

Carbon Dioxide Fixation into Chemicals (Methyl Formate) at High Yields By Surface Coupling Over Pd/Cu/ZnO based NanoCatalyst

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Establishment of Reaction and Analytical Set-ups:

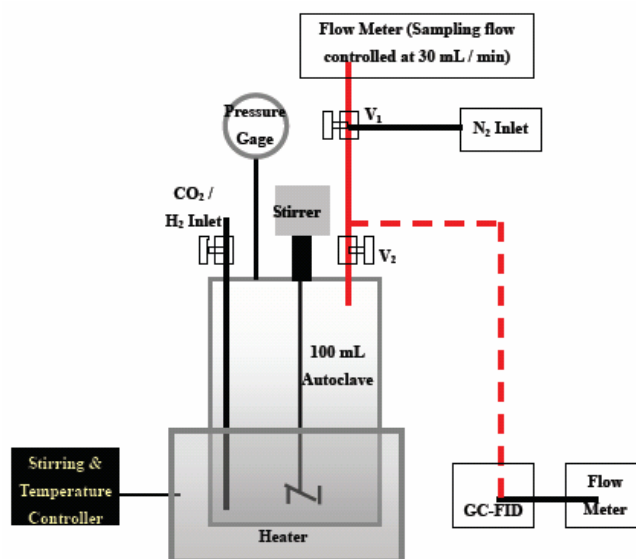


Figure S1. A schematic diagram of the high-pressure rig utilised in the experiments.

Figure S1 presents the 100 mL Parr Series Mini batch reactor (316 stainless steel and equipped with a magnetic driver, by which the stirrer shaft could be driven) used for the study. It was coupled with pipework to create a pressurized testing conditions was purposely-constructed for this work. The maximum working pressure of our setup was of about 250 bar at a maximum temperature of 250 °C. Suitable rupture discs were installed in the autoclave and in the pipelines, which could guarantee the safe operations since the burst of these facile discs could release pressure just above the threshold before a dangerous pressure was reached.

The activation and fixation of CO₂ was carried out in the 100 mL stainless steel reactor. Typically, 0.20 g of catalyst and 10 mL methanol were placed in the reactor, which was then sealed. The reactor was then flushed with pure methane; this gas was used as the internal standard (1 bar). Dried N₂, H₂ and then CO₂ were then pumped into the autoclave reactor to reach the desired pressure at the reaction temperature (150 °C). Gases in the autoclave was carefully released and transferred to the online GC via a heated (~413 K) gas transfer line for analysis. Figure 1 shows a schematic diagram of the reactor and the gas injection setup. Thereafter, extent of the reaction was followed once hydrogen was charged into the reactor. Generally, the gases mixture was allowed to flush the transfer line before making the injection. After the injection was made, nitrogen was allowed to flush the heated transfer line in preparation for the next injection. Also, 3 x 60 mL gas samples were collected before and after the run for injection into a GC-TCD (not connected with the above setup) to determinate the gases contained in the reactor. At the end of a run, the pressure was slowly released where the reactor had been cooled in a dry ice-acetone mixture (-75 °C). The residue in autoclave was used for ¹H-NMR analysis which allows a quantitative analysis for formate production after the run. Finally, all of the solvents were then combined and GC-MS (not connected with the above setup) analysis was carried out for qualitative analysis to conform that there exist no other side products obtained from the run.

Nano-Catalysts Preparation and Characterization:

Catalyst Cu/ZnO/alumina (**Cat**) was prepared using a co-precipitation technique. 3.030 g Cu(NO₃)₂ · 3H₂O (Aldrich), 2.400 g Zn(NO₃)₂ · 6H₂O (Aldrich) and 3.150 g Al(NO₃)₃ · 9H₂O (Aldrich) were dissolved in 500 mL DI water. The solution was stirred and heated to 80 °C. An 0.25 M aqueous solution of Na₂CO₃ (Aldrich) was added to the continuously stirred solution until a pH 7.0 was attained. At this stage, air (20 mL/min) was passed through the solution and the precipitate was aged for two hours while the pH was maintained constant at 7.0. After aging, the precipitate was recovered by filtration, washed with 50 mL hot distilled water for 10 times under suction and dried in air (120 °C for 16 hours) and subsequently calcined in static air (350 °C for 12 h) to produce the

catalyst. The calcined catalyst was reduced with a 20 mL/min flow of 10% H₂/N₂ at 250 °C for 2 hours prior catalyst testing. XRD spectrum (Figure S2) for **Cat** was obtained (where the bulk average particle size of the Cu was determined to be 15 nm. Also, the elemental characteristic of **Cat** after reduction was determined by EDX analysis (Figure S3) where a atomic ratio of Al : Cu : Zn = 1.0 : 1.6 : 1.0 as summarized in Table S1 which agrees to the ratio of the starting precursor salts added.

A 1 w/w % doping of a second metal (Au, Ni, Ru or Pd) was prepared by deposition precipitation directly to **Cat**. The resulting catalysts namely 1% Au-Cu/ZnO/alumina, 1% Ni-Cu/ZnO/alumina, 1% Ru-Cu/ZnO/alumina and 1% Pd-Cu/ZnO/alumina were prepared by using HAuCl₄ (Alfa), Ni(NO₃)₂ · 6H₂O (Aldrich), RuCl₃ (Alfa) and Pd(NO₃)₂ (Alfa) as the precursor salts respectively. EDX analysis was conducted for those catalysts and the resulting atomic ratio agrees with the starting precursor salts added.

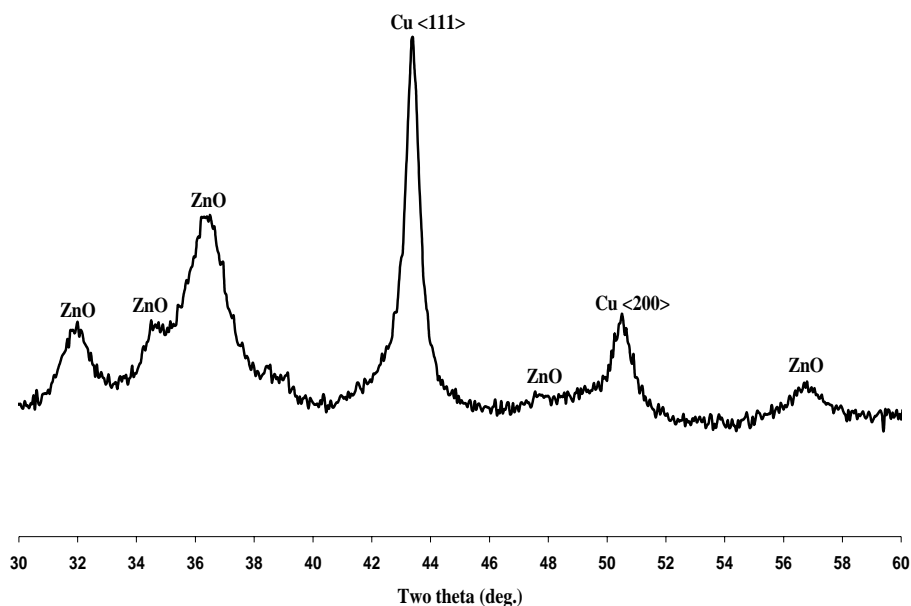


Figure S2. A typical XRD spectrum obtained for **Cat** showing clearly diffraction broadening for both Cu and ZnO.

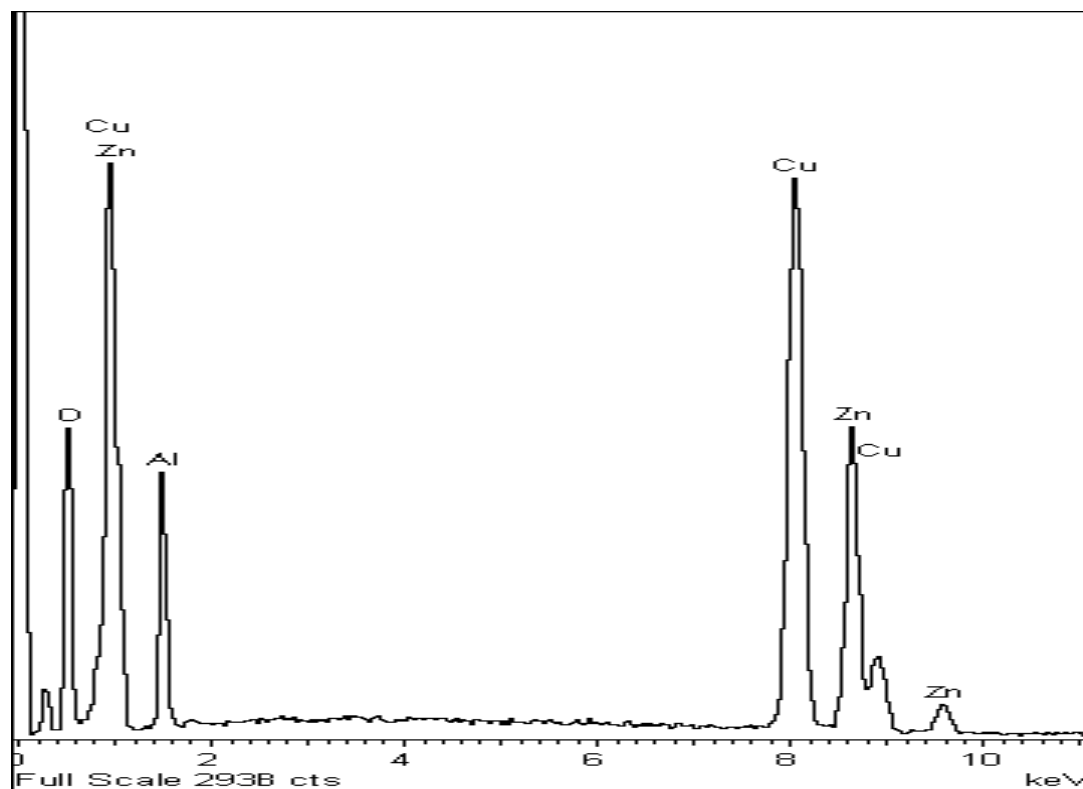


Figure S3. A typical EDX spectrum obtained for **Cat** showing the compositions of Al, Cu and Zn.

Table S1. The average compositions (Al, Cu and Zn) of **Cat** after a detailed analysis with 5 randomly selected areas with taking the ZAF correction

	Al / atomic %	Cu / atomic %	Zn / atomic %
Site of Interest 1	16.13	22.77	14.06
Site of Interest 2	14.07	25.41	15.59
Site of Interest 3	16.11	20.79	12.89
Site of Interest 4	13.69	25.25	15.41
Site of Interest 5	15.22	23.10	14.72
Average atomic %	15.04	23.46	14.53
Standard Deviation	1.13	1.92	1.10

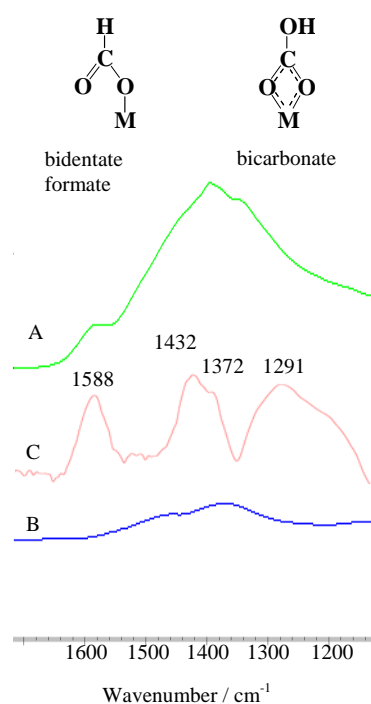
Solvents (in excess) with different properties was attempted to capture the formate intermediate from the catalyst. Table S2 summarized this preliminary study. At this point, it was interesting to observe that only methanol was able to capture formate from the catalyst in form of methyl formate (MF) among those tested solvents. It was likely that esterification (by thermal or acid site from the catalyst) occurred between the surface formate and the methanol

Table S2. Attempts to capture surface formate by different solvents

Solvent	CO ₂ / bar	formate yield / mmol ^c
Hexane	10	0.0
Triethylamine	10	0.0
Methanol	10	5.1
No solvent ^b	10	0.0
No solvent ^{a,b}	10	0.0
Methanol	Nil.	Trace (<0.05)
Methanol ^a	Nil.	0.0

Preliminary studies with CO₂, 50 bar H₂, N₂ (as diluent), 10.0 mL solvent and 0.2 g **Cat** in a 100 mL Parr autoclave reactor at 160 bar and 150 °C for 25 hours otherwise stated as below: ^a absence of **Cat**; ^b 10.0 mL methanol added at room temperature after reaction for NMR analysis; ^c determined by H¹-NMR with chloroform as external standard; ^d determined by calibrated GC-TCD.

An FTIR studies were also conducted at room temperature using a Nicolet 5700 FTIR instrument, equipped with a diamond ATR analyzer and an MCT detector at 0.4 cm⁻¹ resolution in the specific region 1700 – 1100 cm⁻¹. The catalyst powder, **Cat** (before and after the reaction) was compared. Here, the study demonstrated clearly that there were adsorbed formate species with absorption band observed at 1588 cm⁻¹ and 1372 cm⁻¹ (Figure S4). Adsorbed bicarbonate was also found which may due to the reaction between CO₂ and water by-product.

**Figure S4.** FT-IR spectra of adsorbed carbonaceous species found as intermediates of the CO₂ activation. Spectrum A was obtained from **1** after the reaction. Spectrum B was obtained from **1** before the reaction. Spectrum A and spectrum B were ported with common scale. Spectrum C was a subtraction of spectrum B from spectrum A. 1588 cm⁻¹ and 1372 cm⁻¹ corresponding to the ν_{as} (CO₂) and δ (CH) vibration respectively of surface bidentate formate; 1432 cm⁻¹ and 1291 cm⁻¹ corresponding to the ν_s (CO₃) and δ (OH) vibration respectively of surface bicarbonate.¹

Catalyst Activity Evaluation:

XRD spectrum for **Cat** was obtained where the bulk average particle size of Cu was determined to be 15 nm. Thus, the Cu particles contained in **Cat** has a maximum dispersion of 9.1% by assuming that Cu existed as a spherical particle. This means that a maximum of 9.1% of the overall Cu in the **Cat** was being exposed for the CO₂ activation reaction. EDX spectra collected for **Cat** showing that there existed a Cu loading of 23.46 atomic % which equivalent to a Cu loading of 41.38 weight %. Therefore, there was **0.1185 mmol of surface Cu** for every 0.20 g of **Cat** added in each of the testing.

For instance, when 1%Pd-Cu/ZnO/alumina was used as the catalyst for the CO₂ activation reaction (Table 2, 0.20 g 1%Pd-Cu/ZnO/alumina, 10 mL CH₃OH, 1 bar above atmosphere of CH₄ as internal standard, 10bar CO₂, 50 bar H₂ charged @ 150 °C and N₂ as diluent in a 100 mL Parr autoclave reactor at 160 bar reacted for 25 hours), the reaction reached equilibrium with **5.7 mmol MF produced**. Therefore, the final quantity of MF exceeds the surface coverage of the catalyst by 48 times (5.7/0.1185).

The TOF of the reaction was evaluated at the 10th minute of the reaction where time zero counted once CO₂ was charged. Therefore, the TOF for the above testing (with 1%Pd-Cu/ZnO/alumina as the catalyst) was calculated as 38.15 h⁻¹.