

Figure 1S. Cu K-edge XANES spectra of (A) Cu/HT, (B) Cu^{II}/HT, (C) Cu foil, (D) Cu(CF₃SO₃)₂.

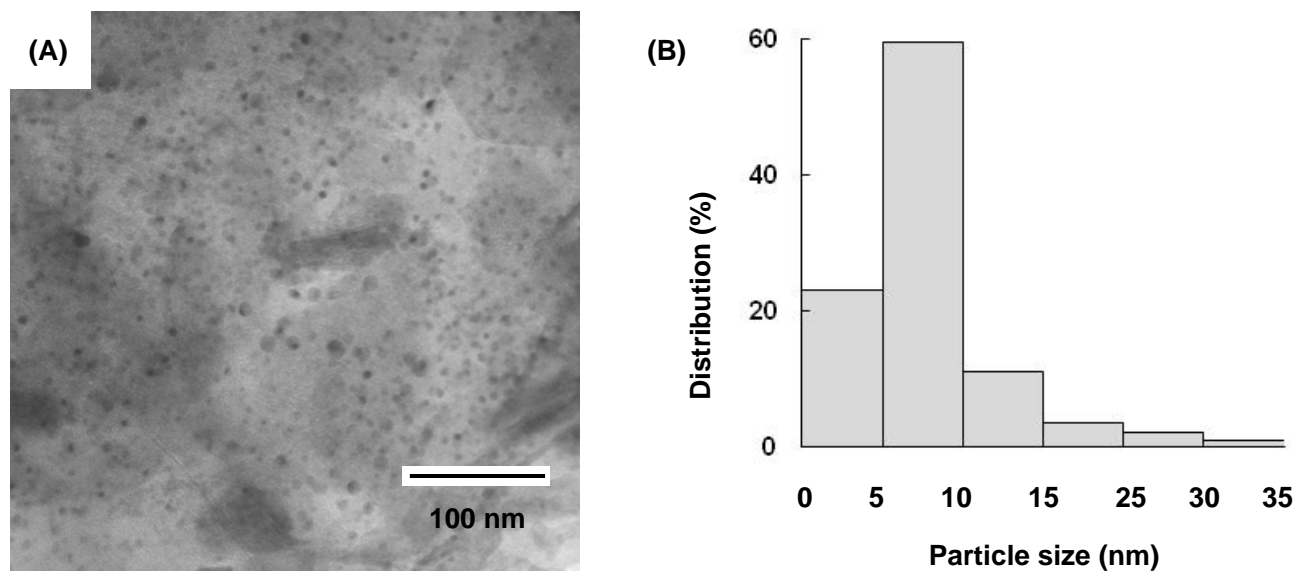


Figure 2S. (A) TEM image of Cu/HT, (B) size distribution diagram of the Cu nanoparticles.

A typical procedure for the dehydrogenation of cyclooctanol by Cu^{II}/HT: Cu^{II}/HT (0.10 g, 0.073 mmol Cu) was placed in a Schlenk tube equipped with a reflux condenser. The vessel was evacuated and filled with 1 atm of molecular hydrogen (H₂) and the solid catalyst was stirred at 180 °C for 0.5 h. After replacing the H₂ with Ar, a mineral oil bubbler was attached to the top of the condenser, *p*-xylene (5 mL) and cyclooctanol (1.0 mmol) were added, and the reaction mixture was vigorously stirred at 130 °C under Ar for 3 h. The solid catalyst was removed by centrifugation and the yield was determined by GC analysis with biphenyl as an internal standard (Shimadzu GC-8A, carrier gas: N₂ (50 kPa), H₂ (50 kPa), and air (50 kPa), column: 5 % KOCL-3000T (5.0 m); oven temperature program: from 100 °C, 16 °C/min up to 220 °C, hold for 10 min, injection and detection temperature: 270 °C, retention time: cyclooctanone (7.7 min), cyclooctanol (8.6 min), biphenyl (11.7 min)).

Measurement of H₂: The dehydrogenation was carried out in a closed vessel under standard reaction conditions. After the reaction, the gas phase was subjected to GC-TCD for qualitative and quantitative analysis of H₂. GC conditions were as follows: GC using thermal conductivity detector (Shimadzu GC-8A, column: molecular sieves 13X (4.0 m), oven temperature: 40 °C, injection and detection temperature: 70 °C, carrier gas: Ar (100 kPa), current: 60 mA, retention time: H₂ (3.0 min)). Evolution of H₂ was also confirmed volumetrically using a gas buret attached to the reactors.

Recycling experiments: another portion of the cyclooctanol (1.0 mmol) was successively added to the reaction mixture after the first and second runs, and the reaction mixture was continuously stirred at 130 °C under Ar for 3 h.

Product purification: after the dehydrogenation reaction, CuHT was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was subjected to silica gel column (Wakogel C-200), and eluted by a mixture of EtOAc and hexane (3:2).

Product identification: the products showed spectra in an excellent agreement with the reported data. All products are commercially available. CAS registry number and references are shown below.

Table 1.

cyclooctanone (entry 1);^{1,2} CAS registry No. [502-49-8]

2-octanone (entry 2);³ CAS registry No. [111-13-7]

Table 2.

cyclododecanone (entry 4);⁴ CAS registry No. [830-13-7]

cyclopentanone (entry 5);³ CAS registry No. [120-92-3]

cyclohexanone (entry 6);³ CAS registry No. [108-94-1]
3-methylcyclohexanone (entries 7 and 8);³ CAS registry No. [591-24-2]
4-ethylcyclohexanone (entries 9 and 10);⁵ CAS registry No. [5441-51-0]
3,5-dimethylcyclohexanone (entries 11 and 12);⁶ CAS registry No. [2320-30-1]
octahydro-1(2H)-naphthalenone (entries 13 and 14);⁷ CAS registry No. [4832-16-0]
4-(1,1-dimethylethyl)cyclohexanone (entries 15 and 16);⁸ CAS registry No. [98-53-3]
2-norbornanone (entries 17 and 18);⁹ CAS registry No. [497-38-1]
2-adamantanone (entries 19);³ CAS registry No. [700-58-3]
5 α -cholestan-3-one (entries 20);¹⁰ CAS registry No. [566-88-1]
acetophenone (entries 22);³ CAS registry No. [98-86-2]
2-acetylpyridine (entries 23);¹¹ CAS registry No. [1122-62-9]
benzaldehyde (entries 24 and 25);¹² CAS registry No. [100-52-7]
octanal (entries 26);¹² CAS registry No. [124-13-0]
benzyl benzoate;¹³ CAS registry No. [120-51-4]
2-cyclopentylcyclopentanone;¹⁴ CAS registry No. [14112-41-5]

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