

Electronic Supplementary Information for

**Synthesis of Cu-Zn-Zr-Al-O catalyst via a citrate complex
route modified by different solvents and their
dehydrogenation/hydrogenation performance**

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The conversion and selectivity of products for the conversion of ethanol or ethyl acetate were calculated based on the following equations [Eq. (1, 2)]:

$$\text{Conversion} = \left(1 - \frac{\text{Amount of feed after reaction (mass)}}{\text{Total amount of feed (mass)}}\right) \times 100\% \quad (1)$$

$$\text{Selectivity} = \frac{\text{Amount of a product (mass)}}{\text{Total amount of feed converted (mass)}} \times 100\% \quad (2)$$

While them for the hydrogenation of diethyl oxalate were calculated as follows [Eq. (3, 4)]:

$$\text{Conversion} = \left(1 - \frac{\text{Amount of DEO after reaction (mol)}}{\text{Total amount of DEO in feed (mol)}}\right) \times 100\% \quad (3)$$

$$\text{Selectivity} = \frac{\text{Amount of a product (mol)}}{\text{Total amount of DEO converted (mol)}} \times 100\% \quad (4)$$

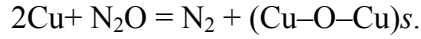
The measurement of specific Cu⁰ surface areas of the catalysts

Catalysts (60 mg) were first reduced in 5% H₂/N₂ mixture at a flow rate of 50 mL/min with a ramping rate of 10 °C/min until 350 °C. The amount of hydrogen consumption in the first TPR (TPR1) was denoted as X. And then the reactor was purged with Ar to 50 °C. N₂O (30 mL/min) was injected to oxidize surface copper atoms to Cu₂O at 50 °C for 15 min. Subsequently, the reactor was flushed with Ar to remove the oxidant. Finally, another TPR experiment was performed. Hydrogen consumption in the second TPR (TPR2) was denoted as Y. The dispersion of Cu and exposed Cu surface area were calculated according to the equations which are shown below:¹

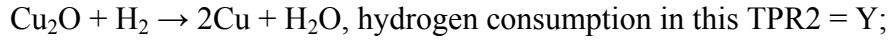
Reduction of all copper atoms:

$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$, hydrogen consumption in the first TPR1 = X.

the decomposition of N_2O on the surface of metallic copper:



Reduction of surface copper atoms only:



And the dispersion of Cu (D) and exposed Cu surface area (S) were calculated as [Eq. (5, 6)]:

$$D = \frac{2Y}{X} \times 100\% \quad (5)$$

$$S = \frac{2Y \times N_{av}}{X \times M_{Cu} \times 1.4 \times 10^{19}} = \frac{1353Y}{X} (\text{m}^2 - \text{Cu} / \text{g} - \text{Cu}) \quad (6)$$

where N_{av} is the Avogadro's constant, M_{Cu} is the relative atomic mass (63.5 g/mol), 1.4×10^{19} comes from that an equal abundance of an average copper surface atom area of 0.0711 nm^2 , equivalent to 1.4×10^{19} copper atoms/ m^2 .²

Average volume-surface diameter ($d_{v.s.}$) of Cu particles can be expressed as a function [Eq. (7)]:

$$d_{v.s.} = \frac{6}{(S \times \rho_{Cu})} \approx 0.5 \frac{X}{Y} (\text{nm}) \quad (7)$$

where, ρ_{Cu} is the density of copper (8.9 g/cm^3).

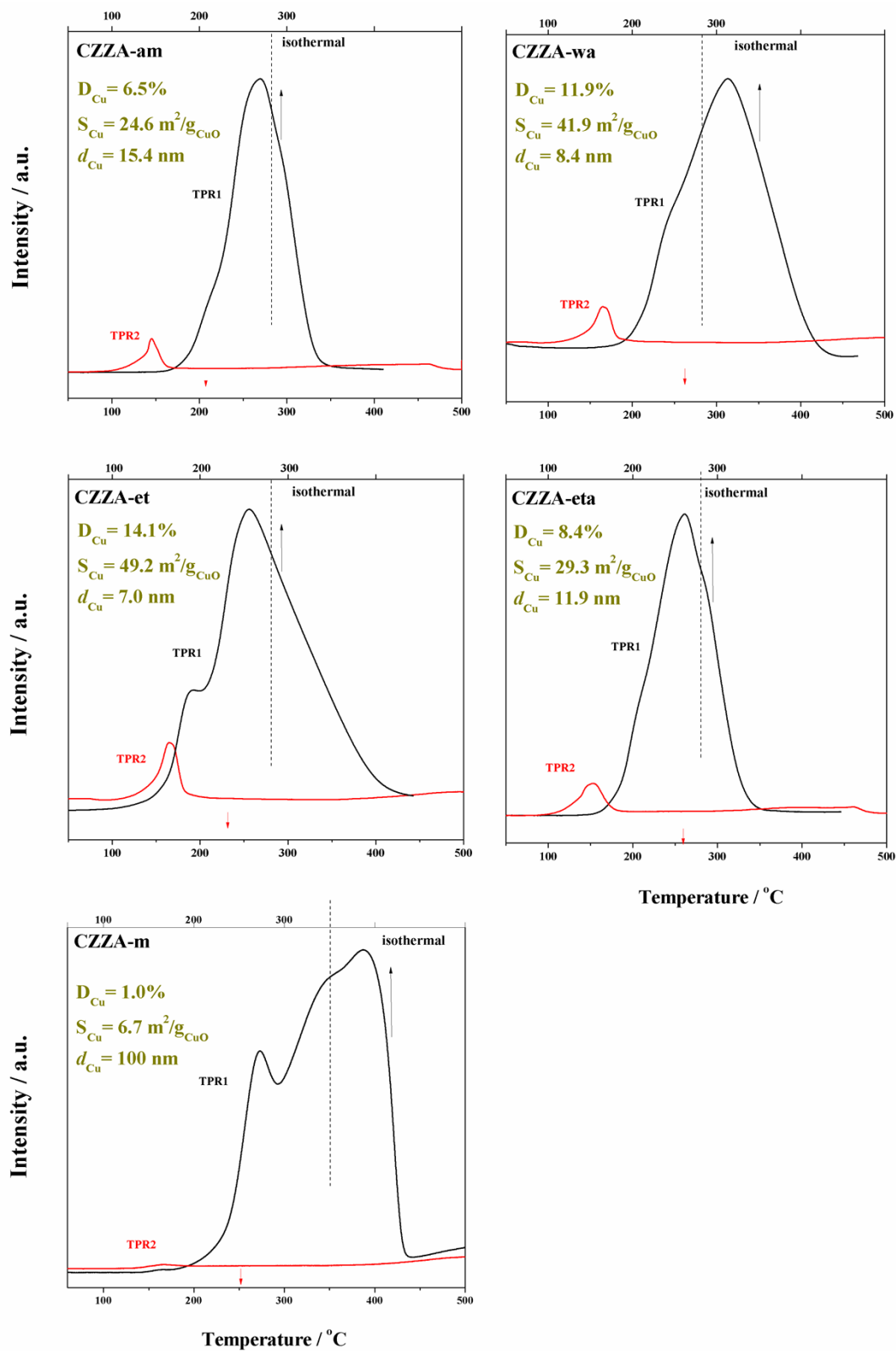


Fig. S1 The profiles of Cu metal surface area of CZZA-x catalysts determined by the N₂O titration method.

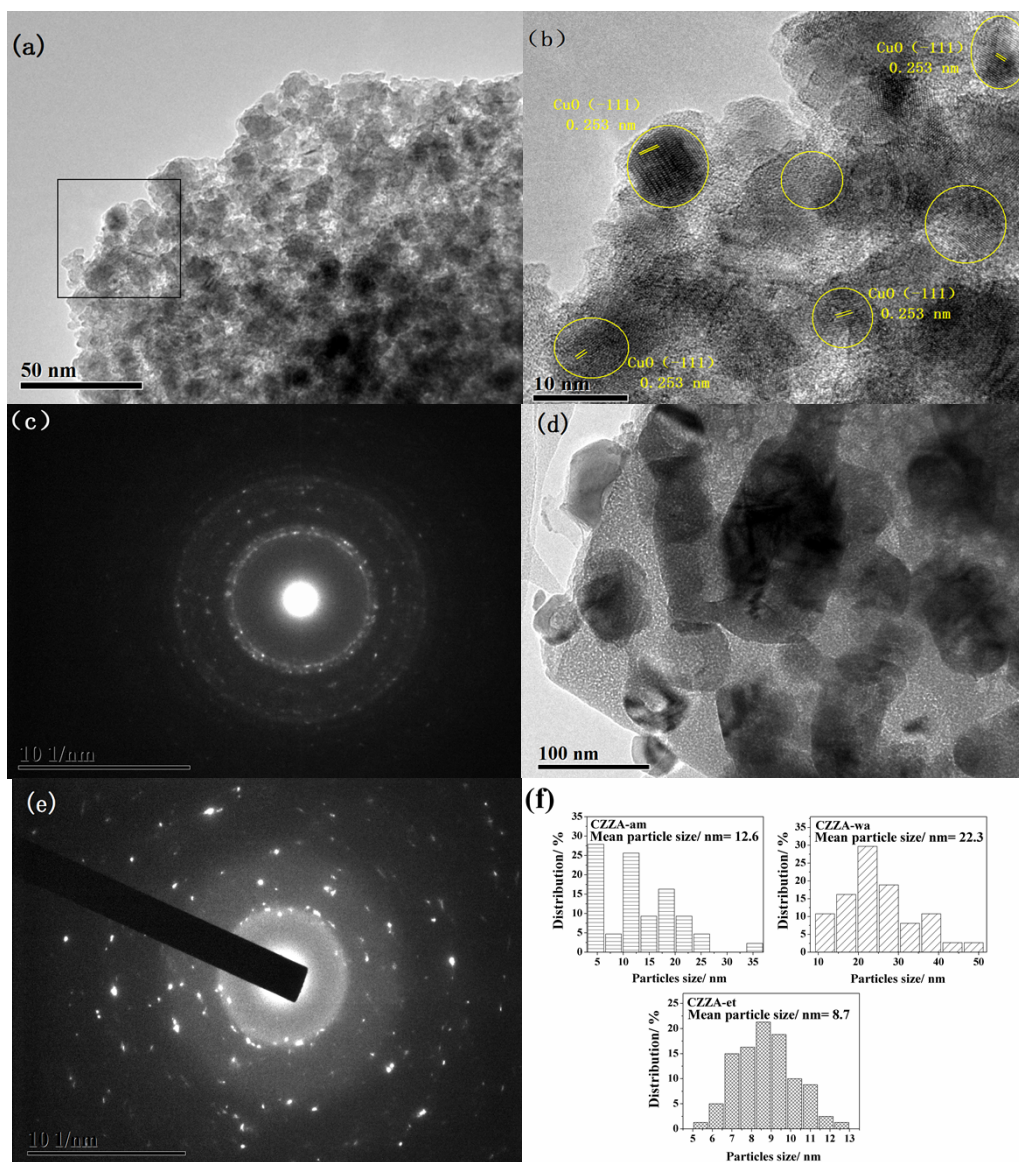


Fig. S2 TEM images of varying magnification of the calcined quaternary catalysts CZZA-et (a and b) and CZZA-wa (d) ; the SAED pattern of CZZA-et (c) and CZZA-wa (e); particles size distribution of the CZZA catalyst as a function of solvents(f).

References

1. Z. Yuan, L. Wang, J. Wang, S. Xia, P. Chen, Z. Hou and X. Zheng, *Appl. Catal., B*: 2011, **101**, 431-440.
2. C. Van Der Grift, A. Wielers, B. Jogh, J. Van Beunum, M. De Boer, M. Versluijs-Helder and J. Geus, *J. Catal.*, 1991, **131**, 178-189.