CO Catalytic Oxidation by Metal Organic Framework Containing High Density of Reactive Copper Sites

Yonggang Zhao,[a,#] Moothetty Padmanabhan, [a,#] Qihan Gong, [a] Nobuko Tsumori,[b,*] Qiang Xu,[c] and Jing Li[a,*]

[a] Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Road, Piscataway, New Jersey, 08854, USA
[b] Toyama National College of Technology, 13, Hongo-machi, Toyama, 939-8630, JAPAN
[c] National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka,563-8577, JAPAN

Supporting Information

1

Experimental Section

Materials: All chemicals were purchased from commercial sources (Alfa Aesar, Acros, Aldrich or TCI America) and used as received.

Compound 1: **1** was prepared by a hydrothermal method. $Cu(CH_3COO)_2 \cdot H_2O$ (0.199g, 1.0 mmol) and *nip* (0.213g, 1.0 mmol) were dissolved in 10mL of water. The mixture was first stirred for 15 mins to form a blue gel,. then sealed in a Parr reaction vessel and heated at 373 K for 2 days. After naturally cooling down to room temperature, very uniform blue crystalline powder (diameter around 50μm) of **1** (0.080g, 88% yield based on metal) was isolated by filtration. The product was washed with water and DMF orderly, and then dried under vacuum.

PXRD Analysis: Powder X-ray diffraction experiments were conducted using a D/M-2200T automated system (Ultima$^+$, Rigaku) with Cu Kα radiation (λ=1.5406 Å). The PXRD patterns were collected between 2θ angles of 3° to 50° at a scan rate of 5 deg·min^{-1}. Graphite monochromator was used and the generator power settings were at 40 kV and 40 mA.

Thermogravemetric Analysis: The thermal properties of the compound were evaluated using a TA Instruments Q50 TG unit. The samples (~10 mg) were loaded onto a sample pan and heated from room temperature to 600 °C at a rate of 10 °C·min^{-1} under N_2 (flow and purge rate at 40 mL·min^{-1} and 60 mL·min^{-1}, respectively).

Catalysis Experiment: The catalytic oxidation of CO was conducted by using a fixed bed plug flow reactor system. Pure CO, O_2 and He were supplied through mass flow controllers and mixed with each other, and then the final reactant gas (37 ml min^{-1}) was passed through the catalyst bed. The catalyst (0.11 g) was mixed with quartz sand

(>300 μm, 0.22 g) and filled in the reactor made of stainless steel and then calcinated in argon at 120^oC for 3 h and in the reaction gas at 250 °C for 1 h. The reaction gas was composed from CO (1 vol. %), O_2 (20 vol. %) and He (balance), and hourly space velocity (SV) was 20,000 $mL \cdot h^{-1} \cdot g(cat.)^{-1}$. The reaction temperature was programmed between room temperature and 250^oC and monitored by thermocouple.

The reactant CO and product CO_2 were analyzed by using an on-line gas chromatograph (GC) system, which was composed of two gas chromatographs; one (GC-8A, Shimadzu) with Molecular Sieve 5A (3 m) for CO and one (GC-2014, Shimadzu) with Porapack Q (4 m) for CO_2, respectively. The retention times of gases were checked by comparison with those of authentic samples. Conversions of CO to CO_2 were calculated from the data (X_{CO}) from the GC for CO according to

$$X_{CO} = (1 - A_{CO} / A_{CO*}) \times 100 \; (\%)$$

where A_{CO*} and A_{CO} are the peak areas of CO before and after the reaction, respectively. Conversions of CO to CO_2 were calculated from the data from the GC (X_{CO2}) for CO_2 according to

$$X_{CO2} = A_{CO2} / A_{CO2*} \times 100 \; (\%)$$

where A_{CO2*} is the peak area of CO_2 after the complete conversion of CO to CO_2 and and A_{CO2} is the peak area of CO_2 after the reaction. The values of X_{CO2} and X_{CO2} are almost in agreement with each other.

Reaction rate (R, mol of CO_2 (mol of Cu . s)$^{-1}$) was calculated as follows:

$$R_{GC} = X_{GC} \times F_{CO} / M_{Cu}$$

3

F_{CO} (mol s^{-1}) is flow rate of CO in reactant gas, and M_{Cu} is the amount of Cu (mol) in used catalyst (0.11g) calculated from the formula weight of proposed dehydrated form [$Cu_5(OH)_2(nip)_4$].

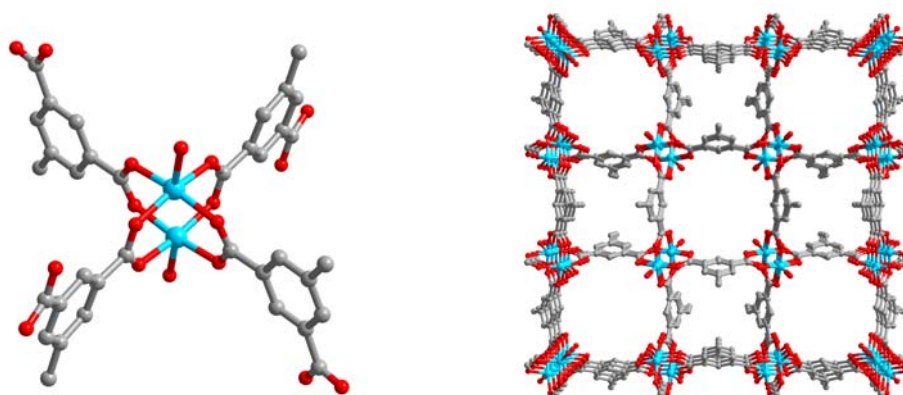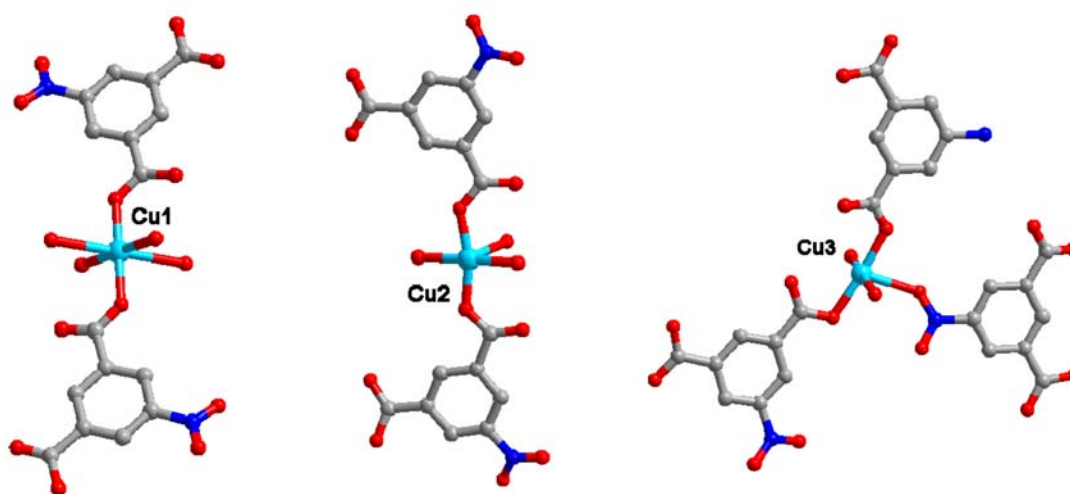**Fig S1**. Paddle-wheel Cu$_2$ building unit and perspective view of the microporous framework of Cu(*mip*)(H$_2$O).

Fig S2. Coordination environment of crystallographically independent copper centers in the pentameric Cu$_5$ building unit.
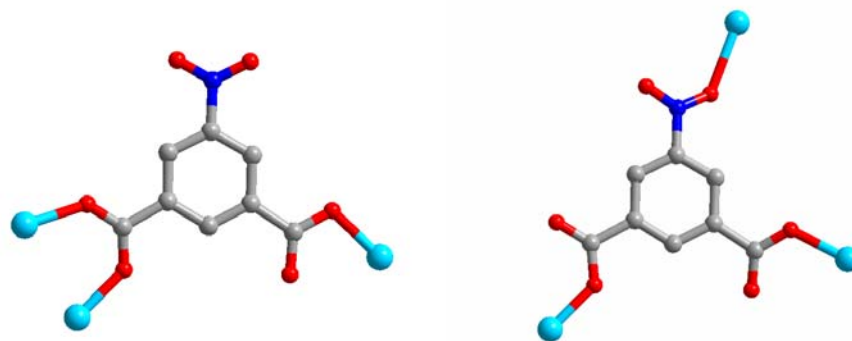
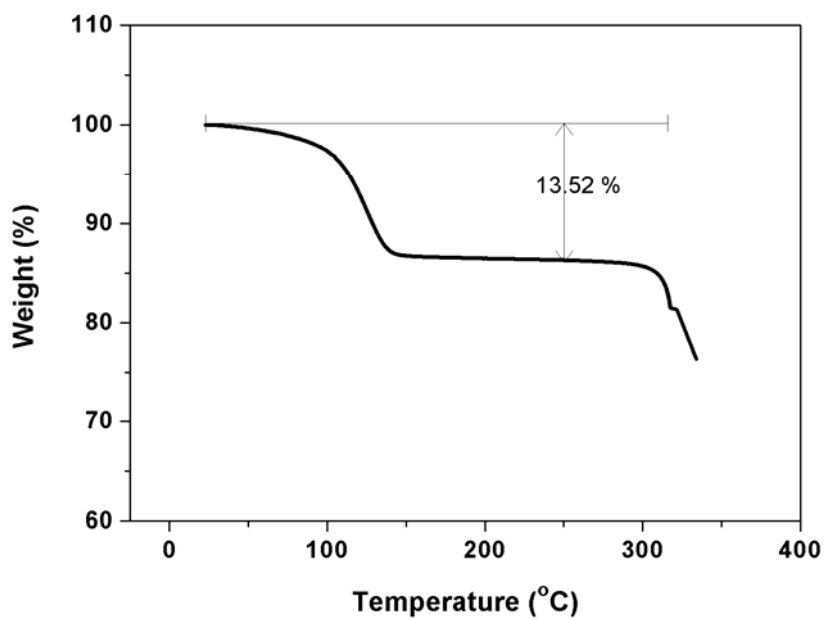**Fig S3**. Two coordinated modes of the *nip* ligand.

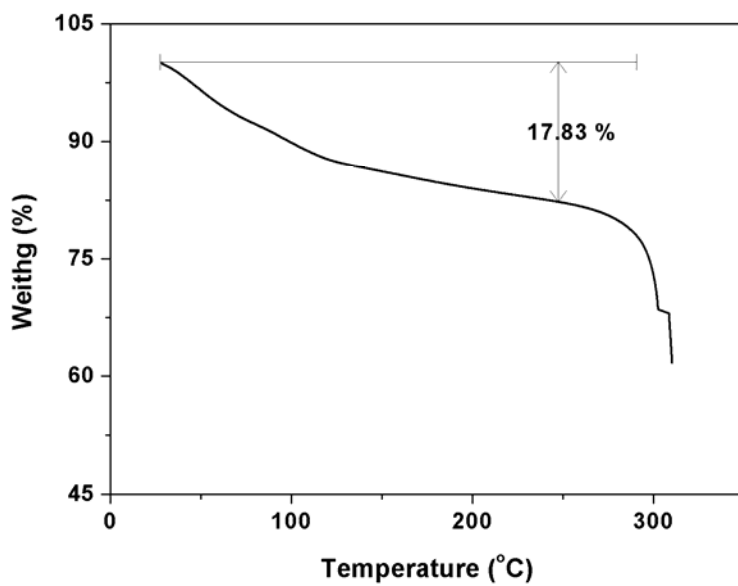**Fig. S4.** Thermogravimetric (TG) profile of compound **1**.

Fig. S5. TG profile of compound **1'** after the adsorption of NH_3.
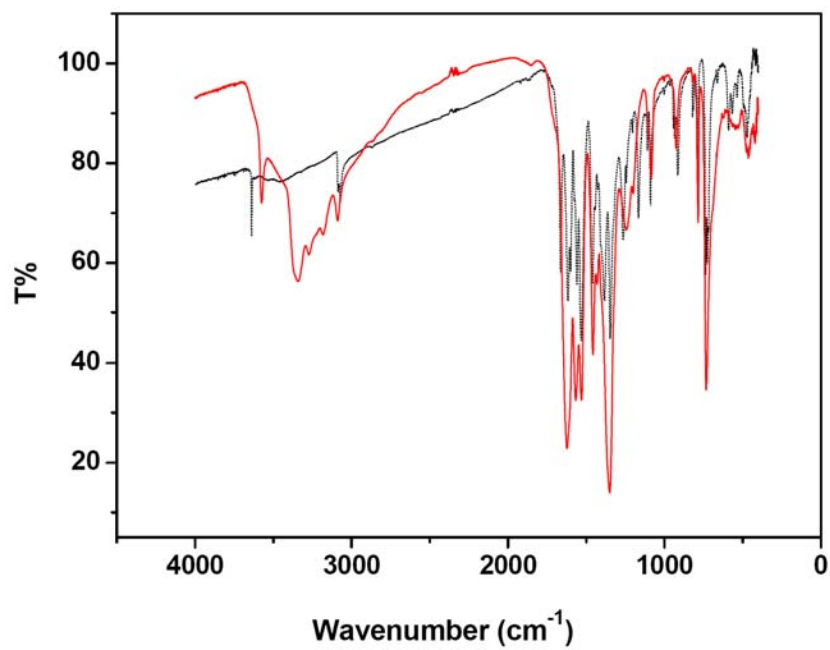

Fig. S6. FT-IR spectra of the compound **1'** (black dot) and **1'** after exposure to vapor of ammonia (red solid).
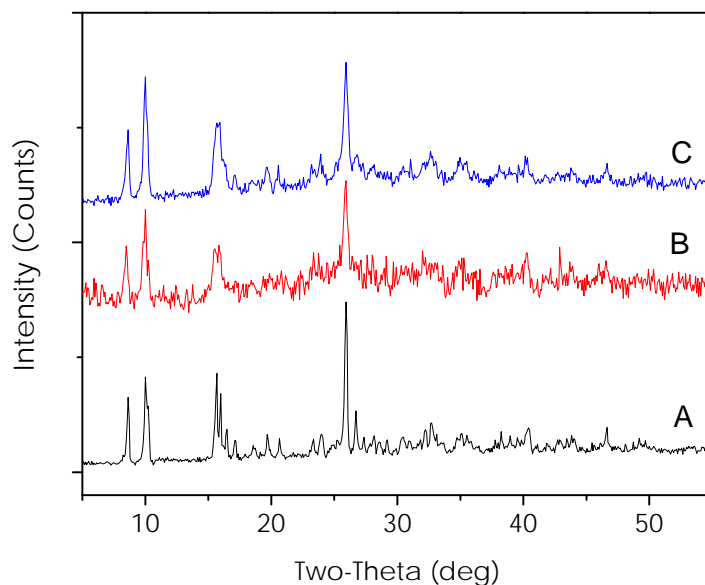
Fig. S7. PXRD patterns of **1**: A) before catalytic reactions; B) after catalytic reaction at 200 ºC for 20 hr and re-exposure to air for a long period of time. Sample was rehydrated by adsorbing water from air; and C) after catalytic reaction at 175 ºC for 20 hr and re-exposure to air for a long period of time.