetramethoxysilane-related species form in methanol vapor and leach from the catalysts. This issue was efficiently avoided with the Cu/Beta-deAl catalyst due to the superior stability of crystallized zeolite in methanol vapor compared with amorphous silica. Theoretical studies were also conducted to calculate the reaction coordinates of the DMO hydrogenation process (**Figure 2(I)**).

In summary, SVUV-PIMS is a powerful technology for observing reactive intermediates in catalytic reactions, but a suitable reactor design and sampling method are important. The study reported by Liu et al. [7] utilized SVUV-PIMS as an advanced characterization technique to investigate the structure and mechanisms of a copper-nanoparticle catalyst supported on dealuminated Beta zeolite for hydrogenation processes. Through SVUV-PIMS, the researchers realized real-time monitoring of surface species and reactions, providing detailed insights into the behavior of copper nanoparticles on the zeolite support. The innovative approach of utilizing SVUV-PIMS technology with a suitable reactor and ionization energy (11.6 eV) successfully captured (CHO)Cu₁^{*} species in dimethyl oxalate hydrogenation, which is expected to apply to other thermal catalysis reactions.

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Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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