

**Electronic supplementary information (ESI†) available: Experimental details and
characterization data.**

Dynamic redox cycle of Cu⁰ and Cu⁺ over Cu/SiO₂ catalyst in ester hydrogenation

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Catalyst preparation

The Cu/SiO₂ catalyst was prepared by the ammonia-evaporation method. 11.4 g of Cu(NO₃)₂·3H₂O (Tianjin Kermel Corp) was dissolved in 150 ml of deionized water and then 18 ml of 28% ammonia aqueous solution (Tianjin Kermel Corp) was added and stirred in 30 min. 12.0 g of SiO₂ (Evonik Degussa) was added into the formed copper ammonia complex solution at 308 K and stirred for 4 h. Then, the temperature of the water bath was increased to 363 K to allow for the evaporation of ammonia and the deposition of copper species on silica. When the pH value of the suspension decreased to 6-7, the evaporation process was terminated. The filtrate was washed with deionized water and dried overnight at 393 K. The catalyst precursor was calcined at 723 K for 4 h, pelletized, crushed and sieved to 20~40 meshes.

Measurement of catalytic activity

The catalytic performance of the catalyst was tested in a continuous-flow fixed-bed reactor. Typically, 1 g catalyst was packed into a stainless steel tubular reactor (internal diameter: 12 mm) with the thermocouple inserted into the catalyst bed. Before reaction, the catalyst was activated at 623 K for 3 h in a pure hydrogen flow with a ramping rate of 1 K/min. Ethyl acetate was injected into the vaporizer, heated and then introduced into the reactor by H₂. The products were

introduced in a gaseous state and analyzed on line by a Varian CP 3800 gas chromatograph with a flame ionization detector (FID).

Catalyst characterization

XRD patterns were obtained on an X'Pert PRO diffractometer (PANalytical). Ordinary XRD characterization was carried out with a Cu-K α radiation of 40 kV and 40 mA and powder catalyst was used. After the treatment with ester and H₂, we use helium to flush and protect the catalyst powder to avoid long time exposure to air. In-situ XRD in Figure S1 was carried out with a Cu-K α radiation of 40 kV and 300 mA. Catalysts samples were shaped into a plate with a diameter of 13mm and a thickness of 1.5 mm before characterizations.

Temperature programmed reduction/oxidation (TPR/TPO) was carried out on a Quantachrome iQ instrument. The consumption of hydrogen or oxygen was monitored with a thermal conductivity detector.

The XPS/XAES analysis was performed on a Vacuum Generator Scientific ESCALAB Mark II system with Al-K α ($h\nu = 1486.6$ eV, 10.0 kV) X-ray radiation. The power of the X-ray source was 100 W and the nominal resolution was higher than 0.1 eV. The Si2p line at 103.4eV was taken as a reference for the binding energy calibration.

Determination of the Cu⁺/Cu⁰ ratio

After the reaction, the catalyst particles were flushed and protected by helium. However, during the transfer from the reactor to Quantachrome iQ instrument, exposure to air was unavoidable. For the catalyst exposed to air, TPO and TPR gave similar value of Cu⁺/Cu⁰ ratio, which proved them feasible and reliable. It also suggests that only very small part of Cu⁰ was

oxidized to Cu^{2+} when exposure to air (if the oxidation took place) and it has no obvious effect on the Cu^+/Cu^0 ratio.

Method I: First, a TPR experiment was carried out with the spent catalyst. This TPR was marked as TPR1. After the reaction, Cu^+ and Cu^0 coexisted in the spent catalyst. The area of the H_2 -consumption peak in TPR1 (S_{TPR1}) was attributed to the reduction of Cu^+ to Cu^0 . Second, the catalyst after TPR1 was oxidized by O_2 at 823 K. At this time, all the Cu^0 was oxidized to Cu^{2+} . Third, another TPR was performed after the oxidation, which was denoted as TPR2. The area of the H_2 -consumption peak (S_{TPR2}) in TPR2 was attributed to the reduction of Cu^{2+} to Cu^0 . The ratio of Cu^+/Cu^0 in the spent catalyst was calculated according to $2S_{\text{TPR1}}/(S_{\text{TPR2}}-2S_{\text{TPR1}})$.

Method II: First, a TPO experiment was carried out with the spent catalyst. This TPO was marked as TPO1. After reaction, Cu^+ and Cu^0 coexisted in the spent catalyst. The area of the O_2 -consumption peak in TPO1 (S_{TPO1}) was attributed to the oxidation of Cu^0 to Cu^{2+} together with the oxidation of Cu^+ to Cu^{2+} . Second, the catalyst after TPO1 was reduced by H_2 at 623 K. At this time, all the Cu^{2+} was reduced to Cu^0 . Third, another TPO was performed after the reduction, which was denoted as TPO2. The area of the O_2 -consumption peak (S_{TPO2}) in TPO2 was attributed to the oxidation of Cu^0 to Cu^{2+} . The ratio of Cu^+/Cu^0 in the spent catalyst calculated according to $(2S_{\text{TPO2}}-2S_{\text{TPO1}})/(2S_{\text{TPO1}}-S_{\text{TPO2}})$.

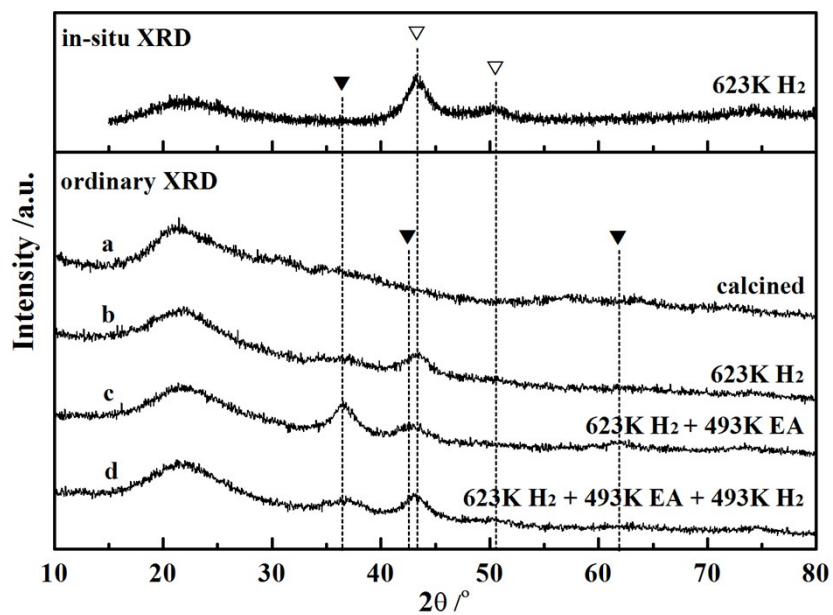


Fig. S1 XRD patterns of Cu/SiO₂ catalyst. Ethyl acetate (EA) was introduced onto the reduced catalyst by a carries gas of helium.

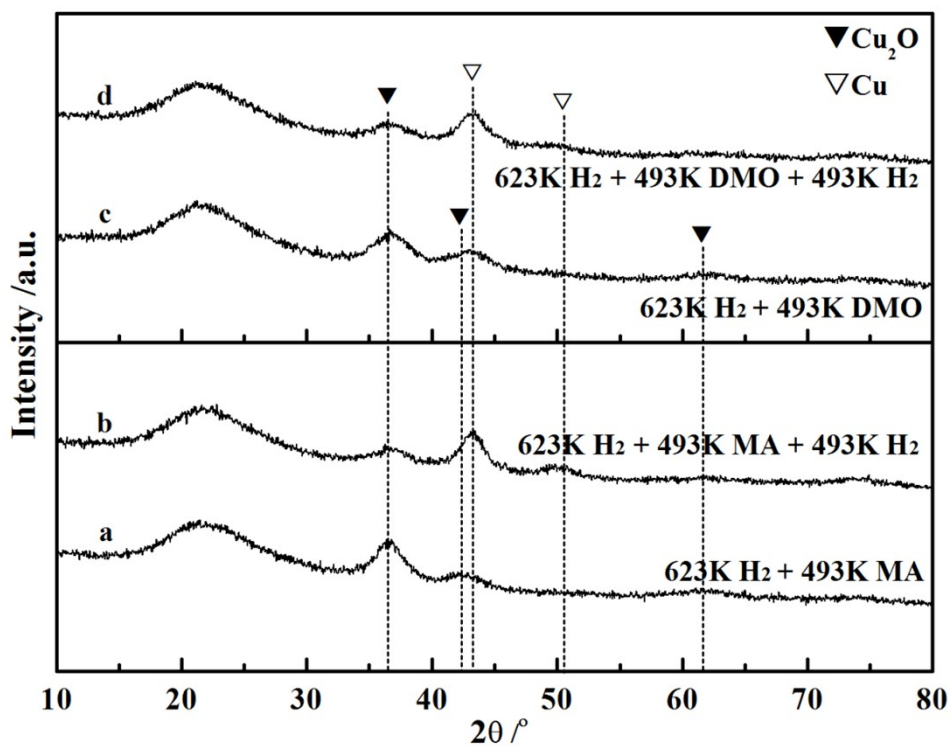


Fig. S2 XRD patterns of Cu/SiO₂ catalyst. Methyl acetate (MA) was introduced onto the reduced catalyst by a carries gas of helium. Dimethyl oxalate (DMO) was dissolved in methanol and introduced onto the reduced catalyst by helium.

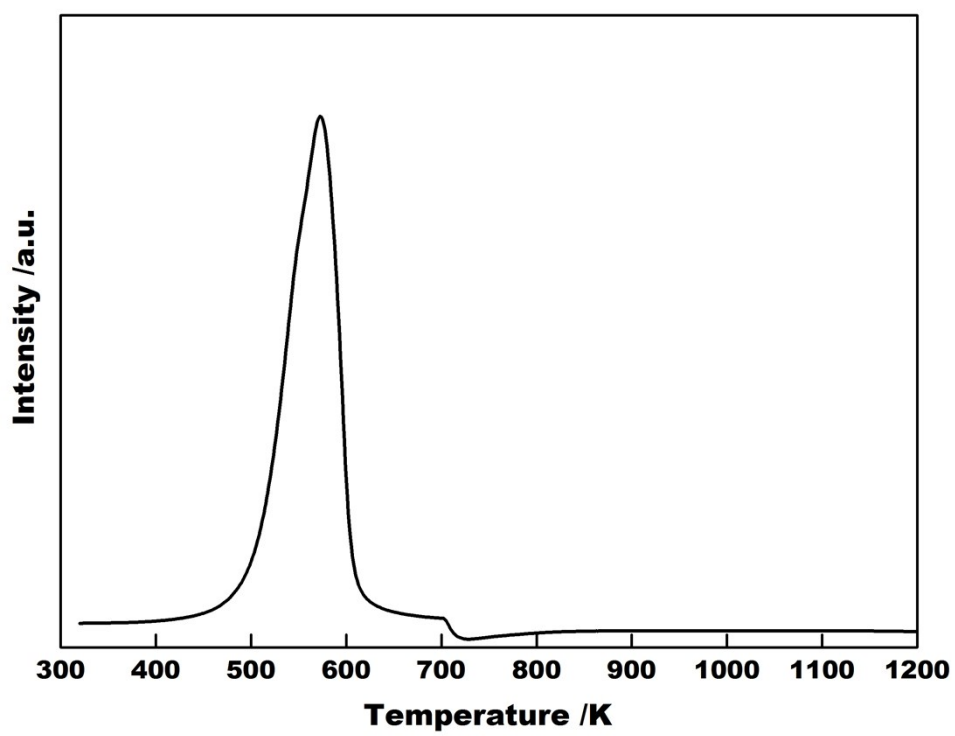


Fig. S3 TPR profile of Cu/SiO₂ catalyst.