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Supporting information:

Ratio-controlled synthesis of phyllosilicate-like materials as precursors for highly efficient catalysis of formyl group

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S1 Experimental details

S1.1 Catalytic test

Activity tests of the samples were executed in a stainless steel fixed bed reactor (i.d. 12 mm, length 600 mm). Initially, the samples (20-40 mesh) were used to fill the isothermal region of reactor tube, and then the samples were adequately reduced at 270 °C with a 5 vol% H_2/N_2 mixture gas. The distilled furfural was brought into an evaporator by a HPLC pump after reduction. Afterward, H_2 was introduced into the system through mass flow controller, and furfural was mixed with pure H_2 at the top of the preheater. Finally, the mixed reactants were introduced into the fixed-bed reactor.

S1.2 Products analysis

Liquid products were collected in a gas-liquid separator with a condenser, and analyzed using an off-line gas chromatograph (GC6890, Agilent, USA). A capillary column (polyethandiol, 30 m × 0.32 mm) and a flame ionization detector were used in the system. The tail gas was also determined using an on-line gas chromatograph (GC6890, Agilent, USA), which was comprised of a flame ionization detector and apolyethandiol capillary column. GC-MS (6890N, Agilent, USA) was employed to identify products in this system. Carbon balance was greater than 96% and the error was about ±3%. Furfural conversion, products selectivity and carbon balance were calculated according to the following equations:

$$Conversion(\%) = \frac{Mole\ of\ furfural\ converted\ (mol)}{Mole\ of\ furfural\ fed\ (mol)} \times 100$$

$$Selectivity(\%) = \frac{Mole\ of\ the\ product\ produced\ (mol)}{Mole\ of\ furfural\ converted\ (mol)} \times 100$$

$$Carbon\ balance(\%) = \frac{Mole\ of\ the\ overall\ carbon\ fed\ (mol)}{Mole\ of\ the\ overall\ carbon\ outflowed\ (mol)} \times 100$$

In order to compare the intrinsic activities of these sample, furfuryl alcohol yield from the hydrogenation of formyl groups were controlled below 10% at low temperature and high weight hourly space velocity. Our date from TOFs were also strictly calculated at below 10% furfural conversion, and the thermal effect from the reaction itself is largely suppressed. Besides, in order to control the conversion of furfural, we only modulate the WHSV at 120 °C to calculate the TOFs. Turnover frequencies (TOFs) were used to compare the intrinsic activities of samples. TOFs based on the hydrogenation of formyl groups were given as follows:

$$TOF = \frac{Furfural\ conversion(\%) \times WHSV\ \div MOlecular\ weight\ of\ Furfural\ \left(mol\ g_{cat}^{-1}\, h^{-1}\right)}{Number\ of\ Cu\ Sites\ (mol\ g_{cat}^{-1})}$$

The weight hourly space velocity (WHSV) is defined as the grams of furfural per hour per gram of catalyst. Molecular weight of Furfural is calculated by 96 g.mol^{-1}. Number of Cu sites were calculated by N_2O titration.

S1.3 N_2O chemisorption:

Copper surface area S_{Cu} and dispersion D_{Cu} (the ratio of surface Cu amounts to total Cu amounts present in the catalyst) were calculated by N_2O decomposition method, which is based on the formation of a monolayer of Cu_2O by the oxidation of surface metal copper with a N_2O flow, then Cu_2O reduced to Cu^0 with H_2 gas:

(a) Total (bulk + surface) copper reduction is measured by means of

Hydrogencomsumption *X*: $CuO + H_2 \rightarrow Cu + H_2O$;

(b) Only surface copper reduction is measured by means of

Hydrogencomsumption *Y*: $Cu_2O + H_2 \rightarrow 2Cu + H_2O$

By assuming spherical shape of copper metal particles and 1.47 × 10^{19} copper atoms/m^2, copper surface area (S_{Cu}) and particles size (d_{Cu}) can be calculated by Eqs. (1) and (2), respectively.

$$S_{Cu} = \frac{2YN_{av}W_{Cu}}{XM_{Cu}1.4 \times 10^{19}} \approx \frac{1353YW_{Cu}}{X}(m^2\ g\ Cat.^{-1}) \qquad (1)$$

$$d_{Cu} = \frac{6w_{Cu}}{S_{Cu}\rho_{Cu}} \approx 0.5 \times \frac{X}{Y}(nm) \qquad (2)$$

where N_{av}: Avogadro's constant, M_{Cu}: relative atomic weight, ρ_{Cu}: copper density =8.92g.cm^{-3}, W_{Cu} (wt%): the content of copper in the catalyst detected by ICP-OES.

Table S1 The relative amount of copper species over x% Cu-phyllosilicate catalysts.

Catalysts	The molar ratio of Cu and Si elements	$[Cu^+/(Cu^0+Cu^+)]\times 100^b$ (%)
8% Cu-Ps	0.09	31.8
16% Cu-Ps	0.19	32.3
24% Cu-Ps	0.33	35.6
31% Cu-Ps	0.49	37.4
39% Cu-Ps	0.75	41.4
43% Cu-Ps	0.89	39.5
46% Cu-Ps	1.10	38.1

[a] the relative amount of different silicon species was determined by FTIR spectra. [b] the relative amount of different copper species over the reduced *x*% Cu-Phyllosilicate catalysts was determined by XAES spectra

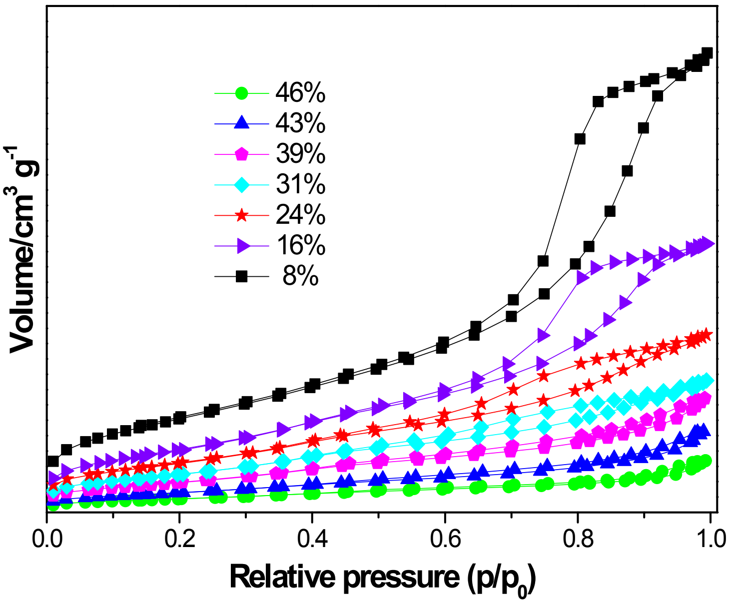

Fig. S1 Adsorption isotherms of the calcined x% Cu-phyllosilicate catalysts

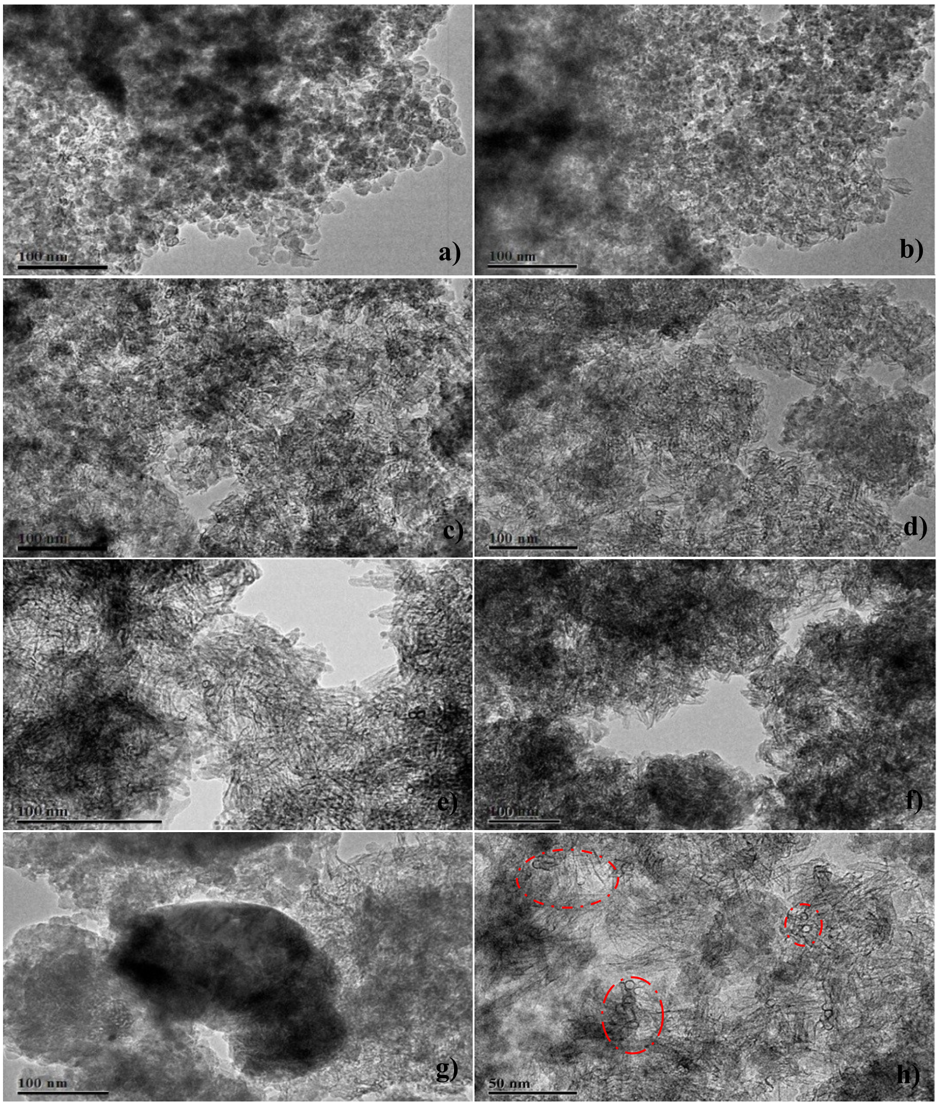

Fig. S2 The Morphology of the calcined x% Cu-phyllosilicate catalysts after calcination at 450 °C: a) 8% Cu-Ps, b) 16% Cu-Ps, c) 24% Cu-Ps, d) 31% Cu-Ps, e) 39% Cu-Ps, f) 43% Cu-Ps, h) 46% Cu-Ps, g) the enlarged view of e) 39% Cu-Ps (50 nm)

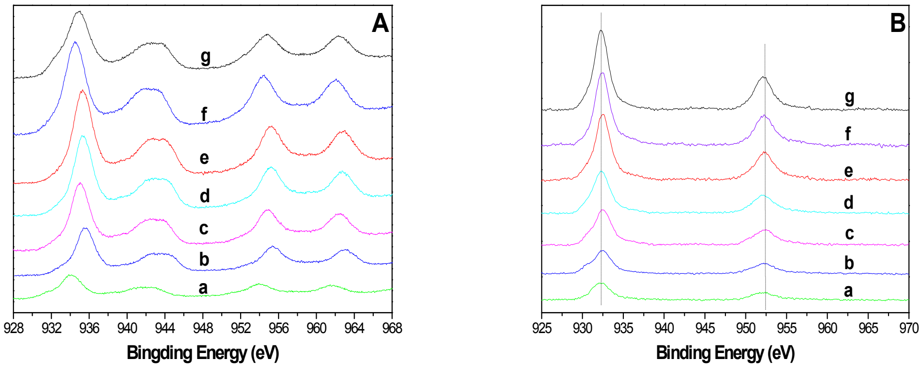

Fig. S3 XPS spectra of A) the calcined and B) the reduced x% Cu-phyllosilicate catalysts (a) 8% Cu-Ps, (b) 16% Cu-Ps, (c) 24% Cu-Ps, (d) 31% Cu-Ps, (e) 39% Cu-Ps, (f) 43% Cu-Ps, (g) 46% Cu-Ps.

The XPS analysis was used to identify surface chemical states and the compositions of reduced catalysts, and the results were exhibited in Fig. S3. According to the former literatures [1,2], the two peaks centered at 932.5 and 952.5 eV were mainly ascribed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks of the reduced copper species (Cu^0 and Cu^+). Because the BE values of Cu^+ and Cu^0 species are almost identical, the distinction between the two species present on the catalyst surface is feasible only through the examination of XAES spectra in Fig. S4.

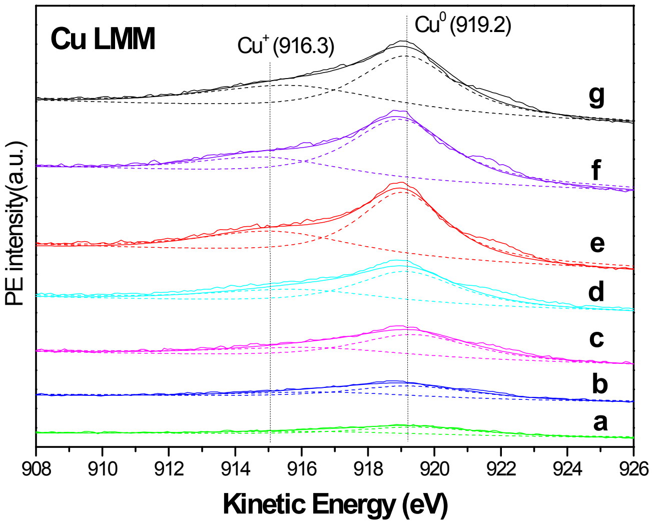

Fig. S4 XAES patterns of the reduced x% Cu-phyllosilicate catalysts (a) 8% Cu-Ps, (b) 16% Cu-Ps, (c) 24% Cu-Ps, (d) 31% Cu-Ps, (e) 39% Cu-Ps, (f) 43% Cu-Ps, (g) 46% Cu-Ps.

From Fig S4, it is clearly known that each Cu LMM spectrum contains one more component as inferred by the broad and asymmetrical peak. Two overlapping Cu LMM Auger kinetic energy peaks of these catalysts centered at 919.2 and 916.3 eV are observed in Fig. S4, indicating that Cu^0 and Cu$^+$ species coexist on the surface of these reduced catalysts. In Table S1, the Cu$^+$/(Cu$^+$ + Cu^0) intensity ratio was obtained by fitting the Cu LMM peak of all *x*%Cu-Ps catalysts, with the maximum value at 39%Cu-Ps sample. It has been authenticated that when CuO species strongly interacted with the support, CuO could be hardly reduced to Cu^0 with completion. The size of Cu$^+$/(Cu$^+$ + Cu^0) ratio in the reduced Cu-Ps catalysts indicates the existence of strong Cu-O-Si bands.

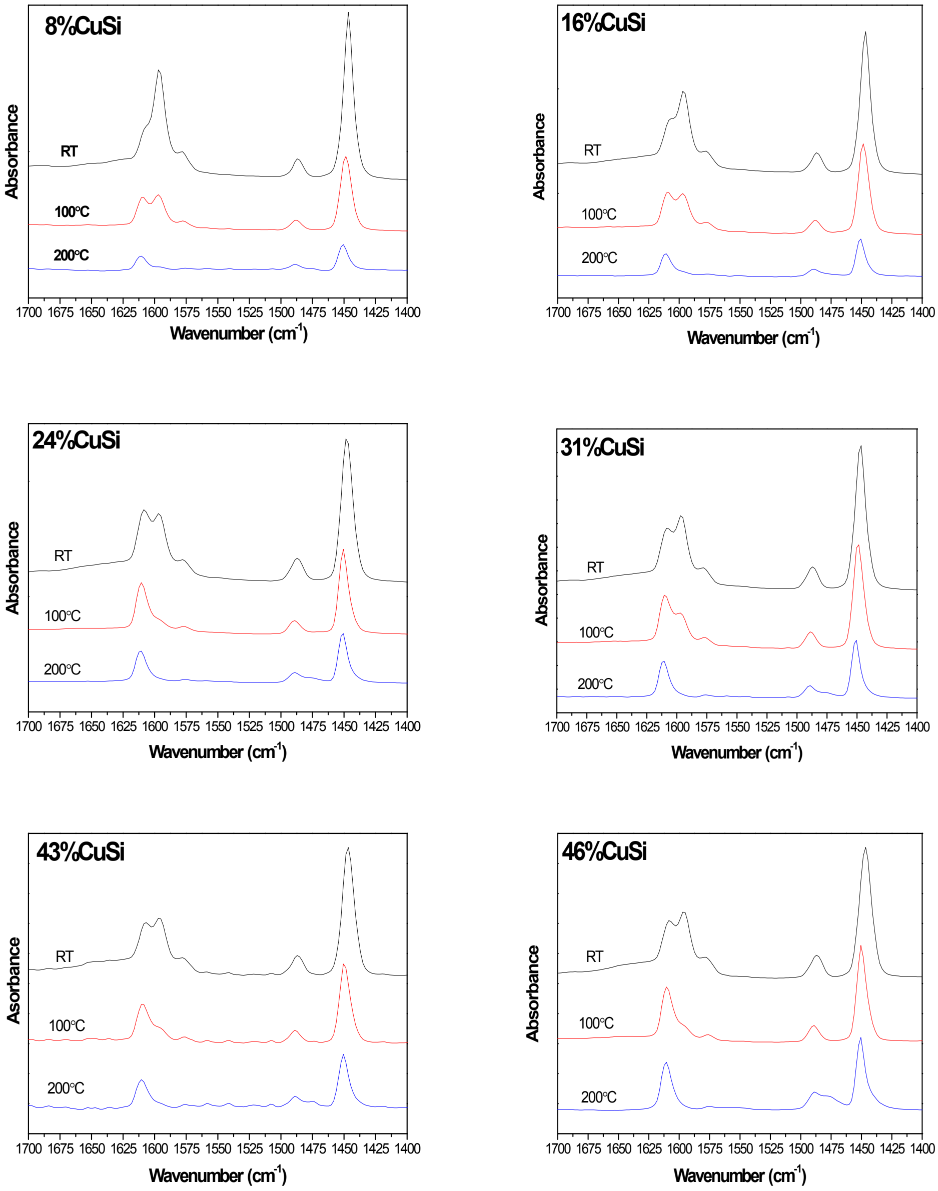

Fig. S5 Py-IR spectra of x% Cu-phyllosilicate catalysts at 30, 100, and 200 °C

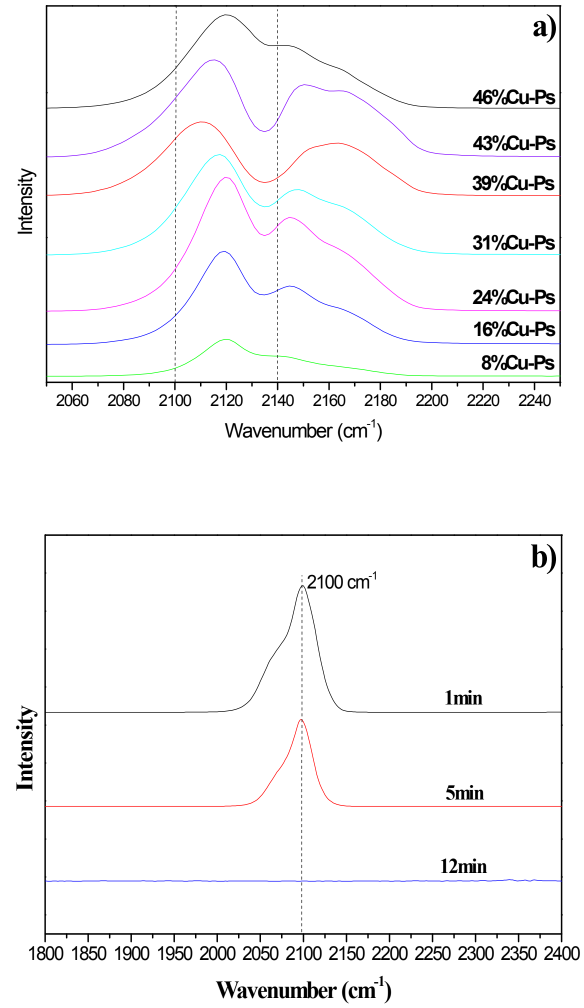

Fig. S6 CO-FTIR spectra of a) the calcined x% Cu-phyllosilicate catalysts (after 10 min), b) the reduced 39% Cu-Ps sample at 20 °C, purged with He for 1, 5, 12 min

CO-FTIR spectra of all the calcined x% Cu-Ps catalysts were conducted to identify chemical environment of copper species in Fig. S6a). According to the former studies [3,4], the adsorption of CO on CuO surface aroused a series of obvious peaks with vibrational frequencies at about 2220-2140 cm^{-1}. In this work, it is discovered that the spectra were shifted the low vibrational frequency at 2220-2080 cm^{-1}. The adsorption of CO below 2140 cm^{-1} was considered to be due to the change of Cu chemical environment [4]. With the increasing of Cu loading, the frequencies of CO bands were shifted to higher frequencies, especially 39% Cu-Ps catalyst. Notably, when Cu loading surpass 43%, the frequencies of CO bands were gradually shifted to lower frequencies. The reason might be attributed to the different interaction of copper and silicon, and the silicon could seize electron from metal copper, which could decrease electron density of C-Cu band and cause the strength of CO band energy. For 39% Cu-Ps catalyst, the interaction of Cu and Si is the strongest, and then the electron density of C-Cu band is least. Besides, it is reasonable that CuO particles were highly dispersed over SiO_2 support, due to the intensity of band as the semi-quantity method for the amounts of copper species [5]. The dispersion of Cu particles derived from CO-FTIR is critically consistent with the results of N_2O titration. In combination with XAES, the shift of peak indicated that chemical environment of copper species on 39% Cu-Ps catalyst changed more obvious than other x% Cu-Ps catalysts because of the different interaction. According to the former literatures [6-8], the Cu^0-CO species is easily decomposed upon evacuation. In this work, the reduced Cu-Ps samples exhibited the weak adsorption peak of CO at 2100 cm^{-1}, which was ascribed to the Cu^0-CO species, and the peak intensity at 2100 cm^{-1} is decreased with 1, 5, 12 min in Fig. S6b). This peak eventually disappeared with the extension of the purge time in pure He gas. Therefore, it is considered that CO the adsorption peak of CO at 2100 cm^{-1} eventually disappeared with the extension of the purge time due to the existence of Cu^0 species after reduction.

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