

Carbon Dioxide Fixation into Chemicals (Methyl Formate) at High Yields by Surface Coupling over a Pd/Cu/ZnO Nanocatalyst

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In recent years, the carbon dioxide (CO₂) issue has become the focus of attention because of the position of CO₂ as the primary greenhouse gas and the implication of its emissions on the problem of climate change. Burning fossil fuels releases the CO₂ stored millions of years ago. Deforestation releases the carbon stored in trees, resulting in more CO₂ in the atmosphere. The resulting climate change is an immediate threat to our security and prosperity, as the global food supplies will be compromised. Therefore, in pursuit of a stable climate, there is an urgent need to construct a low carbon global economy. For example, the U.K. government targets a 60% cut in emissions by 2050¹ as a necessary step for the development of a sustainable economy. Thus, an instantaneous response for research studies in the chemistry of CO₂ including its activation, utilization, and fixation is urgently needed. Apart from the physical storage of CO₂ into depleted oil/gas/coal reservoirs, chemical fixation of CO₂ has attracted additional attention as a possible way to manufacture useful chemicals in some specific locations. As a result, the activation of CO₂ at high yields appears to be the essential step to achieve the above objective. However, there has been limited work in literature reporting a catalytic approach to activate and to fix CO₂ under industrial applicable conditions, despite the fact that this process has been recognized as a significant innovation to chemical industry.² Most previous attempts were unable to attract industrial attention as they suffer from either the use of expensive but non-robust homogeneous catalysts or the use of peculiar reaction conditions (requires excess ligand(s) and solvents at extreme conditions).³ Here, we demonstrate a one-step catalytic fixation of CO₂ to methyl formate (MF) in liquid phase under mild industrial applicable conditions by using a new concept of coupling surface formate species formed from CO₂ on solid catalyst with excess methanol in hydrogen to form the MF, and the quantity of the product is found to greatly exceed the surface coverage of the catalyst by >45-fold. As a result, we report, for the first time, that the optimum Pd/Cu/ZnO/alumina nanocatalyst prepared from simple co-precipitation is capable of activating gaseous CO₂ to condensable MF at high yields (>20%) with excellent selectivity (>96%).

As an initial effort, co-precipitated Cu/ZnO/alumina (**Cat**) was used as the catalyst for the proof of concept of surface coupling with blended molecule, which is an industrial catalyst for water gas shift reaction, WGS (and also reversed reaction, RWGS), where formate species is believed to be the intermediate species.⁴ The use of hydrogen to activate CO₂ to useful chemicals at low temperature could be commercially viable with regard to future hydrogen availability from hydrocarbon reformations with carbon capture/storage and from catalytic water splitting via solar energy. Thus, screening of different solvent molecules in order to identify a candidate that can couple with surface formate to form chemicals under hydrogen and carbon dioxide in presence of **Cat** was carried out. As a result, preliminary studies with 10 bar CO₂, 50 bar H₂,

N₂ (as diluent), 10.0 mL of solvent (hexane, triethylamine, methanol, dichloromethane, DMF, pyridine, no solvent, etc.), and 0.2 g of **Cat** in a 100 mL high-pressure Parr autoclave reactor at the total pressure of 160 bar at 150 °C for 25 h were carried out. It was interesting to find from GC/MS and ¹H NMR that methanol was the only solvent that gave a clean, exclusive condensable product, which was identified to be methyl formate (MF). The noncatalytic methanol conversion to MF and the direct decomposition of methanol to MF in the absence of CO₂ (replaced by N₂) were discounted since only trace MF was observed in both cases.⁵ The yield of MF under CO₂/H₂ in methanol was estimated to be over 45 times that of the complete monolayer of **Cat**, implying that the methanol molecule is capable of coupling the surface formate, dragging the reversed WGS forward (see Supporting Information). It is thus believed that esterification (by thermal means or acid sites from the catalyst) may have taken place quickly between the surface formate and the adsorbed methanol, giving MF which can desorb to the solvent, see Scheme 1. Therefore, a new but clean catalytic reaction route of fixing CO₂ into condensable MF is revealed.

The conditions for optimum MF production were then assessed at 150 °C (Figure 1) which showed a maximum CO₂ conversion at 23.2% through variation of the H₂ to CO₂ molar ratio (*R*) from 0.5 to 12.5 with the MF as a primary product (selectivity >95%). Trace of carbon monoxide (CO) was detected as a byproduct possibly from the RWGS. However, the highest turnover frequency, TOF (evaluated at the first 10 min of the reaction), was achieved at *R* = 5 with a volcano relationship observed, which was attributed to the competition of adsorption sites between H₂ and CO₂ on the catalyst. Under excess H₂ (90 bar, 255.9 mmol), an optimum conversion of CO₂ to MF in function of CO₂ pressure was also assessed (Table 1). It was noted that the % CO₂ conversion to MF could be raised from 10.9 to 19.1% without any noticeable selectivity attenuation simply by reducing the CO₂ pressure under the conditions listed in Table 1.

With reference to the tentative mechanism in Scheme 1, the formation of MF requires chemisorption of at least H₂, CO₂, and methanol on the surface. Doping of the catalyst with more than one metal promoter for co-adsorption of different surface species usually improves the overall reaction rate as this concept has been clearly demonstrated in catalytic hydrogenations.⁶ Thus, an attempt to increase the TOF by doping the **Cat** with 1 w/w % of different metal promoters was carried out, and the results are summarized in Table 2. It is noted that doping the material with precious metals such as Ru, Ni, Au, and Pd metal showed a dramatic effect on TOF: Pd proved to be the best doper that enhanced the TOF by 23.6%, giving activity of 38.15 h⁻¹. This order may relate to the ability of hydrogen activation and transfer of the promoter on the catalyst surface since Pd is also well-known to show the best hydrogen spill-over activity among all precious metals.⁷ Au doper appeared to decrease the TOF, which could be related to its high affinity for Cu, blocking surface sites.

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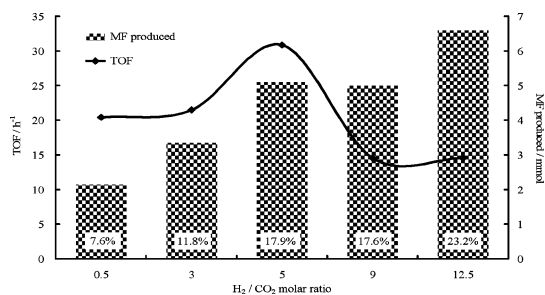


Figure 1. A plot of the total quantity of MF produced (also % CO₂ conv. in white boxes) and initial TOF against H₂ to CO₂ molar ratio, *R*: 0.20 g of **Cat**, 10 mL of CH₃OH, 1 bar CH₄ as internal standard, 10 bar CO₂ (28.4 mmol) with variation of H₂ using N₂ as diluent at 160 bar and 150 °C for 25 h.

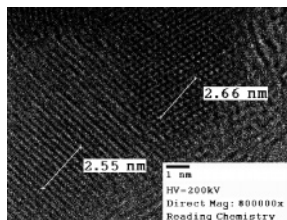


Figure 2. HRTEM image of Pd-doped **Cat** showing the intimate interface between Pd and Cu (PdO <101> and CuO <111> observed⁸ with crystal sizes of 2.66 and 2.55 nm, respectively, after the sample was exposed to air).

Scheme 1. Proposed Capture of Surface Formate over **Cat** by Methanol to Methyl Formate under H and CO₂

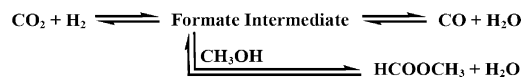


Table 1. Attempts to Optimize % Conversion of CO₂ to MF by Reducing the CO₂ Pressure in the Reaction Mixture^a

	CO ₂ /bar (mmol)	MF yield (mmol)	CO (mmol)	TOF (h ⁻¹)	selectivity ^b (%)	conv. ^c (%)
1	40 (113.7)	12.4	0.27	26.1	97.9	10.9
2	20 (56.9)	9.2	0.20	20.7	97.8	16.2
3	10 (28.4)	5.0	0.16	14.6	96.8	17.6
4	5 (14.2)	2.7	n.d.	n.d.	n.d.	19.1

^a Same conditions as quoted in Figure 1; captions were applied except with variation of CO₂ pressure at 90 bar H₂ (255.9 mmol). ^b Selectivity to MF. ^c % Conversion of CO₂ to MF.

Detailed HRTEM imaging of the Pd-doped **Cat** (Figure 2) was conducted, which showed the intimate interface of Cu and Pd in our co-precipitated nanocatalyst.

Of all catalysts tested, it is interesting to note that the quantity of MF produced was found to level off after a prolonged period of time (see Figure 3). The kinetic poisoning effect by byproducts such as CO and water was discounted since adding excess CO and water prior to reaction showed no significant negative effects on the TOF and the quantity of MF produced. Thus, it is likely the MF production was somehow restricted under a new equilibrium. As shown in Figure 3, the curve with the pre-addition of MF (13.46 mmol) reached the same steady (equilibrium) position as the one without blending the MF, achieving 12.29 mmol MF in both cases. Thus, the results indicate that the CO₂ activation and fixation to MF by these catalytic means with the coupling of methanol can achieve equilibrium for a prolonged period of time. Thus, the future challenge to increase MF productivity from CO₂ activation is to avoid the establishment of equilibrium in liquid by either changing the batch process to a continuous process or/and removing products from recycled mixture.

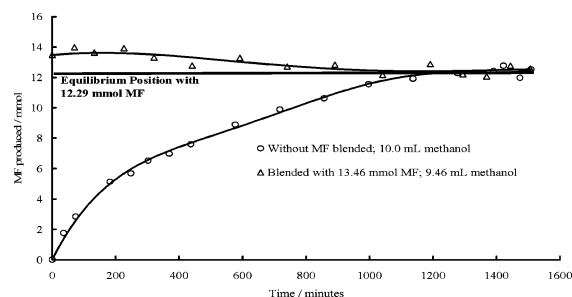


Figure 3. A plot of MF produced against time: (Δ) 35 bar CO₂, 85 bar H₂, 0.830 mL (13.46 mmol) of MF with 113.0 mmol total carbon; (○) 40 bar CO₂, 90 bar H₂ with 113.7 mmol total carbon (0.20 g of **Cat**; 1 bar CH₄ as internal standard; N₂ as diluent in 100 mL of reactor at 160 bar at 150 °C for 25 h).

Table 2. Effect of TOF by Doping the **Cat** with 1% Precious Metals^a

catalyst	TOF (h ⁻¹)
Cu/ZnO/alumina	30.85
1% Ru–Cu/ZnO/alumina	33.62
1% Ni–Cu/ZnO/alumina	37.27
1% Au–Cu/ZnO/alumina	13.42
1% Pd–Cu/ZnO/alumina	38.15

^a Conditions: 10 bar CO₂, 50 bar H₂ at 150 °C.

To conclude, it is demonstrated that, with introduction of methanol to the Pd/Cu/ZnO nanocatalyst under H₂/CO₂, carbon dioxide can be activated and fixed as methyl formate with impressive TOF, yield, and selectivity. Thus, a new route for CO₂ activation by heterogeneous means at ambient conditions is described. This preliminary study also offers directions to rationally design and optimize the required catalyst, reactor, and experimental conditions for this reaction.

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Supporting Information Available: Synthesis of **Cat** and doping, setup, and experimental procedure are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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