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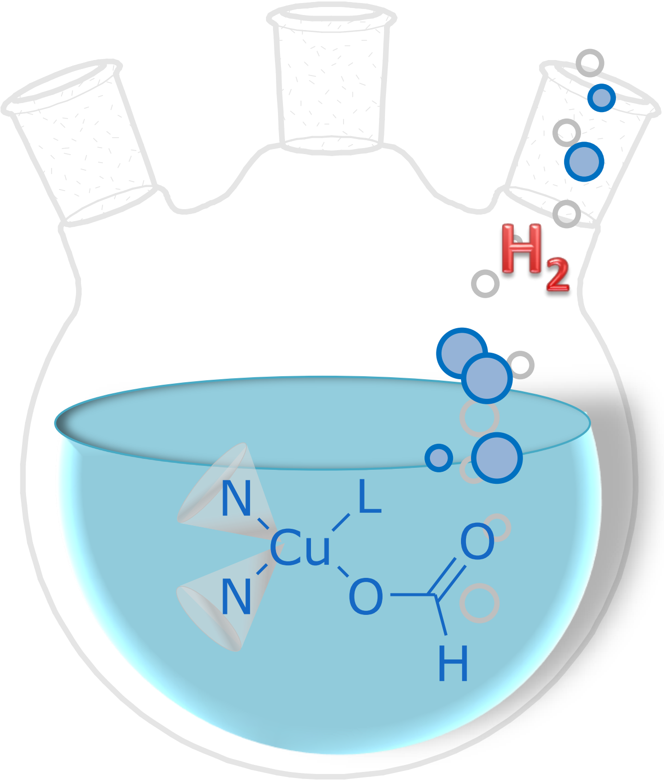

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The production of H_2 from HCOOH was achieved by using simple Cu compounds and different HCOOH/amine adducts. The activity is strongly dependent on the amine, more basic and bulky ones giving better results whereas the use of chelating amines is detrimental.

New catalytic systems for the hydrogenation of CO_2 to formic acid followed by its decomposition to give back CO_2 and H_2 are extremely interesting as the combination of the two reactions would allow one to valorize CO_2 by its transformation in a highly useful instrument for hydrogen storage.

The development of improved technologies for H_2 generation and H_2 storage in a safe and reversible manner is a prerequisite for the utilization of hydrogen as fuel[1]. Moreover formic acid is one of the major by-products of levulinic acid production with the Biofine process.[2] Compared to H_2, formic acid is liquid and easy to store, transport and handle.[3] Besides, HCOOH is considered less hazardous than methanol (its first competitor as hydrogen carrier) and therefore a valuable alternative in spite of its lower hydrogen density (43 vs 125 g/kg).[4]

In the last years some papers, especially from Beller and Laurenczy groups, on formic acid dehydrogenation have been published, reporting promising results, but using expensive catalysts based on noble metals, such as $[\{RuCl_2(p\text{-cymene})\}_2]$ or proton-switchable Ir complexes.[5] Others works report an interesting activity using various heterogeneous system mainly based on Pd, Au and Ag.[5b,6] As far as non-noble metals are concerned, only a few homogeneous iron catalysts are reported to be active in the reaction, in the presence or in the absence of visible light[1,7,8] while the potential of Cu based system is still largely unexplored.

In this paper we wish to report our results in the production of H_2 from formic acid by using simple copper complexes and a HCOOH/amine adduct.

In the absence of catalyst a 5:2 HCOOH/NEt_3 adduct (NEt_3=triethylamine) gave no gas evolution, but as soon as $Cu(OAc)_2$ is added formation of H_2 and CO_2 starts giving in 3 h a total volume of 20 ml. GC analysis of the gas phase of all the experiments showed that H_2 and CO_2 were formed in a 1:1 ratio, together with traces of CO (<150 ppm).

By decreasing the HCOOH/NEt_3 ratio we observed the same trend reported by Beller and coworkers[5a,d], the higher the amine concentration, the higher the conversion, although for ratio lower than 1 the increase was quite limited (Table 1).

Table 1. Decomposition of formic acid using different HCOOH/NEt3 ratio and different Cu precursors

Cu precursor	HCOOH/NEt_3 Ratio	V (ml)			C (%)	TON	TOF
		3 h	6 h	22 h		22 h	
$Cu(OAc)_2$	5/2	20	28	56	4.1	4.4	0.20
$Cu(OAc)_2$	1/1	58	103	234	17.2	18.6	0.85
$Cu(OAc)_2$	2/5	63	112	273	20.1	21.6	0.98
$Cu(OOCH)_2$	1/1	47	88	229	16.8	18.4	0.84
$Cu(acac)_2$	1/1	64	121	253	18.6	20.3	0.92
$Cu(NO_3)_2$	1/1	66	116	231	17.0	18.6	0.85
$CuCl_2$	1/1	17	26	71	5.2	5.7	0.26
CuO	1/1	47	66	249	19.6	19.6	0.89
Cu powder	1/1	8	9	21	1.5	1.7	0.08

Reaction conditions: Cu=0.26 mmol, 95 °C, HCOOH=28 mmol (1.31 g)

On the contrary the use of different copper compounds for the reaction did not lead to important differences in conversion and total volume produced. This could be due to the rapid replacement of pristine ligands by formate and amine, due to their high concentration in the reaction medium. Only $CuCl_2$ was significantly less performant while Cu powder was almost inactive.

A more interesting and evident effect was observed by changing the amine (Table 2). Here the basicity plays an important role. In particular, the lower the basicity of the amine, the lower the activity. Aniline and pyridine, e.g., with high pK_b (9.37 and 8.75) gave negligible conversion after 22 h (0.6% and 2%) whereas highly basic dibutylamine and triethylamine, allowed to reach a conversion around 17% in 22 h (V=221).

Table 2. Decomposition of formic acid with $Cu(OAc)_2$ using different amines: effect of basicity

Amine	pK_b	V (ml)			C (%)
		3 h	6 h	22 h	22 h
Dibutylamine	2.75	53	94	221	16.2
Piperidine	2.88	59	99	164	12.0
Triethylamine	2.99	58	103	234	17.2
Tributylamine	3.11	115	186	349	25.6
Ethylendiamine	3.29[a]	8	8	8	0.6
Tripropyilamine	3.35	160	241	312	22.9
Benzylamine	4.67	13	17	28	2.1
Pyridine	8.75	24	26	28	2.1
Aniline	9.37	11	10	10	0.7
Diphenylamine	13.21	4	5	5	0.4

Reaction conditions: Cat=0.26 mmol, 95°C, HCOOH=28 mmol (1.31 g, 99 wt%), HCOOH/Amine=1; [a] pK_{b1}

However, Fig 1 shows that there is no linear dependence of the activity on basicity. On the contrary a very narrow range of pK_b grants high activity while outside this range activity collapses. Moreover there is no linearity even in the pK_b range ensuring activity, e.g. piperidine is more basic than triethylamine or trybutylamine (pK_b=2.88 vs 2.99 and 3.11) but the volume of gas produced is much lower (t=22h, 156 ml vs 221 and 349). The particular case of ethylendiamine is worth noting: notwithstanding its high basicity the reaction does not almost proceed. This behavior suggests a coordination effect of the amine on the copper center. Ethylendiamine is well known for its chelating properties and could strongly coordinate the Cu atom blocking all the four square planar coordination sites with its bite angle[9] of ~85° and thus inhibiting coordination of the $HCOO^-$ species and forming a very stable and inactive complex.

Therefore we took into consideration other parameters such as nucleophilicity and steric hindrance that can play a role in the coordination chemistry involved in this reaction. Table 3 reports catalytic data related with the nucleophilic constant, n[10] and with the conic angle[11] of the amines. It is apparent from this comparison that activity increases by increasing steric hindrance and by decreasing nucleophilicity, thus suggesting that the role of the amine is not limited to HCOOH deprotonation.

A reaction mechanism may be suggested in which the presence of two bulky amines could favour the elimination of hydrogen and CO_2 from a square planar intermediate.

The catalytic system tends to deactivate with time, as shown by the solution discolouring and by the formation of a reddish precipitate. Reduction of Cu (II) in basic medium by means of weak reducing agents such as reducing sugars, citric and ascorbic acid[12] is well known.

However the catalyst could be easily reactivated, before complete reduction to metallic phase, simply by opening the reactor to air. After a few minutes (5 min) the mixture turns back to blue (Cu(II)) and an increase in activity is observed (Fig.2).

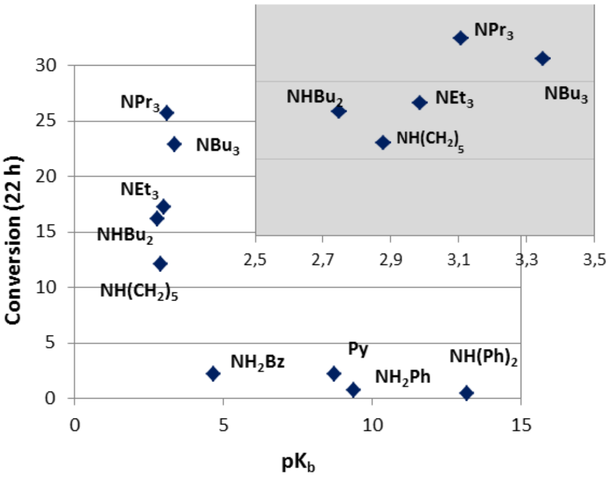

Fig. 1. Conversion vs pK_b for the different amines. The inset shows the region between 2.5-3.5 pK_b

Table 3. Decomposition of formic acid: effect of nucleophylicity

Amine	n[a]	pK_b	θ[b]	6 h	22 h	22 h
				V (ml)		C (%)
Piperidine	5.59	2.88	121	99	164	12.0
Dibutylamine	4.77	2.75	158	94	221	16.2
Triethylamine	4.09	2.99	150	103	234	17.2
Triproylamine	-	3.35	160	241	312	22.9

Reaction conditions: Cat=0.26 mmol, 95 °C, HCOOH=28 mmol (1.31 g, 99 wt%), HCOOH/Amine=1; [a] n= nucleophilic constant; [b] conic angle

To stabilize copper in solution we tried to exploit the chelating ability of ethylendiamine, as we already observed that in the presence of such amine neither decomposition of HCOOH nor discoloring of the solution or separation of solids took place. Results reported in Table 4 show that in fact a stoichiometric amount of ethylendiamine with respect to Cu gave a significant improvement in the performance of the $HCOOH/NEt_3$ adduct. On the contrary, Cu/en ratio other than 1 or a different diamine such as TMEDA had no effect.

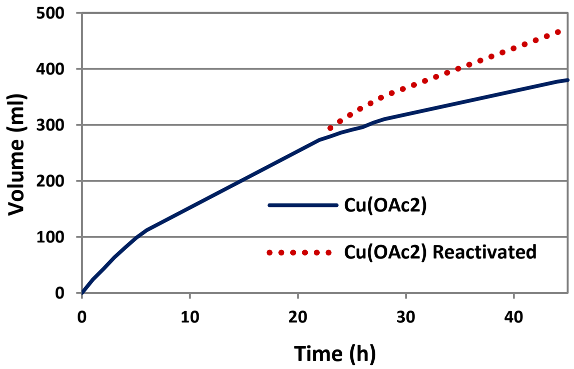

Figure 2. Re-activation of $Cu(OAc)_2$, by exposing the reaction mixture to air after 22 h.

Another chance is to avoid alkalinization of the medium as reduction of copper to form Cu(0) nanoparticles only occurs under basic conditions. Therefore we added an acid other than HCOOH to keep a low pH during the reaction, without affecting the HCOOH/amine ratio. Addition of acetic acid to the $1HCOOH/1NEt_3$ mixture did not modify the reaction profile during the first hours of reaction, but the long term stability increased very much (V=320 vs 220, C=24.5 vs 16.4) as shown in Fig.3.

Table 4. Stabilization of Cu catalyst using stoichiometric amount of Ethylendiamine or TMEDA

Cu/en Ratio	3 h		6 h		22 h	
	V (ml)	C (%)	V (ml)	C (%)	V (ml)	C (%)
Cu/en=1/2	60	4.4	105	7.7	234	17.2
Cu/en=1/1	121	8.9	189	13.9	299	22.0
Cu/en=2/1	59	4.3	98	7.2	223	16.4
Cu/TMEDA=1/1	70	5.2	111	8.2	224	16.4

Reaction conditions: $Cu(OAc)_2$=0.26 mmol, 95 °C, HCOOH=28 mmol (1.31 g, 99 wt%), $HCOOH/NEt_3$=1

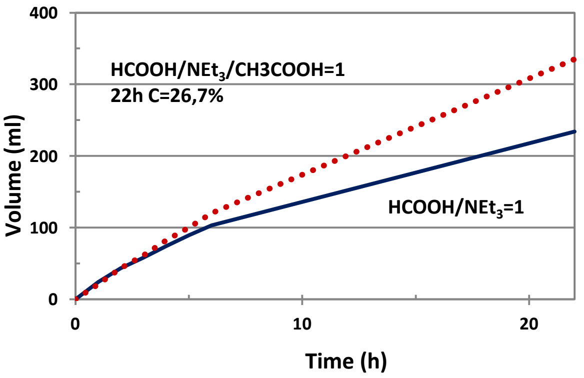

Figure 3. Stabilization of the Cu catalyst by the addition of CH_3COOH to the starting mixture

Finally we tested some precursor with very low potential reduction to metallic copper (Table 5).

Table 5. Decomposition of formic acid using different Cu precursors

Cu precursor	$HCOOH/NEt_3$ Ratio	V (ml)			C (%)
		3 h	6 h	22 h	22 h
CuCl	1/1	32	59	189	14.9
Cu_2O	1/1	79	124	217	16.0
CuI	1/1	110	209	493	36.2
$[(PPh_3)CuH]_6$	1/1	28	47	59	4.3

Reaction conditions: Cu=0.26 mmol, 95 °C, HCOOH=28 mmol (1.31 g)

Cu_2O showed high initial activity but it slowed down reaching at 22 h a conversion comparable to the Cu species reported in Table 1.

On the contrary CuI showed very high activity and stability allowing to reach 36% conversion at 22 h and 66% at 45 h. This matches with a TON value of 72 which is far away from the values obtained with Fe[8] or Ru[5a] that are up to 4 order of magnitude higher.

In conclusion, copper compounds appear as promising catalysts for H_2 production from HCOOH/amine adducts although, so far, neglected by the scientific community.

Their activity can be finely tuned through the choice of the amine while deactivation may be controlled. Work is in progress to get a deeper insight into the mechanism and particularly into the coordination geometry of the active site in order to develop an effective system for hydrogen production from HCOOH in the presence of a non-noble metal.

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Electronic Supplementary Information (ESI) available: experimental conditions (apparatus, catalytic experiments and gas-phase analysis) and reaction profiles. See DOI: 10.1039/c000000x/

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