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Binary metal (Ti, Cu) oxyhydroxy–organic (terephthalate) framework: An interface model nanocatalyst for hydrogen purification

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ABSTRACT

The importance of metal–support interfaces is widely known in commercial and fundamental heterogeneous catalysis; however, it is difficult to characterize the active interface sites. In this study, we synthesize a new class of compound comprising tetragonal $[Ti_8O_8(OH)_4]^{12+}$ clusters interlinked by terephthalates (bdc) and $[Cu_2(OH)_6]^{2-}$ linkers $\{Ti_8O_8(OH)_4, (bdc)_2, [Cu_2(OH)_6]_4\}$. The crystalline structure was refined for X-ray diffraction and direct links between $[Cu_2(OH)_6]^{2-}$ and $[Ti_8O_8(OH)_4]^{12+}$ are confirmed by extended X-ray absorption fine structure. This compound functions very well ($k = 0.117 \text{ min}^{-1}$ in CO 63 Pa + O₂ 76 Pa at 323 K) as a catalytic model of interface Cu sites on ultra-dispersed Ti [hydro]oxide for preferential oxidation of CO in predominantly H₂ gas, that is important for the purification of hydrogen used in fuel cells. In comparison, mean 1.7-nm CuO nanoparticles embedded inside the pores of MIL125 were inert ($k = 0.0035 \text{ min}^{-1}$) because of the absence of links between Cu and $[Ti_8O_8(OH)_4]^{12+}$ clusters. In CO 0.51 kPa + O₂ 0.51 kPa at 323 K, the conversion to CO₂ and CO PROX selectivity using Ti₈O₈(OH)₄(dbc)₂.[Cu₂(OH)₆]₄ (76% and 99%) was significantly higher than that using CuO/CeO₂ (28% and 96%, respectively) for 24 h.

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1. Introduction

Oxyhydroxy metal clusters, e.g., $[Zr_6O_4(OH)_4]^{12+}$ [1], $[Al_{12}O(OH)_{18}]^{16+}$ [2], and $[Ti_8O_8(OH)_4]^{12+}$, [3] were linked using organic molecules containing more than two anionic functional groups, e.g., terephthalate (1,4-benzene dicarboxylate; bdc), 1,3,5-benzene tricarboxylate (btc), and bipyridine [4], to form metal–organic frameworks (MOFs). Cu oxides supported on TiO₂ catalyzed CO oxidation [5,6], methane combustion [7], NO_x decomposition [8], and photocatalytic water splitting [9].

For heterogeneous catalysis, metal–support interfaces have frequently been considered as active sites [10-13]. The interface between the nanoparticles and the metal oxide support is believed to play a crucial role in the catalysis. The examples of metal– support interfaces are copper nanoparticles on zinc oxide for methanol synthesis [10], rhodium nanoparticles on titanium oxide for hydrogenations [11], ruthenium nanoparticles promoted with alkali metal on carbon for ammonia synthesis [12], and gold nanoparticles on TiO₂ for preferential oxidation (PROX) of CO [13]. However, in nature, the interfaces have been difficult to characterize by spectroscopic or physicochemical methods. In this study, exact model composite consisting of $[Ti_8O_8(OH)_4]^{12+}$ clusters and $[Cu_2(OH)_6]^{2-}$ linkers was prepared as a molecular model of Cu oxide/hydroxide on Ti oxide/hydroxide support (supported catalysts).

Recently, nanosized metal oxide/sulfide and layered double hydroxide (LDH) have been synthesized utilizing MOF as a replica for the crystalline morphology [14] and MOF as a core template followed by the elimination of MOF to form hollow LDH, respectively [15]. The synthesis of core–shell nanocomposites of $Cu_3(btc)_2$ and anatase TiO₂ (210-nm thickness) has also been reported [16]. In this study, $[Ti_8O_8(OH)_4]^{12+}$ cluster, tetragonally linked by bdc ligands (MIL125), was chosen as a model of TiO₂ support. The interface between $[Ti_8O_8(OH)_4]^{12+}$ and added Cu species during catalyst synthesis was characterized and evaluated for CO PROX in predominantly H₂ gas.

2. Experimental

2.1. Synthesis of model catalysts

2.1.1. MIL125

MIL125 with a formula of $Ti_8O_8(OH)_4$ (bdc)₆ was synthesized via the reported procedure [3]. In brief, 3.75 mmol of Ti(IV) tetrabutoxide (>95%, Wako Pure Chemical) was mixed with 45 mL of *N*,





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N-dimethylformamide (DMF; >99.5%, Super dehydrated grade, Wako Pure Chemical) and 5.0 mL of methanol (>99.8%, Super dehydrated grade, Wako Pure Chemical). Terephthalic acid (15 mmol, >95%, Wako Pure Chemical) was added to the solution and dissolved. The mixed solution was magnetically stirred for 5 min at 300 rotations per minute (rpm) at 290 K. Subsequently, the solution was transferred into a Teflon-lined autoclave (TVS-N2-100, Taiatsu Techno; the inner volume 100 mL) and heated at 423 K for 20 h. The white precipitate thus obtained was filtered using a 0.2-µm-pore polytetrafluoroethylene membrane filter (Omnipore JGWP04700, Millipore) and washed several times with DMF (total 60 mL) and acetone (total 90 mL; >99.5%, Wako Pure Chemical). The obtained powder was dried in air at 353 K for 12 h and heated in vacuum at 473 K for 6 h.

2.1.2. Solid-state embedding of Cu

Cu was embedded in MIL125 using the following procedure. Using a mortar and pestle, 200 mg of MIL125 and 102 mg of Cu (II) acetate monohydrate (>99.8%, Wako Pure Chemical) were well mixed for 10 min. The mixture was treated in vacuum (10^{-6} Pa) at 290 K for 1 h. The resultant powder was heated at 473 K under 25 kPa of H₂ for 3 h. This reduction step was aimed for the growth of metallic Cu nanoparticles inside the nanopores of MIL125 (Chart 1A). The color of the powder changed from light blue to red, indicating the formation of metallic Cu nanoparticles in the sample. The sample was calcined in air at 573 K for 2 h. If the reduction step in H₂ was skipped, the crystalline of MIL125 was critically decomposed and 15 nm of CuO particles significantly greater than the nanopores (1.7 nm) of MIL125 was formed based on the X-ray diffraction (XRD) analysis. The obtained lime green powder was denoted as Cu/MIL125-S-ratio, in which the ratio was the atomic ratio of Cu/Ti. The atomic ratio of Cu/Ti was fixed at 1/2 (Table 1). During the solid-state embedding procedures, the framework of MIL125 was intact (see Section 3.1).

2.1.3. Cu impregnation

0.4 mL of Cu nitrate (0.5 mmol; >99.9%, Wako Pure Chemical) aqueous solution was prepared and 200 mg of MIL125 was added. The mixture was magnetically stirred at 300 rpm and 290 K for 20 min and the water was evaporated at 353 K. The atomic ratio of Cu/Ti was basically set to 1/2, but varied between 0 and 1 (0/1, 1/4, 1/2, 3/4, and 1/1) by incorporating 0.4 mL of Cu nitrate

(0–1.0 mmol) for comparative purposes (Table 1). The powder was calcined in air at 553–613 K for 2 h. The obtained green samples by impregnation method prepared via impregnation of MIL125 with Cu nitrate aqueous solution and calcination were denoted as Cu/MIL125-I-*T*-ratio, in which *T* was the calcination temperature (K) and the ratio was the atomic ratio of Cu/Ti (1/4, 1/2, 3/4, and 1/1). MIL125-I-573-0/1 was a control sample that was obtained from the impregnation procedure without Cu salt. The reaction of Cu ions with $[Ti_8O_8(OH)_4]^{12+}$ cluster occurred and the framework of MIL125 was lost if the solution was used. Therefore, reduction step in H₂ employed for Cu/MIL125-S-1/2 aiming to grow metallic Cu nanoparticles inside the nanopores of MIL125 was not followed for impregnated samples.

2.1.4. Reference catalysts

JRC-TIO-6 [rutile-type TiO₂, mean particle size 15 nm, the Bru nauer–Emmett–Teller surface area (S_{BET}) 100 m² g⁻¹; Catalysis Society of Japan (CSJ)], JRC-TIO-7 (anatase-type TiO₂, mean particle size 8 nm, S_{BET} 270 m² g⁻¹; CSJ), and P25 (TiO₂, anatase/rutile phase = 8/2, S_{BET} 60 m² g⁻¹; Degussa) [17] were used as references. Cu was embedded via solid-state reaction with or impregnated by the incipient wetness method with these TiO₂ samples and calcined at 573 K. These samples were denoted as Cu/brand of TiO₂-S (via solid-state reaction) and Cu/brand of TiO₂-I (by the incipient wetness method; Table 1).

CuO/CeO₂ catalyst was prepared via co-precipitation method [18]. Aqueous solution of Cu nitrate (0.15 M, 10 mL) and diammonium Ce(IV) nitrate (0.075 M, 100 mL; >95.0%, Kanto Chemical) was prepared, and sodium carbonate aqueous solution (24 mL, 7 wt%) was added to the mixed solution in 1 h at 290 K, and then set still at 290 K for 30 min. The precipitate was filtrated using a JGWP04700 filter and washed several times with deionized water (<0.05 μ S cm⁻¹; total 400 mL). The obtained green powder was dried at 383 K for 18 h, followed by calcination at 573 or 923 K for 4 h. These samples were denoted as CuO/CeO₂-*T* in which *T* was the calcination temperature (K; Table 1).

2.2. Characterizations

N₂-adsorption measurements were performed at 77 K in the pressure range 1.0–40 kPa in a vacuum system (10^{-6} Pa). The samples (10-100 mg) were evacuated and heated from 290 K to 423 K



Chart 1. Proposed structure for Cu/MIL125-S (A) and Cu/MIL125-I (B: side and top views), in which gray sticks/circles indicate $[Ti_8O_8(OH)_4]^{12*}$ clusters, dashed lines indicate terephthalates, and green lines/wedges indicate $[Cu_2(OH)_6(OH_2)_n]^{2-}$ (n = 0-4) linkers. The Model B' is based on Model B' in Chart 3. Hydrogen atoms are abbreviated for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table	1
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List of catalyst samples and the explanation of preparation method.

Catalyst	Synthesis in medium	iesis in medium				itment	Ref.
	Precursors	Atomic ratio of metals	Solvent used	<i>T</i> ^a (K)	<i>T</i> ^a (K)	Gas	
MIL125	$Ti(OC_4H_9)_4$, Terephthalic acid		DMF	423	353 473	Air Vacuum	[3]
Cu/MIL125-S-1/2	MIL125, $Cu(O_2CCH_3)_2 \cdot H_2O$	Cu/Ti = 1/2	None	290	473 573	H ₂ Air	This work
MIL125-I-573-0/1 Cu/MIL125-I-573-1/4 Cu/MIL125-I-573-1/2 Cu/MIL125-I-573-3/4 Cu/MIL125-I-573-1/1 Cu/MIL125-I-613-1/2 Cu/MIL125-I-613-1/1	MIL125, Cu(NO ₃) ₂	Cu/Ti = 0/1 Cu/Ti = 1/4 Cu/Ti = 1/2 Cu/Ti = 3/4 Cu/Ti = 1/1 Cu/Ti = 1/2 Cu/Ti = 1/1	Water	290	573 573 573 573 573 613 613	Air	This work
Cu/P25-S (13.5 wt% Cu)	P25, Cu(O_2 CCH ₃) ₂ ·H ₂ O	Cu/Ti = 1/5	None Water	290 290	473 573 573	H ₂ Air Air	This work
Cu/JRC-TIO-6-I (rutile; 13.5 wt% Cu) Cu/JRC-TIO-7-I (anatase; 13.5 wt% Cu)	JRC-TIO-6, Cu(NO ₃) ₂ JRC-TIO-7, Cu(NO ₃) ₂		Water	290	573	Air	This work
CuO/CeO ₂ -573 CuO/CeO ₂ -923	$(NH_4)_2Ce(NO_3)_6$, $Cu(NO_3)_2$	Cu/Ce = 1/5	Water	290	573 923	Air	This work
Au/TiO ₂	P25, HAuCl ₄ ·4H ₂ O	Au/Ti = 1/48	Water	353	573	Air	[31]

^a Temperature.

at a ramping rate of 4 K min⁻¹ and maintained at 423 K for 2 h as pretreatment. The S_{BET} value was calculated using eight points in the adsorption isotherm.

The XRD pattern was observed using a D8 ADVANCE diffractometer (Bruker) at the Center for Analytical Instrumentation, Chiba University at a Bragg angle (θ_B) of $2\theta_B = 5.0-60^\circ$ with a scan step of 0.02° and a scan rate of 3 s per step. The measurements were performed at 40 kV and 40 mA using Cu K α emission ($\lambda = 0.15419$ nm) [19,20] and a nickel filter. The sizes of crystallines (*t*) were estimated based on the Scherrer equation:

$$t = \frac{0.9\lambda}{\text{Peak width} \times \cos \theta_{\text{B}}}.$$
 (1)

High-resolution transmission electron microscopy (HR-TEM) images were obtained using a Model H-7650 (Hitachi). The samples were mounted on Cu mesh (150 mesh per inch) coated with a copolymer film of polyvinyl alcohol and formaldehyde (Formvar, Monsanto) and deposited carbon. A tungsten filament was used in the electron gun and the electron accelerating voltage was 100 kV. The magnification was between 60000 and 600000 times.

Fourier transform infrared (FTIR) spectra were measured using a Model FT/IR-4200 spectrophotometer equipped with a mer cury–cadmium–tellurium–M detector (JASCO) in the wave number region between 4000 and 650 cm⁻¹. The energy resolution was set to 2 cm⁻¹. A sample disk (ϕ = 20 mm, 4 mg diluted in KBr) was positioned perpendicular to the IR beam.

Ti K and Cu K-edge X-ray absorption fine structure (XAFS) spectra were measured at 290 K in a transmission mode on a beamline 9C in the Photon Factory and NW10A in the Photon Factory Advanced Ring at the High Energy Accelerator Research Organization (Tsukuba). The storage ring energy was 2.5 GeV and the ring current was 450 mA for Ti K-edge. The values were 6.5 GeV and 37–54 mA for Cu K-edge. A Si(111) and Si(311) double-crystal monochromator was inserted in the X-ray beam path. The X-ray intensity was maintained at 65% of the maximum flux using a Piezo translator set on the crystal. The slit opening size in front of the I_0 ionization chamber was 1.0 mm (vertical) × 2.0 mm (horizontal). The I_0 and $I_{transmit}$ ionization chambers were purged with a mixed gas of N₂ (70%) + He (30%) (I_0) and N₂ ($I_{transmit}$) for Ti K-edge. The Ti K and Cu K-edge absorption energy

values were calibrated to 4964.5 and 8980.3 eV, respectively, for the spectra of Ti and Cu metal foils [19,20]. The energy position of the monochromator was reproduced within ± 0.1 eV.

The XAFS data were analyzed using an XDAP package [21]. The analytical procedure has been described previously [22-24]. Multiple shell curve fit (CF) analyses were performed for the Fourier-filtered k^3 -weighted extended XAFS (EXAFS) data in kand *R*-space using empirical amplitude and phase-shift parameters extracted from the EXAFS data of JRC-TIO7 for Ti-O and Ti(-O-)Ti interatomic pairs, CuO powder for Cu-O and Cu(-O-)Cu interatomic pairs, and Cu metal for Cu-Cu interatomic pair. The interatomic distance (R) and its associated coordination number (*N*) values for the Ti–O, Ti(–O–)Ti, Cu–O, Cu(–O–)Cu, and Cu–Cu interatomic pairs were set to an *R* value of 0.1949 nm with an *N* value of 6, an *R* value of 0.3039 nm with an *N* value of 4, an *R* value of 0.1956 nm with an N value of 4. an R value of 0.3028 nm with an *N* value of 10, and an *R* value of 0.2553 nm with an *N* value of 12. respectively, on the basis of their crystal structures [25]. The Debye–Waller factor (σ^2) value was with reference to that for the model parameter ($\Delta \sigma^2$).

2.3. CO PROX tests

Most of the CO PROX reaction tests in predominant H_2 were performed as follows: 50 mg of catalyst was placed in a Pyrex reactor connected to a closed circulating system (total volume 0.142 L) and evacuated (10⁻⁶ Pa) for 2 h at 290 K. Then, the sample was heated to 323 K and reaction gas (H_2 370 µmol, CO 3.7 µmol, O_2 4.5 µmol) was introduced to the system. The gas flow rate was 0.33 L min⁻¹. The products and reactants were analyzed using columns of Molecular Sieve 13X-S and polyethylene glycol-6000 on Flusin P (GL Sciences) set in an online gas chromatograph equipped with a thermal conductivity detector (GC-TCD; Shimadzu, Model GC-8A). Independently, 19 µmol of CO₂ and/or moisture was mixed to above reaction gas ($H_2 + CO + O_2$) and the effects on CO PROX reaction were tested at 323 K.

To evaluate the dependence of reaction system and/or reactant pressure, CO PROX tests in predominant H_2 were also performed using a gas flow system for representative catalysts. 100 mg of catalyst was placed in a Pyrex reactor (internal diameter 4 mm) and 101 kPa of mixed gas (O₂ 1%, N₂ 99%) was flowed at a rate of

10 mL min⁻¹ for 1 h at 323 K. Then, the gas was switched to 101 kPa of reaction gas (CO 0.5%, O₂ 0.5%, H₂ 49.5%, N₂ 49.5%) and the flow rate was 20 mL min⁻¹. The products and reactants in the exit gas (40 mL time⁻¹) were analyzed using GC-TCD in a similar way to that for closed circulating system.

3. Results and discussion

3.1. Cu/MIL125 synthesized via solid-state method

Major XRD peaks for Cu/MIL125-S-1/2 synthesized via the solid-state method, i.e., physical mixing of Cu salt with MIL125 at an atomic ratio of Cu/Ti of 1/2 and heating in H₂ at 473 K (Fig. 1A-b), appeared at 6.89°, 9.58°, 9.83°, and 11.80°, similar to those for MIL125 (6.94°, 9.61°, 9.90°, and 11.82°; Fig. 1A-a). XRD peak intensity decreased to 26-44% of the corresponding peaks for MIL125. The S_{BET} value and mean crystalline size based on Eq. (1) consistently decreased from $852 \text{ m}^2 \text{ g}^{-1}$ and 94 nm for MIL125 to $349 \text{ m}^2 \text{ g}^{-1}$ and 25 nm for Cu/MIL125-S-1/2 (Table 2a and b). The S_{BET} and mean crystalline size for MIL125 were in consistent with reference 3. MIL125 is ultimately dispersed and all the constituent atoms are in contact with the nanopores (Chart 1A). Thus, contribution of the external surface area should be small and smaller mean crystalline size (25 nm) does not necessarily correspond to higher S_{BET} value (349 m² g⁻¹) for Cu/MIL125-S-1/2. One of the major reasons of SBET decrease was that the nanopores of MIL125 were blocked by Cu species (Chart 1A). Furthermore, partial decomposition of MIL125 to less nanoporous structure was also possible for Cu/MIL125-S-1/2.

The Ti K-edge XANES (Fig. S1D-b) of the Cu/MIL125-S-1/2 pattern was very similar to that of MIL125 (spectrum a). Ti K-edge EXAFS peaks for Cu/MIL125-S-1/2 resembled those of MIL125 (Fig. 2b and a). The *N* value for the Ti(-O-)Ti pair at 0.270 nm remained at 0.4, while the *N* value for the Ti(-O-)Ti pair at 0.314 nm increased from 1.6 to 2.2 (Table 3b and a) probably due to the local distortion of the framework. Thus, the framework of MIL125 was basically retained in Cu/MIL125-S-1/2.

From Cu K-edge EXAFS CF analysis, formation of mean 1.7-nm metallic Cu nanoparticles was suggested on the basis of the N value of a Cu–Cu interatomic pair (9.1) [26] after solid-state mixing and heating at 473 K in H₂. Due to the high Cu content (13.5 wt%) in the sample, the Cu⁰ nanoparticles should ideally occur in the pores of MIL125 (Chart 1A). The lattice parameters (a = 1.85 nm; c = 1.80 nm) based on 011 and 002 diffraction for Cu/MIL125-S-1/2 (Fig. 1A-b) are negligibly different from the values of MIL125 (a = 1.86 nm; c = 1.81 nm). As the mean size for metallic Cu was almost the upper limit of the pore space of MIL125 (Chart 1A), on the basis of the *N* value (2.2) for Cu(-O-)Cu interatomic pairs obtained from Cu K-edge EXAFS (Fig. 2d and Table 3d), the mean size of Cu oxides formed by calcination at 573 K in Cu/MIL125-S-1/2 would be 1.7 nm. The 1.7-nm CuO particles were not detected by XRD above the detection limit. 5.9-nm mean size CuO particles were observed in HR-TEM attached to the MIL125 crystallines' external surfaces (Fig. 3B); however, the number was very few and corresponded to approximately 8 atomic%. The population of CuO nanoparticles for CuO (13.5 wt%)/SiO₂ was used as a standard in HR-TEM image. As the result, CuO seen for Cu/MIL125-S was 8% of that for CuO (13.5 wt%)/SiO₂.

3.2. Cu/MIL125 synthesized via impregnation method

The framework structure for Cu/MIL125-I-573-1/2 was altered from that of MIL125, as demonstrated by XRD. The peak pattern for MIL125 (Fig. 1A-a) changed to totally different one for



Fig. 1. (A and B) XRD patterns for MIL125 (a), Cu/MIL125-S-1/2 (b), MIL125-I-573-0/1 (c), Cu/MIL125-I-573-1/4 (c'), Cu/MIL125-I-573-1/2 (c''), Cu/MIL125-I-573-1/2 (c''), Cu/MIL125-I-573-1/2 (c''), Cu/MIL125-I-573-1/2 (d), Cu/MIL125-I-613-1/1 (d'), and Cu/MIL125-I- model B' (Chart 1 and see later description in text) (e and f). Patterns e (panel A) and f (panel B) were theoretically generated using Diamond 3.2 [27] and refined by Rietveld algorithm using TOPAS 4.2, respectively. The residue was between pattern c'' and f (panel B). (C) FTIR spectra for MIL125 (a), Cu/MIL125-I-553-1/2 (b), Cu/MIL125-I-573-1/2 (c), and Cu/MIL125-I-613-1/2 (d).

Table 2

Particle sizes of MIL125, compound **1**, and CuO based on XRD peak width^a, specific surface area, and CO PROX reaction performances in H₂^b using MIL125, Cu/MIL125, Cu/MIL125, Cu/TiO₂, CuO/CeO₂, and Au/TiO₂.

Entry	Catalyst	Mean crystalline size (nm) ^a			$S_{\rm BET} (m^2 { m g}^{-1})$	Time (h) ^c	Rate const. $k (10^{-3} \text{ min}^{-1})$	Conv. (%) ^d	Selec. (%) ^e
		MIL125	Compound 1	CuO					
a	MIL125	94			852	3	0.6	4.9	94
b	Cu/MIL125-S-1/2 ^f	25			349	3	3.5	42	98
с	MIL125-I-573-0/1	68				3	0.8	9.9	25
d	Cu/MIL125-I-573-1/4		92		165	3	0.5	8.4	79
e	Cu/MIL125-I-573-1/2		106		320	2	45	99	98
e′	Cu/MIL125-I-573-1/2 ^g		92		238				
f	Cu/MIL125-I-573-3/4		51	9.2	250	2	47	99	93
g	Cu/MIL125-I-573-1/1		68	8.6	215	2	69	100	100
h	Cu/MIL125-I-613-1/2		101	7.2	337	1	117	97	98
h′	Cu/MIL125-I-613-1/2 ^g		90		332				
i	Cu/MIL125-I-613-1/1			13	185	2	50	100	100
j	Cu/P25-S (13.5 wt% Cu)			19		3	9.2	73	94
k	Cu/P25-I (13.5 wt% Cu)			23	58	3	3.4	39	58
1	Cu/JRC-TIO-6-I (rutile; 13.5 wt% Cu)			37		3	0.3	3.8	53
m	Cu/JRC-TIO-7-I (anatase; 13.5 wt% Cu)			<4		3	0.9	14	80
n	CuO/CeO ₂ -573					2	30	95	93
0	CuO/CeO ₂ -923					1	85	98	90
р	Au/TiO ₂ ^h					1	141	100	93

^a Based on Scherrer equation (Eq. (1)) for MIL125 (011), Compound 1 (011), and CuO ($\overline{1}11$) + (002) reflection peaks.

^b Initial gases: CO 3.7 μmol, O₂ 4.5 μmol, H₂ 370 μmol. At 323 K.

^c Reaction period.

^d [CO]/[CO]_{0min} \times 100.

 $e [CO_2]/([CO_2] + [H_2O]) \times 100.$

^f Calcined sample.

^g After CO PROX test of entry e or h.

^h Sample 10 mg, reaction temperature 293 K; Ref. [31].

Cu/MIL125-I-573-1/2 (Fig. 1A-*c*"). Main peaks appeared at 8.38° and 9.22°. The peaks at 6.94° and 9.61° for tetragonal MIL125 were assigned to the 011 and 020 diffractions [3]. Assuming that the tetragonal and body-centered framework for MIL125 (a = 1.86 nm; c = 1.81 nm) was preserved in this unknown structure for Cu/MIL125-I-573-1/2, the two peaks can be ascribed to the 011 and 020 planes, respectively, with lattice parameters a = 1.936 nm and c = 1.277 nm (see also Rietveld refinement below).

This assumption of tetragonal body-centered structure was justified based on the theoretical XRD pattern using Diamond version 3.2 obtained by calculating crystal structure factors (Fig. 1A-e) [27]. The angle and the intensity ratio for major peaks at 8.38°, 9.22°, 12.42°, and 16.72°, assignable to the 011, 020, 121, and 022 diffractions (Fig. 1A-c"), were exactly reproduced in the theoretical pattern (8.29°, 9.21°, 12.40°, and 16.62°, respectively) calculated for the model structure containing MIL125 sheets and $[Cu_2(OH)_6]^{2-}$ linkers (Chart 1B'; vide infra). Furthermore, the model structure was refined via the Rietveld algorithm using TOPAS 4.2 (Bruker). The refined pattern resembled pattern e given by Diamond 3.2; however, if the anisotropy in the direction of 010 and 121 was also considered in the refinement, the theoretical pattern (8.37°, 9.21°, 12.43°, 13.96°, and 16.72°) assignable to the 011, 020, 121, 002, and 022 diffractions was nearly completely reproduced (Fig. 1A-f).

A weak peak in the theoretical pattern f, the 031 plane at 15.47°, did not clearly appear in experimental pattern c", and the 040 peak at 18.41° in pattern c" was weak in pattern f probably because of imperfect crystallinity, anisotropy, and/or the detection limit of the apparatus. Moreover, the weak experimental peak at 8.93° and 17.83 (pattern c") was absent in pattern f, presumably due to formation of a different very minor crystal lattice.

In the Cu/MIL125-I-573-1/2 HR-TEM images, fringes with an interval of 4.1 nm were observed that crossed the other fringes perpendicularly with the same interval (Fig. 3C, inset). Considering the spatial resolution (2–3 nm) of the HR-TEM apparatus, three

repetitions of perpendicular 110 and $1\overline{10}$ planes would be observed with intervals of 1.37×3 nm (*a* = 1.936 nm).

In the FTIR spectra for Cu/MIL125-I-1/2 (Fig. 1C), the peak intensity centered at 1546, 1397, and 1019 cm⁻¹ because of coupling modes of $v(C=C) + \beta(CCH) + v(CH)$, $v(C=C) + \delta(C=C-C)$, and γ (CCC) + β (CCH) due to terephthalate [28] decreased to two-thirds, one-half, and one-third by calcination at 553, 573, and 613 K, respectively (Fig. 1C-b-d), compared with intact MIL125 (a).

For determining the crystal structure of Cu/MIL125-I, the compressed *c* length by a factor of 0.71 needs to be explained as compared with MIL125, while *a* length remained constant (1.04 times). We concluded that one-third of terephthalates in the *ab*-plane for MIL125 [Ti₈O₈(OH)₄·(bdc)₆] remained for Cu/MIL125-I-613-1/2; those connecting [Ti₈O₈(OH)₄]¹²⁺ clusters in neighboring [Ti₈O₈(OH)₄·(bdc)₂]⁸⁺ sheets were replaced by shorter [Cu_x(OH)_{2x+2}(OH₂)_y]²⁻ (*x* = 2, 3, or 4) linkers. In this model, the nearest interatomic distance between Ti atoms in neighboring [Ti₈O₈(OH)₄·(bdc)₂]⁸⁺ sheets [the length (*L*) of green sticks in Chart 1B] was 0.874 nm.

$$L = \sqrt{\left(\frac{a}{\sqrt{2}} - 2r\right)^2 + \left(\frac{c}{2}\right)^2}$$
$$= \sqrt{\left(\frac{1.936}{\sqrt{2}} - 2 \times 0.386\right)^2 + \left(\frac{1.277}{2}\right)^2} = 0.874 \text{ nm.}$$
(2)

in which r is the distance between the center of Ti₈ octagon and the middle point of two neighboring Ti atoms (Chart 2).

Based on the Cu—O and Ti—O interatomic distances determined by EXAFS for Cu/MIL125-I-573-1/2 (both 0.195 nm; Table 3c and e) and assuming complete tetrahedral (T_d) or octahedral (O_h) coordination around Cu, three plausible Cu linker models were drawn (Chart 3).

The first model is $[Cu_2(OH)_6]^{2-}$, in which the Cu sites are T_d coordinated (Chart 3A). The second and third are $[Cu_2(OH)_6(OH_2)_4]^{2-}$ and $[Cu_4(OH)_{10}(OH_2)_6]^{2-}$, in which the Cu sites are O_h coordinated (Chart 3B and C, respectively).



Fig. 2. Ti K-edge (a–c) and Cu K-edge (d and e) EXAFS for MIL125 (a), Cu/MIL125-S-1/2 (b and d), and Cu/MIL125-I-573-1/2 (c and e). The k^3 -weighted EXAFS χ -function (1), its associated Fourier transform (3), and the best CF for Fourier-filtered data in k-space (2) and R-space (4).

In models A, B, and C, the nearest distances between Ti atoms in the neighboring $[Ti_8O_8(OH)_4(bdc)_2]^{8+}$ sheets (green bar length in Charts 1B and 2) were calculated as 0.838, 0.936, and 1.100 nm, respectively (Chart 3). Thus, model C was rejected as the linker in comparison with the experimental value: 0.874 nm (Eq. (2)). If the O—Cu—O angles for central Cu₂O₂ core in model A were slightly distorted from 109.5° (T_d) to 96.1° (model A', Chart 3) or if the dihedral angle of two CuO₄ planes was distorted from 180° to 132° (model B'), the Cu linker length *L* became 0.874 nm, in agreement with XRD.

Based on the Ti K-edge EXAFS CF analyses for Cu/MIL125-I-573-1/2 (Table 3c and Fig. 2c), the Ti(-O-)Ti interatomic distance changed from 0.305 nm (mean) for MIL125 (Table 3a) to 0.276 nm. Its associated *N* value increased from 2.0 to 3.8. In addition, a new farther peak appeared at 0.33 nm (phase shift uncorrected; Fig. 2c3), that can be ascribed to a Ti(-O-)Cu interatomic pair fitted with the *R* value 0.380 nm and *N* value 2.6 (Table 3c), strongly suggesting that new Ti(-O-)Cu interatomic links formed around the [Ti₈O₈(OH)₄]¹²⁺ clusters. The *N* value was consistent with models A' or B' for Cu/MIL125-I (Chart 3) within variation of ±0.6 (Table 3c), because the models assumed that two-thirds of terephthalates coordinated to the Ti atoms in MIL125 were replaced by $[Cu_2(OH)_6]^{2-}$ linkers; thus, the *N*[Ti (-O-)Cu] value was two. The distance (0.380 nm; Table 3c) was in agreement with the Ti···Cu interatomic distance in model B' (0.373 nm; Chart 3) rather than 0.355 nm in model A'. The formula would be $Ti_8O_8(OH)_4 \cdot (bdc)_2 \cdot [Cu_2(OH)_6]_4$ (Compound 1) for Cu/MIL125-I-613-1/2. Model B' in Chart 3 is also drawn in Chart 1B'.

The connection between $[Cu_2(OH)_6]^{2-}$ linkers and $[Ti_8O_8(OH)_4]^{12+}$ clusters was investigated by Cu K-edge EXAFS. The *N* value for Cu—O pairs (3.6; Table 3e and Fig. 2e) supported the coordination of four O atoms in both models A' and B' (Chart 3) within the variation of ±0.6 (Table 3e). The *N* value for Cu(—O—)M (M = Cu or Ti) was shown to be 2.8 (Table 3e), consistent with coordination to one Cu and two Ti (Chart 3A' and B'). The interatomic distance for Cu(—O—)M (0.310 nm; Table 3e) was consistent with model A': $2/3 \times 0.355 + 1/3 \times 0.261 = 0.324$ nm and model B': $2/3 \times 0.373 + 1/3 \times 0.259 = 0.335$ nm.

Table 3
Best-fit results of Ti and Cu K-edge EXAFS analyses for MIL125 and CuO supported on/in MIL125 and TiO ₂ . ^a

Catalyst	Ti—O		Ti(—O—)Ti		Ti(—O—)Cu		Cu—O		Cu(—O—)M (M = Ti, Cu)	
	Ν	<i>R</i> (nm)	N	<i>R</i> (nm)	N	<i>R</i> (nm)	N	<i>R</i> (nm)	Ν	<i>R</i> (nm)
(a) MIL125	4.4 (±1.5) 1.6 (±1.8)	0.175 (±0.003) 0.2174 (±0.0008)	0.4 (±0.3) 1.6 (±0.3)	0.271 (±0.001) 0.314 (±0.003)						
(b and d) Cu/MIL125-S-1/2	2.6 (±1.2) 2.4 (±0.6) 0.9 (±0.3)	$\begin{array}{c} 0.169 \\ (\pm 0.003) \\ 0.192 \\ (\pm 0.004) \\ 0.220 \\ (\pm 0.002) \end{array}$	0.4 (±0.9) 2.2 (±0.6)	0.270 (±0.02) 0.314 (±0.003)			3.2 (±0.6)	0.1956 (±0.0008)	2.2 (±0.6)	0.307 (±0.003)
(c and e) Cu/MIL125-I-573-1/2	5.2 (±1.2)	0.1945 (±0.0004)	3.8 (±0.3)	0.276 (±0.002)	2.6 (±0.6)	0.3797 (±0.0008)	3.6 (±0.6)	0.195 (±0.001)	2.8 (±2.2)	0.310 (±0.006)
(f) Cu/P25-I							3.2 (±1.5)	0.196 (±0.002)	9.2 (±1.2)	0.303 (±0.008)
(g) Cu/JRC-TIO-7-I							3.1 (±0.6)	0.194 (±0.001)	4.9 (±2.7)	0.308 (±0.004)
(a') MIL125 (X-ray crystallography) ³	2 1 3	0.1894 0.1941 0.1982	1 1	0.2761 0.3543						

^a The values in parenthesis are fit errors.



Fig. 3. HR-TEM images for MIL125 (A), Cu/MIL125-S-1/2 (B), and Cu/MIL125-I-573-1/2 (C).



Chart 2. The diagram for length of Cu linker in the crystal structure of Chart 1B.

The theoretical XRD pattern (Fig. 1A-e and B-f) calculated for model B' (Chart 1) was similar to experimental one (Fig. 1A-c"), as discussed above. The theoretical Ti and Cu K-edge X-ray absorption near-edge structure (XANES) pattern generated using ab initio multiple scattering calculation code, FEFF8.4 [29] and the greater Cu 1s-3d pre-edge peak intensity [30] directly supported model B' as linkers for Cu/MIL125-I. However, model A' may be also acceptable (Fig. S1B and C; Supplementary material).

3.3. CO PROX tests

CO PROX activity was tested, and the rates were evaluated assuming first-order kinetics of CO pressure (P_{CO}):

$$-dP_{\rm CO,t}/dt = kP_{\rm CO,t}.$$
(3)

We performed three CO PROX tests under the same conditions and the data (rate constant *k*, conversion, and selectivity) variation was within 5%. The data for all the catalysts were nicely fit to the equation, suggesting stability of these catalysts (Fig. 4A). The *k* value was 0.0006 min⁻¹ for MIL125 (Table 2a). Introducing Cu species in MIL125 by the impregnation method improved the activity by a factor of 200 to 0.117 min⁻¹ (Cu/MIL125-I-613-1/2; Table 2h and Fig. 4A-e). The performance was due to the formation of Compound **1** and maximal S_{BET} value (Table 2h) due to the desorption of extra terephthalates (Eq. (5); see discussion below). This value was superior to 0.085 and 0.030 min⁻¹ using CuO/CeO₂-923 and CuO/ CeO₂-573, respectively (Table 2o and n and Fig. 4A-h) and comparable to 0.141 min⁻¹ using Au/TiO₂ [31] (Table 2p) if the difference in reaction conditions (50 versus 10 mg of catalyst, 323 versus 293 K, respectively) was not considered.

The mass was nicely balanced for the reaction $2CO + O_2 \rightarrow 2CO_2$ for Cu/MIL125-S-1/2, Cu/MIL125-I, and Cu/P25-I (Fig. 4A-a-g and



Chart 3. Plausible Cu hydroxide linker models. The Cu–O and Ti–O interatomic distances were fixed at 0.195 nm based on EXAFS. (A, A', and B') $[Cu_2(OH)_6]^{2-}$, (B) $[Cu_2(OH)_6(OH_2)_4]^{2-}$, and (C) $[Cu_4(OH)_{10}(OH_2)_6]^{2-}$. The Cu site symmetry was T_d (A and A'), planar (B'), and O_h (B and C).

B) whereas CO decrease was greater than the stoichiometry for Cu/ MIL125-I-573-1/1 (Fig. 4A-d) and O₂ decrease was smaller than the stoichiometry for Cu/MIL125-I-613-1/1 (Fig. 4A-f). We suspect that extra adsorption of CO or the consumption of surface O species occurred for the catalysts because the population of Compound **1** was quite low for these samples of Cu/Ti ratio = 1/1 as demonstrated by XRD (Fig. 1A-*c*^{'''} and d'). CO₂ formation was smaller than the stoichiometry for CuO/CeO₂-923 (Fig. 4A-h) because CeO₂ should adsorb significantly CO and O₂ especially at the initial stage of reaction test. Preferable adsorption of CO on Cu¹ sites [32,33] and CuO nanoclusters [34] for CuO/CeO₂ catalysts and the adsorption of O₂ on defect sites of CeO₂ were reported [35,36].

For Cu/MIL125-I-573-1/2, the *k* value was smaller by a factor of 0.38 (0.045 min⁻¹; Table 2e and Fig. 4A-b) compared with that using Cu/MIL125-I-613-1/2. The XRD pattern (Fig. 1A-c", and d), crystalline size (106–101 nm; Table 2e and h), and S_{BET} values (320–337 m² g⁻¹) were comparable for the two catalysts. We consider the formation reactions for Compound **1** as follows:

$$\begin{split} & \text{Ti}_8 O_8(\text{OH})_4 \cdot (\text{bdc})_6 + 4\text{Cu}^{2+} \\ & \rightarrow \text{Ti}_8 O_8(\text{OH})_4 \cdot (\text{bdc})_2 \text{ layer} + 4\text{Cu}(\text{bdc}) \quad (aq., 290 \text{ K}) \\ & \rightarrow 0.5 \text{Ti}_8 O_8(\text{OH})_4 \cdot (\text{bdc})_2 \cdot [\text{Cu}_2(\text{OH})_6]_4 + 0.5 \text{Ti}_8 O_8(\text{OH})_{12} \\ & \quad \cdot (\text{bdc})_2 \quad (\text{vacuum}, 613 \text{ K}) \end{split}$$

Thus, Cu(bdc) remaining until the heating at 613 K was inactive for the CO PROX reaction and Compound **1** should be the active species. The terephthalates coordinated to Cu^{2+} ions progressively desorbed as the temperature rise in vacuum (Fig. 1B), and resultant

Cu hydroxides would link $[Ti_8O_8(OH)_4]^{12+}$ clusters as in Charts 1 and 3B'.

The stability of Cu/MIL125-I-573-1/2 and Cu/MIL125-I-613-1/2 catalysts was checked by XRD and S_{BET} after CO PROX tests (Table 2e, e'; h, h' and Fig. 5A). Mean crystalline size based on Eq. (1) of Compound **1** after PROX was 87–90% of that before PROX. Conversely, the changes of S_{BET} values and the amount of terephthalate critically depended on samples: 74 versus 99% (S_{BET}) and 80 versus 96% (the amount of bdc; Fig. 5B-a–d), respectively. Thus, Eq. (5) was almost completed and the structure was stabilized for Cu/MIL125-I-613-1/2 whereas Compound **1** was gradually formed during CO PROX test for Cu/MIL125-I-573-1/2. Accordingly, the PROX activity of Cu/MIL125-I-613-1/2 was completely preserved for six cycles (2 h cycle⁻¹; Fig. 4B).

The effects of CO₂ and/or moisture, that are plausible impurity gases for CO PROX prior to hydrogen supply to fuel cells, on the PROX activity using Cu/MIL125-I-573-1/2 were also checked. 19 μ mol of CO₂ and 19 μ mol of moisture mixed to reaction gas reduced the rate constant to 38% and 44% (Table 4b and c), respectively, of that free from CO₂ and moisture (Table 4a). Moreover, if both 19 μ mol of CO₂ and 19 μ mol of moisture mixed, the rate constant further reduced to 24% of that free from CO₂ and moisture (Table 4c). The trend suggested these polar molecules would block a part of the Cu linker sites for CO activation (Scheme 1).

Next, CO PROX activity was compared by varying the Cu/Ti atomic ratio between 0 and 1 for Cu/MIL125-I-573 (Table 1). The framework of MIL125-I-573-0/1, i.e., the control sample free from Cu, was the same as that of MIL125 (Fig. 1A-a and c). The control sample was inert ($k = 0.0008 \text{ min}^{-1}$; Table 2c), demonstrating that



Fig. 4. (A) Time course of PROX tests in CO (63 Pa) + O₂ (76 Pa) + H₂ (6.3 kPa) using Cu/MIL125-S-1/2 (a), Cu/MIL125-I-573-1/2 (b), Cu/MIL125-I-573-3/4 (c), Cu/MIL125-I-573-1/1 (d), Cu/MIL125-I-613-1/2 (e), Cu/MIL125-I-613-1/1 (f), Cu/P25-I (g), and CuO/CeO₂-923 (h). Catalyst amount 50 mg, temperature 323 K. (B) Durability test of CO PROX using Cu/MIL125-I-613-1/2. The reaction conditions were similar to A except for the catalyst amount (20 mg). The gases were removed in vacuum from the reactor after each cycle before introducing new gases.

Cu was indispensable for CO PROX. Notably, other than Compound 1 for Cu, no other diffraction peaks were detected for Cu/MIL125-I-573 series (Fig. 1A-c-c''').

The Compound **1** crystalline phase determined for Cu/MIL125-I-573 was more stable when the atomic ratio of Cu/Ti was 1/2 rather than 1/4, 3/4, or 1, based on 011 diffraction intensity. The diffraction intensity decreased to 47% (Cu/Ti = $\frac{1}{4}$), 32% (Cu/Ti = 3/4), and 18% (Cu/Ti = 1) of that for a Cu/Ti ratio of 1/2, respectively (Fig. 1A-c'-c""). The S_{BET} value was maximal when the atomic ratio was 1/2 (320 m² g⁻¹; Table 2d–g). The *k* values exponentially increased as the Cu/Ti atomic ratio increased to 1/2 (Table 2c–e and Fig. 4A-b). This trend can be explained that remained inert Cu(bdc) (Eq. (4)) was significant if the Cu/Ti ratio was less than 1/2 and the sample was heated below 573 K (Fig. 1B).

When the atomic ratio of Cu/Ti was 1, the initial reaction in aqueous solution for the catalyst synthesis should be



Fig. 5. (A) XRD patterns for Cu/MIL125-I-573-1/2 before (a) and after PROX test (b) and Cu/MIL125-I-613-1/2 before (c) and after PROX test (d). (B) FTIR spectra for Cu/MIL125-I-573-1/2 before (a) and after PROX test (b) and Cu/MIL125-I-613-1/2 before (c) and after PROX test (d).

$$\begin{split} & Ti_8O_8(OH)_4\cdot(bdc)_6+8Cu^{2+} \\ & \to Ti_8O_8(OH)_4\cdot(bdc)_2 \ layer+4Cu(bdc)+4Cu^{2+} \quad (aq.,290 \ \text{K}). \end{split}$$

Thus, extra Cu²⁺ ions more than the Cu/Ti ratio of 1/2 would not be in close contact with Ti and/or bdc species and thus did not increase the crystallinity of Compound **1** (Fig. 1A-*c*", *c*"', and *c*""). Conversely, extra Cu²⁺ ions in Eq. (6) contributed to add smaller crystallines of Compound **1** and accordingly to reduce the *S*_{BET} values from 320 to 250 and then to 215 m² g⁻¹ (Table 2e–g). As the result, the effective interface of Cu linker with $[Ti_8O_8(OH)_4]^{12+}$ cluster (Scheme 1) increased moderately and the *k* values for CO PROX gradually increased from 0.045 to 0.046 and then to 0.069 min⁻¹ starting from Cu/Ti ratio of 1/2 to 1/1 (Table 2e–g and Fig. 4A-b, c, and d)). In these comparisons, the conversion (99–100%) and selectivity (93–100%) for 1–2 h were quite excellent for these catalysts (Table 2e–g).

TiO₂ surface is weakly acidic. The specific surface area should correlate positively with the number of the weak acid sites. However, rate constants in Table 2 basically unrelated to S_{BET} values. If the atomic ratio of Cu/Ti was fixed to 1/2 (entries b, e, and h), the S_{BET} values were nearly the same (349, 320, and 337 m² g⁻¹), whereas the rate constants changed by a factor of 33 (0.0035, 0.045, and 0.117 min⁻¹, respectively). Thus, the concentration of acid sites was not influential factor for the PROX activity using composite catalysts of Cu and MIL125.

The *k* value was the maximum for Cu/MIL125-I-613-1/2 (0.117 min⁻¹; Table 2h and Fig. 4e). Compared to the *k* value for Cu/MIL125-I-573-1/2 (0.045 min⁻¹; Table 2e and Fig. 4b), heating effect to remove Cu(bdc) on the activity was apparent. In these comparisons, the conversion (97–99%) and selectivity (98%) for 1–2 h were quite excellent for the two catalysts (Table 2e and h). Conversely, the XRD peak intensity did not change significantly between these Cu/MIL125 samples (Fig. 1A-c" and d).

The *k* value decreased for Cu/MIL125-I-613-1/1 as compared to Cu/MIL125-I-613-1/2 (Table 2h and i and Fig. 4A-e and f). The active sites at the boundary between $[Cu_2(OH)_6]^{2-}$ and $[Ti_8O_8(OH)_4]^{12+}$ (Scheme 1) formed via Eq. (5) would be partially decomposed by heating for Cu/MIL125-I-613-1/1 because the



Scheme 1. Proposed reaction sites for CO PROX reaction using Cu/MIL125-I catalysts.

XRD peaks due to Compound **1** almost disappeared (Fig. 1A-d'). Compound **1** was favorably formed for Cu/MIL125-I-1/2 (Fig. 1A-c" and d) rather than Cu/MIL125-I-1/1 (c"", d') probably because extra amorphous phase, e.g. $Ti_8O_8(OH)_{12}$ ·(bdc)₂ or TiO₂, stabilized Compound **1**.

The *N* value for Cu(-O-)M (M = Ti, Cu) interatomic pair was quite small for Cu/MIL125-I-573-1/2 (2.8; Table 3e and Fig. 2e). The mean size of CuO in Cu/JRC-TIO-7-I was less than 4 nm based on XRD peak (Table 2m), and the *N* value for Cu(-O-)M was 4.9 (Table 3g and Fig. S2c) by far smaller than 9.2 for Cu/P25-I (Table 3f and Fig. S2d). The significantly smaller *N*[Cu(-O-)M] value for Cu/MIL125-I-573 and no diffraction peaks other than Compound **1** for Cu (Fig. 1A) supported that Cu₂ linker structure (Model B' or A', Chart 2) was predominant in Cu/MIL125-I catalysts.

The activity of Cu/MIL125-S-1/2 was 7.8% of Cu/MIL125-I-573-1/2 (Table 2b and Fig. 4A-a). For Cu/MIL125-S-1/2, direct links between Cu sites of mean 1.7-nm CuO nanoparticles and $[Ti_8O_8(-OH)_4]^{12+}$ clusters were not detected by EXAFS (Fig. 2b, d and Table 3b, d). Various reference Cu/TiO₂ catalysts tested by varying the catalyst preparation (solid state embedding/impregnation) and crystalline phase of TiO₂ (anatase and/or rutile) showed small *k* values: 0.0003–0.0092 min⁻¹ (Table 2j–m and Fig. 4A-g).

For CO oxidation using Cu/TiO₂ catalysts, CO is proposed to adsorb on smaller CuO, while O₂ preferably dissociates on rutile-type TiO₂ [6]. The relatively greater *k* value (0.0092 min⁻¹) using Cu/P25-S, in which TiO₂ is 80% of the anatase phase and 20% of the rutile phase [17], would result from relatively smaller CuO (mean 19 nm; Table 2j) on the anatase for CO adsorption and effective contact of the smaller CuO with rutile for O₂ dissociation. Atomically dispersed $[Cu_2(OH)_6]^{2-}$ should be advantageous for CO adsorption and $[Ti_8O_8(OH)_4]^{12+}$ would be more effective than rutile TiO₂ for O₂ dissociation using Compound **1** (Scheme 1).

Finally, in comparison with lower-pressure CO PROX tests (CO 0.063 kPa, O₂ 0.076 kPa, H₂ 6.3 kPa; Table 2 and Fig. 4), relatively high-pressure CO PROX tests (CO 0.51 kPa, O₂ 0.51 kPa, H₂ 50.1 kPa) were also performed using a flow reaction system at the same reaction temperature (323 K; Fig. 6). The amount of catalyst was increased from 50 mg to 100 mg.

Using Cu/MIL125-I-613-1/2, the best catalyst among Cu/MIL125 and Cu/TiO₂ catalysts in lower-pressure tests (Table 2), CO oxidation rate became stabilized at 3 h from the start of reaction (Fig. 6A1) and the conversion to CO₂ was stabilized at 67–76% at 3–24 h (Fig. 6A2). Water was detected until 4 h from the start of reaction, but the amount was negligible at 4–24 h (Fig. 6A1).

Table 4

Comparisons of CO PROX reaction performances in H2^a at 323 K using Cu/MIL125-I-573-1/2 in the presence/absence of CO₂ and/or H2O.

-		-								
Entry	Catalyst	CO (µmol)	O_2 (µmol)	H_2 (µmol)	CO_2 (µmol)	H_2O (µmol)	Time (h) ^b	Rate const. $k (10^{-3} \text{ min}^{-1})$	Conv. (%) ^c	Selec. (%) ^d
a	Cu/MIL125-I-573-1/2	3.7	4.5	370			2	45	99	98
b		3.7	4.5	370	19		2	17	80	97
с		3.7	4.5	370		19	2	20	86	
d		3.7	4.5	370	19	19	2	11	63	

 a Initial gases: CO 3.7 μ mol, O₂ 4.5 μ mol, H₂ 370 μ mol. At 323 K.

^b Reaction period.

 c [CO]/[CO]_0min \times 100.

^d $[CO_2]/([CO_2] + [H_2O]) \times 100.$



Fig. 6. (A) Time course of PROX tests in CO $(0.5\%) + O_2 (0.5\%) + H_2 (49.5\%) + N_2 (49.5\%) at a flow rate of 20 mL min⁻¹ using Cu/MIL125-I-613-1/2 (A) and CuO/CeO₂-923 (B). Catalyst amount 100 mg, temperature 323 K. (1) The amounts of CO₂, CO, and H₂O in exit gas (40 mL) and (2) the conversion to CO₂ = 100 × [CO₂]_{exit gas}/[CO]_{feed gas} (<math>\blacksquare$, square) and CO PROX selectivity = 100 × [CO₂]_{exit gas}/([CO]_{exit gas}) (\blacktriangle , triangle).

Accordingly, CO PROX selectivity was 98-99% at 4-24 h (Fig. 6A2) in consistent with 98% for lower-pressure test for the catalyst (Table 2h). When the CO PROX test was repeated for used catalyst without the contact with air, initial water formation was negligible. This fact suggested that the water in 0-4 h in Fig. 6A1 exclusively desorbed from catalyst and was not catalytic product derived from H₂ and O₂ gas.

In contrast, using CuO/CeO₂-923 (Table 2o and Fig. 4A-h), CO oxidation rate increased proportionally until 4 h from the start of the test and gradually increase continued for 24 h (Fig. 6B1). Correspondingly, the conversion to CO₂ gradually increased from 16% (@4 h) to 28% (@24 h; Fig. 6B2). Conversely, the CO PROX selectivity was stabilized at 93–96% at 4–24 h (Fig. 6B2) nearly in consistent with 90% for lower-pressure test for the catalyst (Table 2o).

In summary, under the reaction conditions of Fig. 6, the conversion to CO_2 using Cu/MIL125-I-613-1/2 was higher by 4.3–2.7 times than that using CuO/CeO₂-923, demonstrating practical importance of binary metal (Ti, Cu) MIL125-derived catalyst.

The binary MOF $Ti_8O_8(OH)_4 \cdot (bdc)_2 \cdot [Cu_2(OH)_6]_4$ synthesized in this study is a crystalline model of active site at the metal–support interface, and can pave the way for various binary MOF model catalysts of Zr, Al, and Ti clusters linked by V, Fe, Co, Ni, Cu, Ru, Rh, Ag, Pt, and Au (hydro)oxides.

4. Conclusions

Solid-state embedding of Cu(II) and Cu(II) impregnation with MIL125 [$Ti_8O_8(OH)_4$ ·(bdc)₆] was investigated in this study as the interface model of Cu sites on TiO₂. Mean 1.7-nm CuO nanoparticles were formed embedded inside the pores of MIL125 via

solid-state embedding. No Cu...Ti interatomic pair was detected by EXAFS, demonstrating no direct links between Cu sites and [Ti₈₋ $O_8(OH)_4|^{12+}$ clusters. The sample was inert for CO PROX reaction in predominant H₂ ($k = 0.0035 \text{ min}^{-1}$ in CO 63 Pa + O₂ 76 Pa at 323 K) due to the lack of interface sites. In clear contrast, Cu(II)impregnated samples did not retain the framework of MIL125, but transformed to new tetragonal binary MOF, Ti₈O₈(OH)₄·(bdc)₂· $[Cu_2(OH)_6]_4$ (*a* = 1.936 nm, *c* = 1.277 nm), based on XRD. The direct links between Cu sites and $[Ti_8O_8(OH)_4]^{12+}$ clusters were demonstrated by the appearance of Ti(-O-)Cu peak at 0.380 nm and the increase of coordination number by one for Cu(-O-)M (M = Ti, Cu) peak by Ti and Cu K-edge EXAFS. Due to the direct links between Cu sites and $[Ti_8O_8(OH)_4]^{12+}$ clusters, the impregnated samples functioned far better in CO PROX reaction in predominant H₂ $(k = 0.117 \text{ min}^{-1})$ than reference Cu/TiO_2 catalysts $(k = 0.0003 - 0.0092 \text{ min}^{-1})$ and equivalent to CuO/CeO₂-923 and Au/TiO₂. Furthermore, in CO 0.51 kPa + O_2 0.51 kPa at 323 K, the conversion to CO2 and the CO PROX selectivity using Ti₈O8(OH)4- $(bdc)_2$ (Cu₂(OH)₆]₄ (67–76% and 98–99%) were significantly higher than that using CuO/CeO2 (16-28% and 93-96%, respectively) for 24 h. Extra terephthalates (bdc) than the formula Ti₈O₈(OH)₄. (bdc)₂·[Cu₂(OH)₆]₄ blocked the active Cu sites below 613 K as sample pretreatment, whereas best atomic ratio of Cu/Ti was 1/2 for CO PROX activity presumably because extra Ti^{IV} species stabilized the catalytically active Ti₈O₈(OH)₄·(bdc)₂·[Cu₂(OH)₆]₄ crystallines.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2015.09.007.

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