

Carbon Dioxide Hydrogenation to Formic Acid by Using a Heterogeneous Gold Catalyst**

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Formic acid is an important chemical with numerous applications. The industrial methods used for its production employ CO as a raw material.^[1] As an alternative, the hydrogenation of abundant and inexpensive CO₂ could be advantageous and deserves exploration.^[2] Furthermore, a convenient HCOOH production by CO₂ hydrogenation would complete the long desired chemical loop for hydrogen storage using CO₂.^[3] The complementary step, that is, the catalyzed decomposition of HCOOH to pure H₂ together with easily removable and reusable CO₂, has been firmly established.^[3b-f,i-k,q,u,4] The direct catalyzed CO₂ hydrogenation to HCOOH is, however, thermodynamically disfavored ($\Delta G^\circ_{298} = +33 \text{ kJ mol}^{-1}$). Even under especially favorable conditions, namely H₂O solvent and low temperatures, very high CO₂/H₂ pressures must be used to reach a scant HCOOH equilibrium concentration.^[5] Jessop has shown that “the hydrogenation of CO₂ to formic acid is thermodynamically unfavorable unless a base is present; the proton transfer to the base drives the reaction”.^[6] Accordingly, methods intended for HCOOH formation via CO₂ hydrogenation propose the use of high-boiling nitrogenous bases in polar solvents. Ammonium formate salts are quantitatively obtained; HCOOH can be freed from these by thermal splitting.^[7] These methods, however, have not yet been applied industrially. The main hindrances are the laborious removal of catalyst and solvent as well as the limited amounts of HCOOH formed per mol of high-molecular-weight amine.

Recently, we showed that the low-molecular-weight amine NEt₃ is quantitatively converted into HCOOH/NEt₃ adducts in the absence of foreign polar solvents. With [RuCl₂(PMe₃)₄] as homogeneous promoter at 40 °C and under 1:1 CO₂/H₂ at a pressure higher than 41 bar, neat NEt₃ was quantitatively converted into adducts with an acid/amine molar ratio AAR > 1.33.^[8]

The drawback of this procedure remains the separation of the homogeneous catalyst. This is a crucial step, as the catalyst promotes the reverse decomposition reaction to CO₂, H₂, and

liquid NEt₃ when the pressure is lowered. To solve this problem, we searched for a heterogeneous supported metal catalyst from which the HCOOH/NEt₃ adducts could be separated simply by drawing them, catalyst-free, directly from the reactor under pressure. To simplify the search, we first considered finely divided Groups 8–10 metals. Because, as mentioned above, a catalyst for the production of adducts necessarily promotes their decomposition, we found it convenient to test whether iron powder, Raney nickel and Co, Ru, Rh, Ir, Pd, and Pt metal black cause gas evolution when contacted with the HCOOH/NEt₃ adducts. Each metal sample (5 mmol) was suspended into 50 mL of HCOOH/NEt₃ adduct with AAR = 1.33.^[9] In none of these cases was gas evolution observed during one week at 40 °C.^[10] Upon considering that copper and gold catalyze CO₂ hydrogenation to methanol,^[11] it seemed appropriate to extend our systematic investigation to the Group 11 elements, whose active black forms, however, are not commercially available. We reported that the reduction of CuO with alkaline formaldehyde yields an extremely reactive, pyrophoric, copper material permeated by nanocavities.^[12] We extended this reduction method to Ag₂O and Au(OH)₃. Neither copper nor silver so obtained caused adduct decomposition. Gas evolution and release of amine in a lighter phase were only promoted by Au black obtained by reducing a freshly prepared Au(OH)₃/H₂O slurry with diluted cold alkaline formaldehyde (Figure 1).

Gold black was then tested as a promoter for the direct formation reaction of HCOOH/NEt₃ adducts. A 120 mL rocking stainless-steel autoclave was charged with 1 g (5 mmol) of gold black, 10 mL (62 mmol) of the adduct with AAR = 1.33, 40 mL (286 mmol) of amine, and pressurized with 14 g of a 1:1 CO₂/H₂ mixture (each 304 mmol). At 40 °C, a slow gas absorption took place, but the catalyst deactivated quickly: the 180 bar starting pressure leveled to 107 bar, far

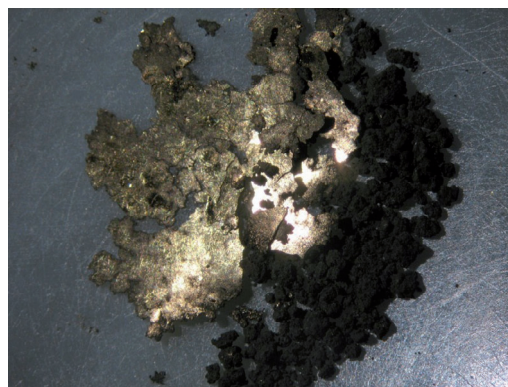


Figure 1. Au black with a shining zone obtained by compression.

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from the 41 bar CO_2/H_2 1:1 pressure equilibrating the amine and the 1.33 adduct^[8] (Supporting Information, Figure S1). The reason for the failure of the catalyst can be understood by comparing the SEM images of gold black before and after its use: metal particle aggregation is evident (Figure 2).

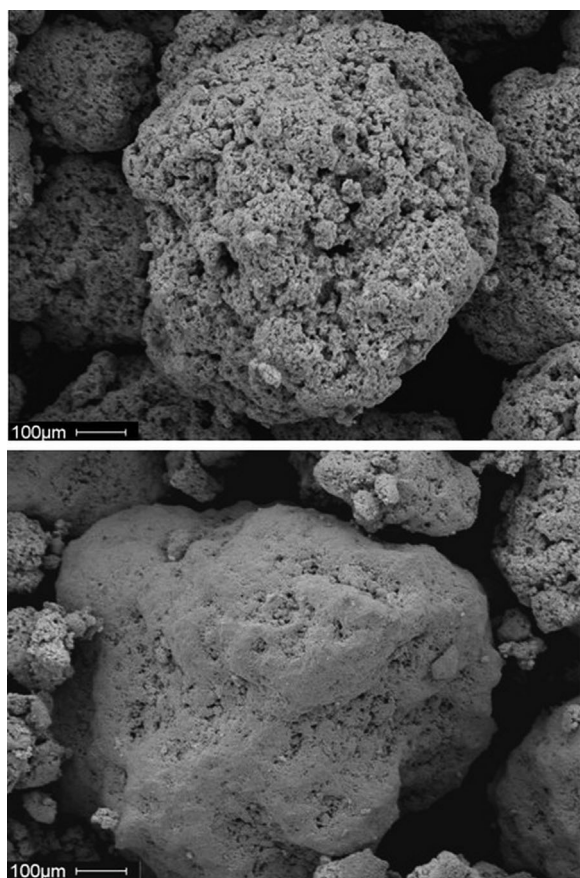


Figure 2. SEM images of Au black before (above) and after (below) its use as catalyst for the formation of the 1.33 adduct.

The catalytic activity of gold for the $\text{HCOOH}/\text{NEt}_3$ adducts formation from CO_2 , H_2 , and neat NEt_3 and the necessity of a support for the metal particles is apparent from these results. We therefore extended our investigation to titania-supported gold. Reproducible results were obtained by employing commercial AUROLite (Mintek; 1 wt % Au/TiO_2 , extrudates). AUROLite is fully characterized (BET $40\text{--}50\text{ m}^2\text{ g}^{-1}$; average gold crystallite size ca. 2–3 nm). Furthermore, the extrudate sticks can be immobilized in a steel net cage and be brought into contact with a stirred liquid without releasing powder. AUROLite (13 g; Au 0.7 mmol) immobilized in a ring-shaped cage was placed in

a 320 mL magnetically driven Parr autoclave equipped with temperature and pressure sensors and a dip tube to remove liquid samples (Supporting Information, Figure S3). The autoclave, connected to a high-pressure reservoir to supply 1:1 CO_2/H_2 and to a HPLC pump to supply NEt_3 , was charged with 140 mL (1 mol) of NEt_3 and pressurized with 1:1 CO_2/H_2 to 180 bar at 40°C . Gas absorption took place, and the pressure was restored to 180 bar when it dropped to 130 bar. After every six pressurizations and about every three days (Figure 3), 100 mL of liquid adduct with an AAR of about 1.7 were taken out and the amount of amine incorporated into the adduct restored into the autoclave. The gasses, mainly consisting of CO_2 , released during the liquid drawing under pressure were also taken into consideration (see the Supporting Information).

The reaction rate changed little during 37 days of production. In this time, a total of 1.326 kg of adduct with $\text{AAR} = 1.715$ was produced and 18040 mol of H_2 per mol of Au incorporated into CO_2/NEt_3 . No other organic products were detected by NMR spectroscopy. Surprisingly, 9% CO with respect to H_2 was found accumulated in the residual gasses. This did not significantly affect the selectivity, as only 63 mmol of CO, with a molar ratio of 5.0×10^{-3} with respect to the incorporated H_2 , were formed during the 37 days of adduct production. The unexpected presence of CO suggests a remarkable tolerance of the gold catalyst towards CO. Presumably, CO formation is due to a gold-catalyzed reverse water gas shift reaction occurring at an unusually low temperature. A lower ΔG°_f of H_2O in the adduct medium could account for this reaction.

The conditions for the production of the adducts have not been optimized, and no supported gold catalysts other than AUROLite were tested. However, it has been shown that titania-supported gold 1) allows one to avoid solvents as the conversion of neat amine into adducts is complete under CO_2/H_2 1:1 pressure higher than 41 bar at 40°C ; 2) is a highly stable catalyst; and 3) permits a continuous process for the production of catalyst-free adducts. Necessary precautions are the recompression into the reactor of gases released during liquid product removal and the periodic replacement of gases in the reactor when CO accumulation slows down the reaction rate by lowering the CO_2/H_2 partial pressure.

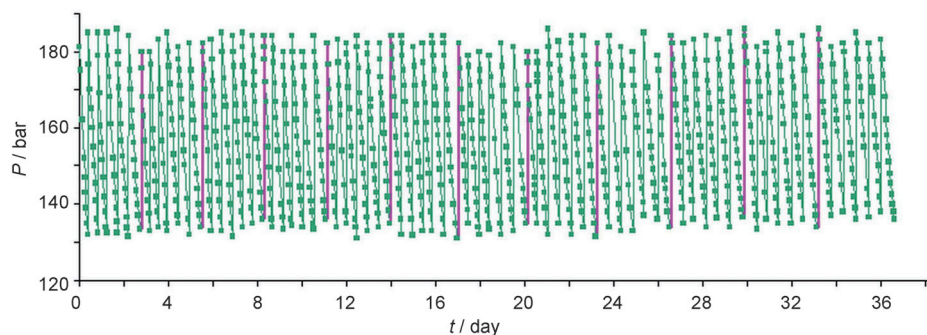


Figure 3. Pressure–time curve for the production of $\text{HCOOH}/\text{NEt}_3$ adduct (1.326 kg, 7.365 mol) with an acid/amine ratio $\text{AAR} = 1.7$ from CO_2/H_2 (1:1) and NEt_3 and catalyzed by AUROLite (13 g, Au 0.7 mmol) in a steel net cage. Green vertical lines: reactor re-pressurizations with gaseous mixture; crimson: liquid drawn from and reloaded into the reactor.

No other homogeneous or heterogeneous catalyst can simultaneously display all of these properties for the CO₂ hydrogenation in the presence of nitrogenous bases. The stripping of HCOOH from the HCOOH/NEt₃ adducts still remains to be done, however. Direct thermal splitting of the HCOOH/NEt₃ adducts into HCOOH and NEt₃ does not occur. Upon increasing the temperature, the adduct with AAR = 1.7 loses NEt₃ progressively until the adduct with AAR = 2.35 is formed at 160 °C. Beyond this temperature, decomposition takes place and a CO₂/H₂/CO mixture together with condensable H₂O and NEt₃ are formed. To recover HCOOH, we exploited an amine-exchange method that has been suggested in the patent literature.^[7a,b] High-boiling tri-*n*-hexylamine was added to HCOOH/NEt₃ adduct with AAR = 1.715 in a molar ratio HCOOH/(*n*-C₆H₁₃)₃N = 2. A biphasic system was obtained (see the Supporting Information) and fractionated under reduced pressure (90 mmHg). A liquid fraction consisting of pure NEt₃ (90% yield) was collected. At higher temperatures, a fraction consisting of 85 wt % HCOOH, contaminated by NEt₃ (11.5 wt %) and (*n*-C₆H₁₃)₃N (3.5 wt %) was recovered. Pure anhydrous HCOOH was obtained by re-distilling the high-boiling fraction at atmospheric pressure. Overall, HCOOH was recovered from the HCOOH/NEt₃ adduct with AAR = 1.715 in 83% yield.

In conclusion, a new catalytic property of gold has been discovered: it promotes the CO₂ hydrogenation in the presence of neat NEt₃ to form HCOOH/NEt₃ adducts. A continuous production process for catalyst- and solvent-free adducts has been demonstrated using a robust titania-supported gold catalyst. The adducts have been split into pure HCOOH (anhydrous) and neat NEt₃ with the help of high-boiling (*n*-C₆H₁₃)₃N. When coupled with the catalytic HCOOH decomposition to CO-free hydrogen together with easily removable and reusable CO₂,^[3b-f,i-k,q,u,4] these findings complete the chemical loop for the long-sought-after hydrogen storage with CO₂. Finally, it remains to be seen whether the method reported herein for HCOOH production that employs CO₂ and H₂ raw materials beats those requiring high-purity CO.^[1] The former would prevail if inexpensive CO₂/CO-contaminated H₂ (CO₂-enriched syngas) could be used as the raw material. Such an opportunity is suggested by the abovementioned observation that the gold-catalyzed HCOOH/NEt₃ adduct production is not inhibited by the self-generated CO.

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