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# Electronic Supplementary Information

# New findings and current controversies on oxidation of benzyl alcohol by a copper complex

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## Experimental

### Materials and methods

All reagents and solvents were purchased from the commercial sources and were used without a further purification: 1,10-Phenanthroline monohydrate (Sigma-Aldrich), $Cu(ClO_4)_2 \cdot 6H_2O$ (Sigma-Aldrich) and acetonitrile (Merck).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out with LEO 1430VP and Philips CM30 devices, respectively. The X-ray powder patterns were recorded with a Bruker D8 ADVANCE diffractometer ($CuK_\alpha$ radiation).

X-ray absorption spectra of these materials at Cu K-edge were measured at 1D XRS KIST-PAL beamline at Pohang Light Source (PLS, Pohang, Republic of Korea), operating at 3.0 GeV with a storage current of 300 mA. The beamline is a bending magnet X-ray Scattering (XRS) beamline which uses an Si(111) double crystal monochromator to give a wide range of monochromatic energies (4–16 keV). To measure XANES spectra of these materials, higher harmonics were removed by detuning incident beam intensity upto 60% of maximum intensity. Three ionization chambers filled with He and $N_2$ gases were used to record the intensity of the incident and the transmitted X-rays, respectively. The materials are placed between the first and second ionization chamber, while a reference foil (Cu) for energy calibration is placed between the second and third ionization chamber. Under stationary conditions, XANES measurements were performed for the

Cu K-edge in a step scanning mode. Fourier transform infrared (FTIR) spectra were recorded using the Bruker FT-IR spectrometer. A sample pellet was prepared with mixture of collected solid and KBr.

After 90 minutes under reaction, the mixture was filtered, and the solid was washed 4 times with DI water and then particles were removed by the centrifuge. The collected solid was dried in 50 °C. For measurement DLS, the collected solid sonicated in water for 15 min, and DLS measurements were carried out at 25.0 ◦C by using a Malvern DLS instrument.


Fig. S1 Color changes during the reaction. Reagents and conditions: **1** (5% mmol), benzylalcohole (1 mmol), $K_2CO_3$ (2 eq) temperature (80 °C), Toluene (5 ml), and under $O_2$.

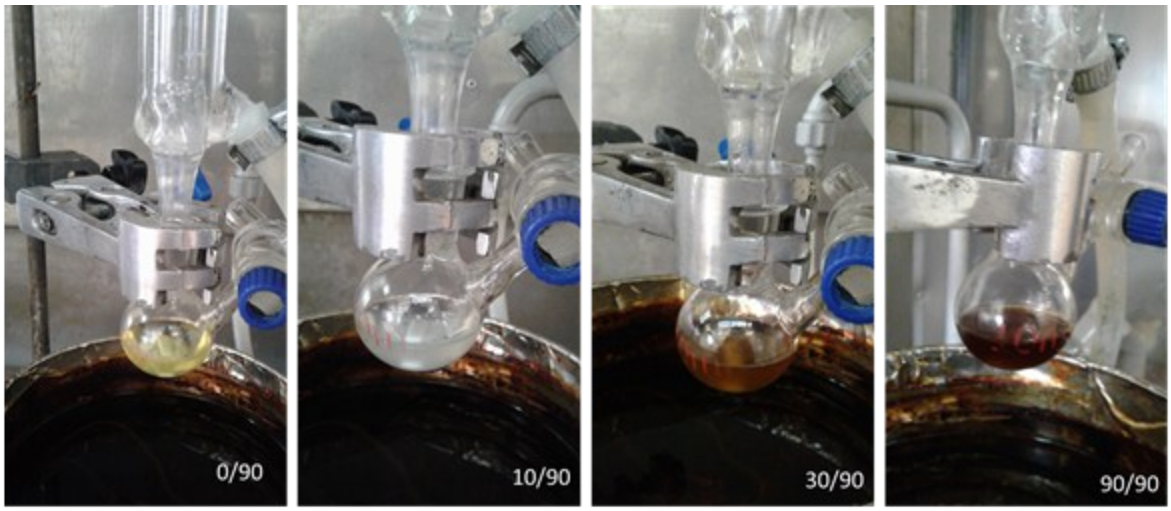



Fig. S2 Color changes during 90 minutes. Reagents and conditions: CuCl (5% mmol), 1, 10 phenantroline (%5), DIAD (%5) benzylalcohole (1 mmol), $K_2CO_3$ (2 eq), temperature (80 °C), and Toluene (5 ml) under $O_2$.

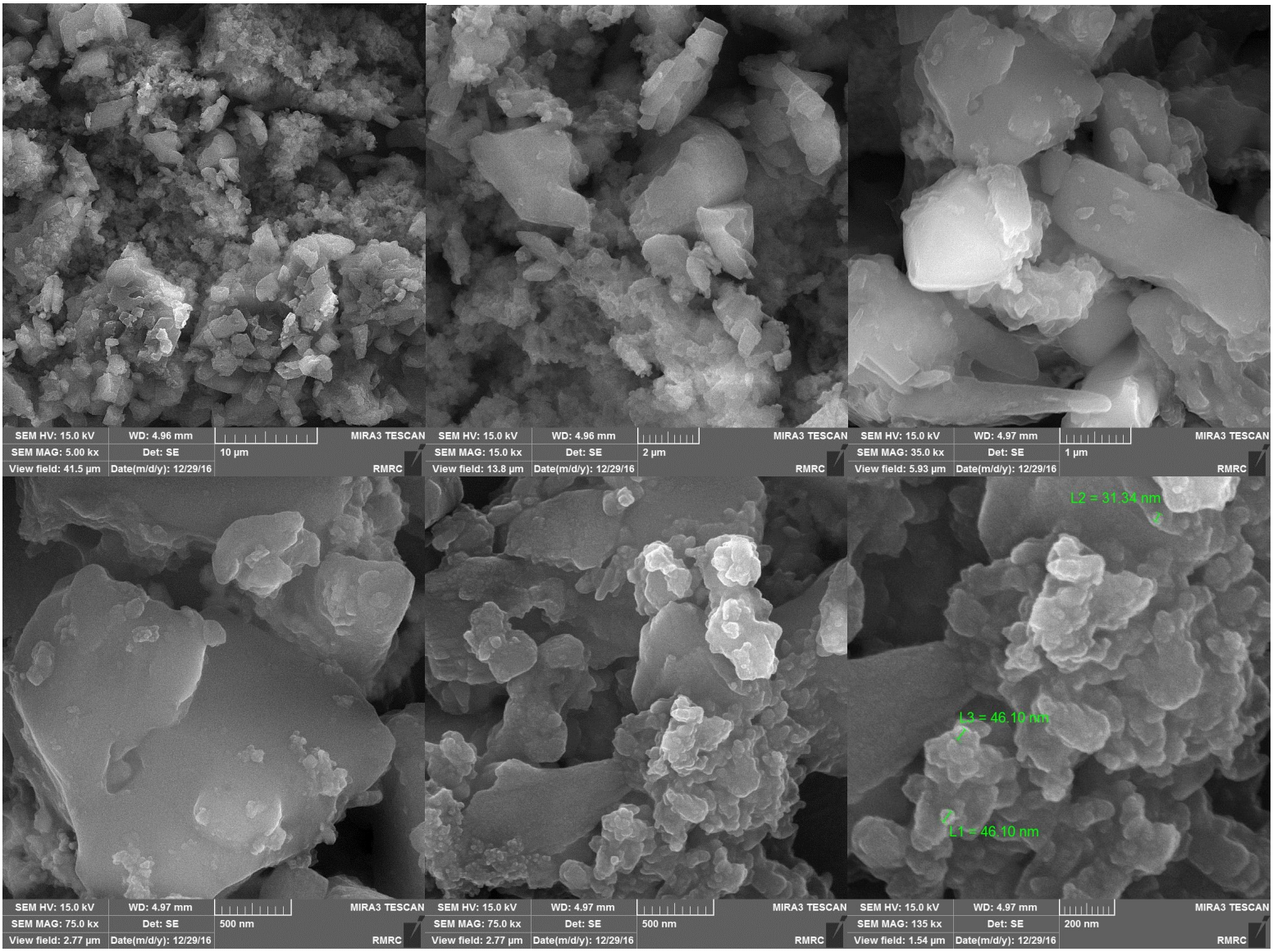


Fig. S3 SEM images of the centrifuged particles from the reaction of **1** under Marko's conditions.

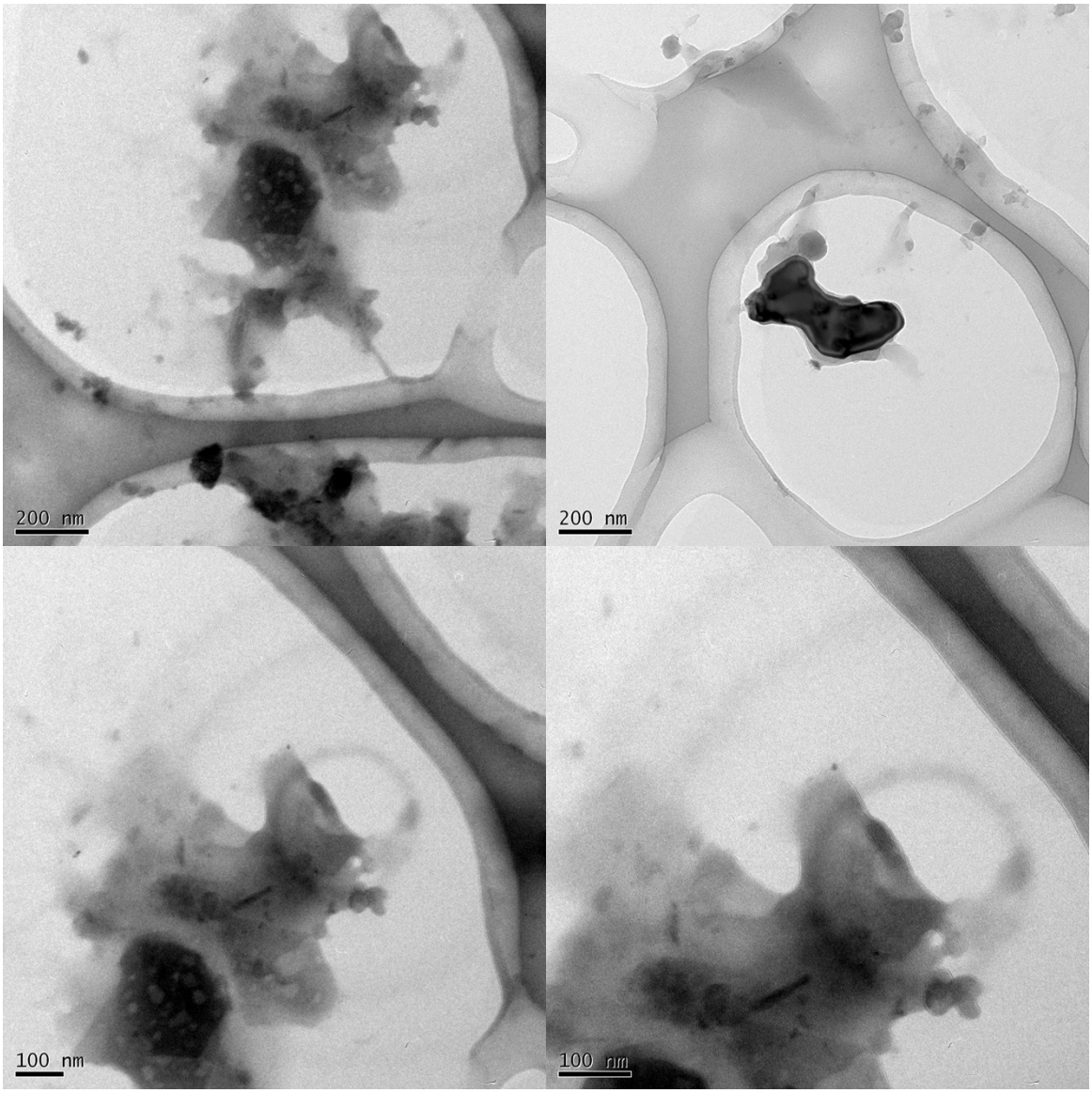



Fig. S4 TEM images of the centrifuged particles from the reaction of **1** under Marko's conditions.

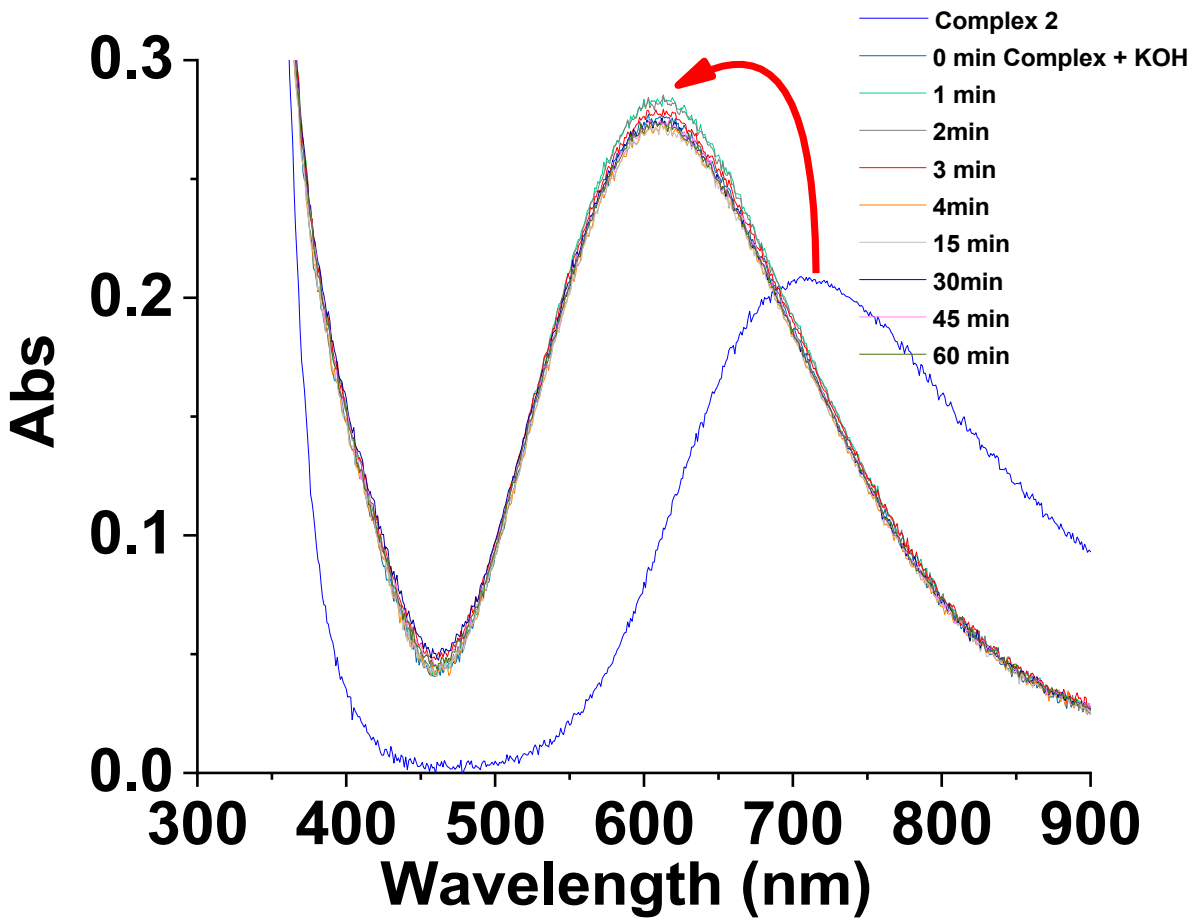
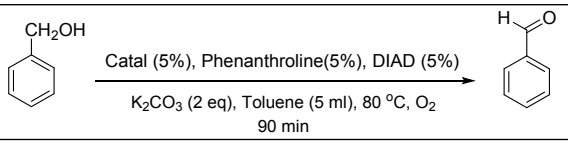
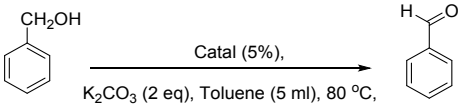
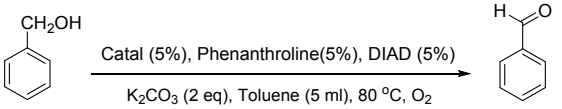
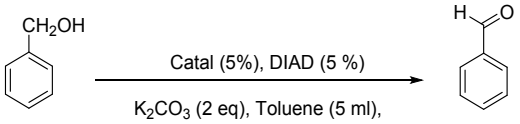
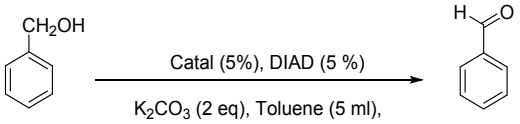
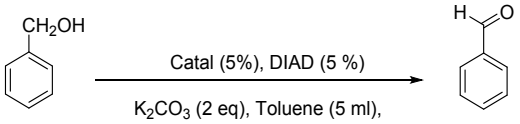
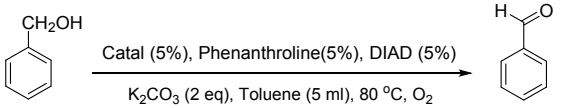
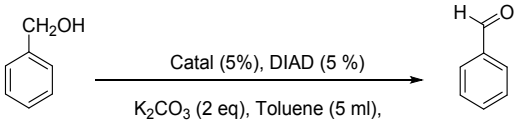
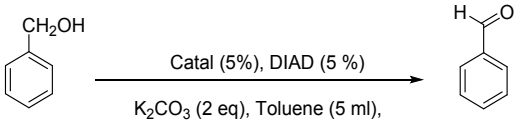
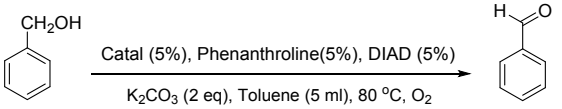
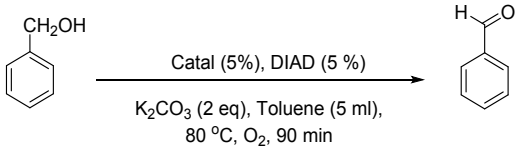
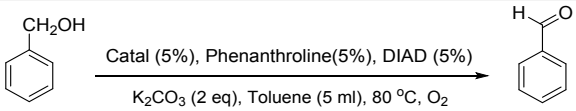
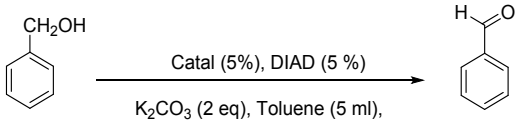
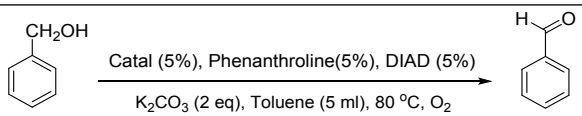



Fig. S5 UV-Vis spectroscopy of **2** (3.0 mM) before and after adding KOH (the final concentration is 2.0 M).

**Table S1** benzyl alcohol oxidation by the catalyst, and the centrifuged nanoparticles from the reaction

| Entry | Catalyst | Benzyl alcohol (%) | Benzaldehyde (%) | Condition |
|---|---|---|---|---|
| 1 | CuCl | 22 | 78 |   |
| 2 | CuO | 99-95 | 1-5 |   |
| 3 | CuO | 99-95 | 1-5 |   |
| 4 | Complex (**2**) | 99-95 | 1-5 |   |
| 5 | Complex (**1**) | 75 | 25 |   |
| 6 | centrifuged solid from the reaction of entry **1** | 62 | 38 |   |
| 7 | $Cu(ClO_4)_2$ | 85 | 15 |   |
| 8 | CuCl | 99-95 | 1-5 |   |
| 9 | CuI | 99-95 | 1-5 |   |
| 10 | CuI | 22 | 78 |   |

| | | | | |
|---|---|---|---|---|
| 11 | $K_2Cu(CO_3)_2$ | 99-95 | 1-5 |   |
| 12 | $K_2Cu(CO_3)_2$ | 99-95 | 1-5 |   |
| 13 | $CuCO_3$ | 99-95 | 1-5 |   |
| 14 | $CuCO_3$ | 99-95 | 1-5 |   |