Supplemental Information

Methanol Synthesis and Decomposition Reactions Catalyzed by a Model Catalyst Developed from bis(1,5-Diphenyl-1,3,5-pentanetrionato)dicopper(II)/Silica

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1 Elemental Analysis of Silica-supported Cu$_2$(dba)$_2$ Catalysts.

The change in UV-vis absorbance of Cu$_2$(dba)$_2$ was used to calculate the amount of metal complex absorbed onto the Cab-O-Sil. The maximum absorbance peak at 444 nm was used for all the calculations of the concentration of complex remaining in solution. With high metal loadings, UV-vis absorption spectra were recorded after 24 h of stirring and then the amount of metal complex left in the solution was calculated. This remaining amount was subtracted from the initial mass of the metal complex and the copper wt% on silica was calculated. The calculated wt% of carbon and copper are shown in Table S-1. To determine whether the ligands were kept intact on the surface after the adsorption of each metal complex, elemental analysis was performed and those results are combined with the UV-Vis results in Table S-1. Using the carbon wt% found by elemental analysis and Cu wt% estimated by changes in the UV-Vis spectra (Table S-1), predicted C and Cu wt%’s were calculated for supported samples of Cu$_2$(dba)$_2$. Moles of C observed by elemental analysis in each sample were plotted versus the moles of Cu observed in the sample (Figure S-1). These observed values (filled circles) were compared to the predicted values obtained using the stoichiometry of the parent metal complex (filled squares). The parent metal complex of Cu$_2$(dba)$_2$ shows a C/Cu ratio of 17. The agreement between the observed and predicted C/Cu ratios suggests that the Cu$_2$(dba)$_2$ complex did not lose any of its ligands upon coordination with the Cab-O-Sil.

### Table S-1 Copper and carbon weight percentages of silica-supported Cu$_2$(dba)$_2$.

| Mass of Cu$_2$(dba)$_2$ used (mg) | Mass of silica used (g) | Elemental analyses--Measured | Elemental analyses -- UV-Vis |
|-----------------------------------|------------------------|-----------------------------|----------------------------|
| 10                                | 0.25                   | Cu% 0.73 C% 2.36             | Cu% 0.73 C% 2.34            |
| 15                                | 0.25                   | Cu% 1.06 C% 3.62             | Cu% 1.1 C% 3.53             |
| 20                                | 0.25                   | Cu% 1.36 C% 4.47             | Cu% 1.33 C% 4.27            |
| 40                                | 0.25                   | Cu% 2.64 C% 8.11             | Cu% 2.65 C% 8.51            |
| 60                                | 0.25                   | Cu% 3.91 C% 11.95            | Cu% 3.71 C% 11.95           |
| 80                                | 0.25                   | Cu% 4.34 C% 13.82            | Cu% 4.64 C% 14.09           |

Measured values determined by elemental analysis (col’s 3 & 4); other values were calculated from UV-vis experiments (col’s 5 & 6).
Figure S-1: Comparison of elemental analyses results and UV-Vis calculated results of silica supported Cu$_2$(dba)$_2$: a) wt% Cu by UV-Vis and C predicted from Cu wt% and b) found by elemental analyses.
Figure S-2: PXRD of Silica-Supported Cu$_2$(dba)$_2$ as a Function of Metal Complex Loading

PXRD patterns of supported Cu$_2$(dba)$_2$, (a) 0.73 wt% (b) 1.06 wt% (c) 1.36 wt% (d) 2.64 wt% (e) 3.91 wt% (f) 4.34 wt% Cu metal, and (g) unsupported Cu$_2$(dba)$_2$. 
Figure S-3  DRIFTS of Cu$_2$(dba)$_2$/silica at copper loadings of (a) 0.73 wt% (b) 1.06 wt% (c) 1.36 wt% (d) 2.64 wt% (e) 3.91 wt% (f) 4.34 wt% and (g) unsupported Cu$_2$(dba)$_2$. 1440 cm$^{-1}$ peak is marked by the dashed vertical line.
The EPR spectra of a) unsupported Cu$_2$(dba)$_2$ b) 0.73 wt% Cu Cu$_2$(dba)$_2$/silica and c) 4.34 wt% Cu Cu$_2$(dba)$_2$/silica

2. Temperature Programmed Decomposition of Polycrystalline and Silica-supported Cu$_2$(dba)$_2$

Pure Cu$_2$(dba)$_2$ was thermally decomposed in the TGA under a stream of helium to determine the percent weight loss. Expected weight changes were calculated for the unsupported sample by assuming the following reactions.

\[
\text{Cu}_2\text{(dba)}_2 \rightarrow 2 \text{Cu(OH)}_2 + \text{volatiles} \quad \text{Eq (S.1)}
\]

Experimental weight changes, Figure 5, of unsupported Cu$_2$(dba)$_2$ were consistent with the reactions shown in Eq. (S-1). This total weight change (70%) is very close to the predicted weight change (70.24%) calculated assuming the formation of two Cu(OH)$_2$ molecules after thermolysis of Cu$_2$(dba)$_2$.

The weight changes attending the thermolysis of silica-supported Cu$_2$(dba)$_2$ are shown in Table S-2. The predicted weight changes were determined using the Cu elemental analysis determined by Galbraith Laboratories and the formula weight of Cu$_2$(dba)$_2$. Furthermore, it is hypothesized that the final product is Cu$_2$O, suggesting that the cupric ions of the metal complex was reduced to cuprous ions.
Figure S-5 Thermal decomposition of Cu$_2$(dba)$_2$/silica; (a) 0.73 wt% (b) 1.06 wt% (c) 1.36 wt% (d) 2.64 wt% (e) 3.91 wt% (f) 4.34 wt%

Table S-2 TGA Weight Changes of Silica-supported Cu$_2$(dba)$_2$

| Wt% Cu | Total weight loss calculated, % | Total weight loss found, % | % error |
|--------|---------------------------------|-----------------------------|---------|
| 0.73   | 2.96%                           | 3.63%                       | -22.5%  |
| 1.06   | 4.30%                           | 4.44%                       | -3.2%   |
| 1.36   | 5.52%                           | 5.04%                       | 8.7%    |
| 2.64   | 10.72%                          | 10.80%                      | -0.8%   |
| 3.91   | 15.87%                          | 14.90%                      | 6.1%    |
| 4.34   | 17.62%                          | 17.94%                      | -1.8%   |

St’d Deviation 11%
3. Derivation of Equations to Extract Rate Constants from Isothermal, Batch Reactor Data

Data of total pressure versus time can be used to estimate reaction rate constant for the dominant reaction at low conversions of the limiting reactant. For the present case, the reacting gas was equi-molar in CO and H$_2$ with H$_2$ being the limiting reactant. Consider the stoichiometry of the methanol synthesis reaction:

$$
N_{H_2} = N_{H_2}^o(1-f); N_{CO} = N_{CO}^o - N_{H_2}^o f/2; N_{MeOH} = N_{H_2}^o f/2; N_T = N_{H_2}^o + N_{CO}^o + N_{H_2}^o[f/2 - f - f/2]
$$

$$
N_T = N_{H_2}^o + N_{H_2}^o - N_{H_2}^o
$$

$$
f = N_T^o (1-f/2)
$$

(1)

where $N_{H_2}^o$ and $N_{CO}^o$ are the initial moles of H$_2$ and CO, $N_{H_2}$, $N_{CO}$, and $N_{MeOH}$ are the moles of H$_2$, CO, and methanol, respectively at a given time and f is the conversion factor.

Using the ideal gas law, isothermal reactor data of total moles can be related to total pressure as follows:

$$
N_T^o = P_T^o; N_T = P_T
$$

$$
P_T/P_T^o = (1-f/2);
$$

$$
f = 2(1 - P_T/P_T^o)
$$

This last expression can be used to determine the fractional conversion of the limiting reagent as a function of time using only the total pressure data.

We can repeat this analysis for the MeOH decomposition reaction using the following stoichiometric equations:

$$
N_{MeOH} = N_{MeOH}^o(1-f); N_{CO} = f N_{MeOH}^o; N_{H_2} = 2f N_{MeOH}^o
$$

$$
N_T = N_{MeOH}^o(1-f) + f N_{MeOH}^o + 2f N_{MeOH}^o
$$

$$
N_T = (1+2f)N_{MeOH}^o
$$

(2)

Using the ideal gas law we can relate isothermal reactor data of total moles to total pressure as follows:

$$
N_T^o = P_T^o; N_T = P_T
$$

$$
P_T/P_T^o = (1+2f); f = (P_T/P_T^o - 1)/2
$$
Figure S-6(a): Fractional Conversion of Hydrogen vs. Time x mass of Cu; a) 3.70 wt% Cu$_2$(dba)$_3$/silica catalyst, filled squares, and b) 41.20 wt% commercial catalyst, filled circles.

4. Integral Method of Analysis

Data of hydrogen fractional conversion vs. time were fit to first order kinetics on an integrate rate plot to determine the goodness of fit and to determine the first order rate constant.
The data for the commercial and model catalyst can be fit to first order kinetics by the integral method of analysis. However, the equations fit to these processed data both show, non-zero, positive intercept values. These non-zero values are found when processing batch reactor data when the time for initiating the reaction is not known.

The data can also be fit to irreversible, pseudo second order kinetics: \( r = k[\text{CO}]_0[H_2]^2 \) by assuming that the concentration of CO changes very little at low hydrogen conversions and assuming this concentration of CO can be approximated by its initial value: \([\text{CO}])_o\). Next, the rate expression can be re-expressed in terms of hydrogen fractional conversion and installed into the design equation for an isothermal, batch reactor, where \( M_{\text{Cu}} \) = mass of total Cu in the catalyst.

\[
t = -\int[H_2]_0 df/[kM_{\text{Cu}}[\text{CO}]_0[H_2]^2_o f(1-f)^2]
\]

\[
t kM_{\text{Cu}}[\text{CO}]_0[H_2]_o = -df/[1-f]^2 = f/(1-f)
\]

5. Differential Method of Analysis – MeOH Synthesis Reaction

The data of total pressure vs time can be processed again to determine the kinetic parameters. As before, the pressure data are converted to fractional conversion of hydrogen, the limiting reagent. These data were used to estimate the conversion rate, df/dt, by a simple Euler’s method (df/dt ~ Δf/Δt. The Δ operator means to use data at adjacent times, see Table S-3). The total pressure data are converted to absolute pressure (psia) before the ratio’s P/P_o are calculated in column 4. Adjacent values of the fractional conversion data, column 6, are averaged to form the entries in column 7. Estimates of the
fractional conversion rate, column 8, are plotted vs. the average values of the fractional conversion data, column 7.

### Table S-3  Differential Method of Analysis Data

| Time (h) | Pressure (psig) | $t^*M_{Cu}$ | P/P$_o$ | F | $(1-0.5f)(1-f)^2$ | Average | $\Delta f/\Delta t$ |
|----------|----------------|-------------|---------|---|-----------------|---------|----------------|
| 0        | 860            | 0           | 1       | 0 | 1               | 0       | 0              |
| 8        | 820            | 1.48        | 0.954   | 0.901 | 0.788         | 0.894   | 0.062          |
| 9.33     | 800            | 1.73        | 0.931   | 0.137 | 0.693         | 0.741   | 0.186          |
| 17       | 760            | 3.15        | 0.886   | 0.229 | 0.527         | 0.610   | 0.064          |
| 22       | 740            | 4.07        | 0.863   | 0.274 | 0.454         | 0.491   | 0.049          |

6. Analysis of Reaction Products

The condensed products from the MeOH synthesis reaction over the commercial and model catalysts are shown in Figures S-7 and S-8.

![Figure S-7: GC-MS analysis of products of MeOH synthesis reaction over commercial catalysts](image)

Each catalyst produced MeOH as the major liquid product.
7 Calculation of Crystallite Size from Scherrer Equation

The powder, x-ray diffractograms were recorded on a Siemens D5000 Powder XRD for the model, Cu/silica (3.7 wt%) and the commercial Cu/ZnO/alumina catalyst (41.2 wt% Cu, Katalco, 51-8 PPT) so as to estimate the average Cu crystallite size, Figure S-9 and Figure S-10. These catalysts were examined after they were used in the MeOH synthesis and the MeOH decomposition reactions.

Figure S-9: PXRD of Cu/ZnO/alumina Commercial Catalyst (Katalco, 41.2 wt% Cu, 51-8 PPT)

Figure S-8: GC-MS analysis of products of MeOH synthesis reaction over model catalyst
The Scherrer equation [1], \( L = K\lambda/(\beta \cos \theta) \), was used to estimate the average crystallite size, \( d \), in nanometers from a knowledge of the wavelength of radiation used (0.1540 nm), the angle of the reflection, the factor \( K \) (~0.9), and the broadening of the peak due to the instrument, \( b_{\text{inst}} = 0.2 \) degrees, and the measured peak broadening, \( b_{2\theta} \). The factor, \( \beta \), used in the Scherrer equation is determined from these two broadening factors assuming that the peaks are Gaussians: \( \beta^2 = b_{2\theta}^2 + b_{\text{inst}}^2 \).

Table S-4 Determining the factors \( \beta \) and \( \cos \theta \)

|                  | \( 2\theta \) | \( b_{2\theta} \) degrees | \( b_{\text{inst}} \) degrees | \( \beta \), degrees | ln(\( \beta \)) | ln(1/cos\( \theta \)) |
|------------------|---------------|--------------------------|-------------------------------|---------------------|----------------|---------------------|
| Commercial Catalyst | 43.24         | 0.45                     | 0.2                           | 0.403               | -4.957         | 0.514               |
|                  | 50.37         | 0.609                    | 0.2                           | 0.575               | -4.601         | 0.482               |
| Model Cu\(_2\)(dba)\(_2\)/silica | 43.24         | 0.53                     | 0.2                           | 0.491               | -4.760         | 0.514               |
|                  | 50.37         | 0.705                    | 0.2                           | 0.676               | -4.440         | 0.482               |

Note: values for \( \beta \) and \( \theta \) used in right-most columns are radians

Monshi, et al. showed how to use the peak data from more than one peak in the PXRD spectrum to determine the average crystallite size [2]. The procedure involves fitting the data of \( \beta \) and \( \cos \theta \) from at least two peaks in the PXRD, Table S-4, so as to determine the value of \( K \). That is, one plots \( \ln \beta \) versus \( \ln(1/\cos \theta) \), Figure S-11, to determine the intercept: \( \ln(K\lambda/L) \) for each catalyst, see Table S-5. Using the value of the radiation wavelength, 0.1540 nm, and these intercepts, it is possible to determine the values of the crystallite sizes, \( L \), using all of the peak data. For the present case, only two peaks were recorded that were characteristic of Cu metal (~43 and 50°).
These estimates of L can also be used to determine the % dispersion of the Cu crystallites, D (Table S-5).

Table S-5 Calculation of Cu Crystallite Sizes for Catalysts

|                     | ln(K\(\lambda\)/L) | (K\(\lambda\)/L) | L, nm | D   |
|---------------------|--------------------|------------------|-------|-----|
| Commercial Catalyst | 0.3409             | 1.4062           | 5.25  | 11.0% |
| Model Catalyst      | 0.7075             | 2.0289           | 3.64  | 15.9% |

The fractional dispersion may be determined by assuming that the Cu atoms pack into the fcc (face centered cubic, cartoon S-1) Cu crystal having a cube dimension of a = b = c = 0.3619 nm and a density of 8.92 g/cm\(^3\). One could model the number of surface atoms per unit area of the crystal by the (111) index plane which shows a number density of 22.1 surface atoms/nm\(^2\). In addition we assume that each cubic crystal shows 5 out of the total of six faces.

It must be noted that this method ascribes a single characteristic dimension to describe what a collection of crystallites having different sizes is. This distribution of particle sizes is evident from the TEM micrographs, Figures S-12 to S-14. The PXRD data, Figure S-10, for the commercial catalyst may also show a feature in the peak at 2\(^\theta\) = 43\(^\circ\), which could be interpreted as a shoulder, see arrows on image. That is, the observed peak could be a composite of two or more peaks thus suggesting that more than one size of crystallites could be interrogated by this peak.
8. Estimating the Crystallite Size from TEM Data

Estimates of the fractional dispersion could also be determined from a consideration of crystallite size determined from TEM data of the model catalyst (Figure S-12 and 13). Some of the features appearing in this figure S-12 show regular square shapes, as might be expected of Cu cubic metal crystals. One might consider as a control sample, the same catalyst examined by TEM before the MeOH synthesis and decomposition reactions. Figure S-13 showed no square shaped features in this image. We estimate that the Cu crystallites appearing in Figure S-12 show sizes ranging from 2-10 nm. For a crystal ~ 10 nm in size, the fractional dispersion is 0.059; whereas, a crystal 2 nm in size shows a fractional dispersion of 0.29. The TEM micrograph for the commercial catalyst, Figure S-14, also shows regularly-shaped features, ranging from 5-20 nm in size. The Cu dispersion for a crystallite 20 nm in size is 0.045.

Figure S-12: Cu_2(dba)_2/silica catalyst after methanol decomposition reaction. Features marked by circles show rectangular shape and have characteristic dimensions ~ 2-10 nm.
Figure S-13: Cu$_2$(dba)$_2$/silica catalyst before methanol decomposition reaction. No “regularly-shaped” features can be identified in this image.
We may compare our results against those reported in the literature for the same catalysts. Literature data for Cu/ZnO/Al₂O₃ catalysts show Cu crystallite sizes of 30.7 and 37.1 nm [3] for which we estimate the fractional Cu dispersion to be 0.032 and 0.026. Smaller Cu crystallites, 2-10 nm, were observed in another study [4] for a Cu/ZnO catalyst. In yet another study, a commercial Cu/ZnO/alumina catalyst showed Cu crystallites of ~9 nm in size, for which the dispersion would be 0.064 [5]. Our results of 3-5 nm estimated from the PXRD data appear to be similar to some of the results reported in the literature.

9. EPR data for Cu 2,2’-bipyridine dimer and monomers

Data were recorded for the supported Cu 2,2’ bipyridine dimer, Figure S-15, on Cab-O-Sil, spectrum B, and for the unsupported metal complex, Figure S-16, spectrum A. See reference 49 for details of the EPR analysis by us. The EPR spectrum for the supported metal complex is consistent with that for coppers in an axial field that are magnetically isolated; whereas, the EPR spectrum of the unsupported metal complex is quite different. The discussion of these results in the original publications were explained by a model where the Cu’s in the supported complex were interacting strongly is the the silica surface. This strong interaction produced an environment not unlike observed for the EPR spectra of a monolayer filme of the mononuclear Cu complex, Cu(acac)₂, supported on silica. The fitted parameters, Table S-6, for the supported mononuclear Cu(acac)₂/silica are not much different from those found for the Cu 2,2’-bipyridine dimer on silica.
We now reinterpret these data to conclude that the Cu 2,2' bipyridine dimer complex dissociates upon contacting the surface of the silica to form two monomeric Cu species that show environments not too different from supported Cu(acac)$_2$/silica. These mononuclear Cu fragments decompose upon heating to air to form highly dispersed Cu ions that are separated by a distance < 0.4 nm.

Table S-6  EPR Parameters for Other Cu Complexes

| Species                  | $g_{||}$ | $g_{\perp}$ | $A_{||}, \text{cm}^{-1}$ |
|--------------------------|----------|-------------|--------------------------|
| Cu bipy dimer/silica    | 2.34     | 2.09        | 0.0184                   |
| [Cu 2,2'-bipy]$^{2+}$   | 2.307    |             | 0.017                    |
| [Cu 2,2'-bipy OH]$^{1+}$| 2.253    |             | 0.0177                   |
| [Cu 2,2'-bipy (OH)$_2$] | 2.232    |             | 0.0196                   |
| Cu(acac)$_2$/silica     | 2.26     | 2.06        | 0.0200                   |

Figure S-15  ORTEP Diagram for Copper 2,2'-Bipyridine Dimer

Figure S-16: EPR Spectrum of Supported and Unsupported Cu 2,2'-bipyridine dimer on silica
10. References

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