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

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Supporting Information
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$_3$COO)$_2$·H$_2$O (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.

Thermogravimetric 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°C for 3 h and in the reaction gas at 250°C for 1 h. The reaction gas was composed from CO (1 vol. %), O₂ (20 vol. %) and He (balance), and hourly space velocity (SV) was 20,000 mL·h⁻¹·g(cat.)⁻¹. The reaction temperature was programmed between room temperature and 250°C and monitored by thermocouple.

The reactant CO and product CO₂ 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 CO₂, respectively. The retention times of gases were checked by comparison with those of authentic samples. Conversions of CO to CO₂ 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 CO₂ were calculated from the data from the GC (X_CO₂) for CO₂ according to

\[ X_{CO2} = A_{CO2} / A_{CO2}^* \times 100 \, (%) \]

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

Reaction rate \((R, \text{ mol of CO}_2 (\text{mol of Cu s})^{-1})\) was calculated as follows:

\[ R_{GC} = X_{GC} \times F_{CO} / M_{Cu} \]
$F_{CO}$ (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 NH3.

**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 °C 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 °C for 20 hr and re-exposure to air for a long period of time.