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A new Cu-based system for formic acid dehydrogenation

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Supporting Information

Catalytic test set-up

The experiments were carried out in a 5 ml glass flask equipped with reflux condenser and connected to a gas burette as shown in Figure S1.

Figure S1. Experimental equipment

In a standard reaction, 28 mmol (1.31 g) of HCOOH were carefully mixed with the desired amount of the amine, then the mixture was pre-heated to the reaction temperature (95 °C, oil bath temperature) under N_2 atmosphere and stirring (1250 rpm). The copper catalysts was added to the reaction mixture thanks to a small glass crucible. The volume was measured thanks to the gas-burette and gases were analyzed by GC equipped by TCD (see further).

Analysis of the gas mixture

The gas produced was analyzed by GC (Agilent 6890N) equipped with a TCD detector and two columns: the first one (bonded, divinylbenzene/ethylene glycol dimethacrylate) for CO_2 detection and the second (19095P-MS0E molecular sieve) for H_2, and CO detection and separation. The analysis was carried out with the following temperature ramp: 4 min at 40°C, heating at 10°/min till 100°C,1 min at 100°C.

For the quantitative analysis an external calibration with three different standard mixtures was carried out. The chromatograms of reaction gas phase put in evidence that H_2 and CO_2 were produced in equal amount. The H_2/CO_2 ratio were around 0.93-0.95 and this value is comparable to the one obtained in our hand with the already reported [$\{RuCl_2(p\text{-cymene})\}_2$] (0.93)[Beller et al. Angew. Chem. Int. Ed. 2008, 47, 3962 –3965].

Traces of amine were detected by analysis of the gas phase with GCMS (GC Agilent 7890A – MS 5975C) equipped with a 5%-phenyl- methyl polysiloxane column

Reaction Profiles

In Figure S2 are reported typical reaction profiles for the formic acid dehydrogenation using copper catalysts.

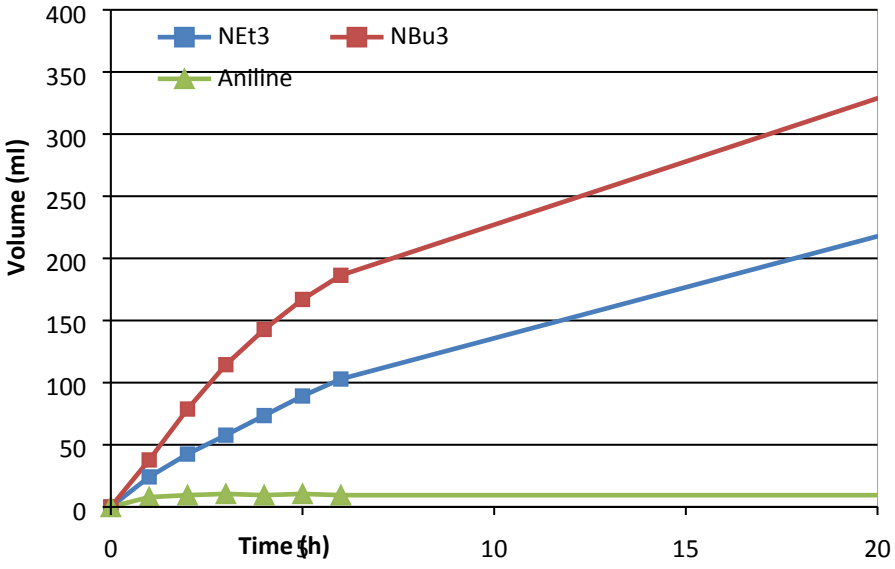

Figure S2. Reaction profile for NEt_3, NBu_3 and aniline in the presence of $Cu(OAc)_2$ catalyst (conditions: Cat=0.26 mmol, 95°C, HCOOH=28 mmol, HCOOH/Amine=1)

Full catalytic results (volume, conversion and TON) at 3, 6 and 22 h

Table S1. Decomposition of formic acid using different $HCOOH/NEt_3$ ratio and different Cu precursors

Cu precursor	$HCOOH/NEt_3$ Ratio	V (ml)			C (%)			TOF			TON		
		3 h	6 h	22 h	3 h	6 h	22 h	3 h	6 h	22 h	3 h	6 h	22 h
$Cu(OAc)_2$	5/2	20	28	56	1.5	2.0	4.1	0.53	0.37	0.20	1.6	2.2	4.4
$Cu(OAc)_2$	1/1	58	103	234	4.2	7.6	17.2	1.53	1.37	0.85	4.6	8.2	18.6
$Cu(OAc)_2$	2/5	63	112	273	4.6	8.3	20.1	1.67	1.48	0.98	5.0	8.9	21.6
$Cu(OOCH)_2$	1/1	47	88	229	3.5	6.5	16.8	1.27	1.18	0.84	3.8	7.1	18.4
$Cu(acac)_2$	1/1	64	121	253	4.7	8.9	18.6	1.70	1.62	0.92	5.1	9.7	20.3
$Cu(NO_3)_2$	1/1	66	116	231	4.8	8.5	17.0	1.77	1.57	0.85	5.3	9.4	18.6
$CuCl_2$	1/1	17	26	71	1.2	1.9	5.2	0.43	0.35	0.26	1.3	2.1	5.7
CuCl	1/1	32	59	189	2.3	4.3	14.9	0.83	0.77	0.68	2.5	4.6	14.9
CuO	1/1	47	66	249	3.5	7.3	19.6	1.23	1.32	0.89	3.7	7.9	19.6
Cu_2O	1/1	79	124	217	5.8	9.1	16.0	2.10	1.67	0.80	6.3	10.0	17.5
CuI	1/1	110	209	493	13.0	15.4	36.2 (45h =66. 0)	2.93	2.78	1.80 (45h =1.6 0)	8.8	16.7	39.5 (45h =72. 0)
Stryker	1/1	28	47	59	2.1	3.5	4.3	0.77	0.63	0.21	2.3	3.8	4.7
Cu powder	1/1	8	9	21	0.6	0.7	1.5	0.23	0.13	0.08	0.7	0.8	1.7

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

Table S2. Decomposition of formic acid with $Cu(OAc)_2$ using different amines: effect of basicity

Amine	pK_b	V (ml)			C (%)			TOF			TON		
		3 h	6 h	22 h	3 h	6 h	22 h	3 h	6 h	22 h	3 h	6 h	22 h
Dibutylamine	2.75	53	94	221	3.9	6.9	16.2	1,40	1,23	0,80	4.2	7.4	17.5
Piperidine	2.88	59	99	164	4.3	7.3	12.0	1,57	1,30	0,59	4.7	7.8	13.0
Triethylamine	2.99	58	103	234	4.2	7.6	17.2	1,27	1,18	0,84	3.8	7.1	18.4
Tributylamine	3.11	115	186	349	8.4	13.7	25.6	3,03	2,47	1,26	9.1	14.8	27.7
Ethylendiamine	3.29[a]	8	8	8	0.6	0.6	0.6	0,20	0,10	0,03	0.6	0.6	0.6
Tripropyilamine	3.35	160	241	312	11.7	17.7	22.9	4,23	3,18	1,13	12.7	19.1	24.8
Benzylamine	4.67	13	17	28	0.9	1.2	2.1	0,33	0,22	0,10	1.0	1.3	2.2
Pyridine	8.75	24	26	28	1.8	1.9	2.1	0,63	0,35	0,10	1.9	2.1	2.3
Aniline	9.37	11	10	10	0.8	0.8	0.7	0,27	0,13	0,04	0.8	0.8	0.8
Diphenylamine	13.21	4	5	5	0.3	0.4	0.4	0,10	0,07	0,02	0.3	0.4	0.4

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

Table S3. Stabilization of Cu catalyst using stoichiometric amount of Ethylendiamine or TMEDA

Cu/en Ratio	3 h				6 h				22 h			
	V (ml)	C (%)	TOF	TON	V (ml)	C (%)	TOF	TON	V (ml)	C (%)	TOF	TON
Cu/en=1/2	60	4.4	1.57	4.7	105	7.7	1.38	8.3	234	17.2	0.84	18.5
Cu/en=1/1	121	8.9	3.20	9.6	189	13.9	2.50	15.0	299	22.0	1.08	23.8
Cu/en=2/1	59	4.3	1.57	4.7	98	7.2	1.30	7.8	223	16.4	0.80	17.7
Cu/TMEDA=1/1	70	5.2	1.87	5.6	111	8.2	1.47	8.8	224	16.4	0.80	17.7

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

Comparison of TONs with the literature

Catalyst	**TON (3h)**	**Ref**
CuI	9	*This paper*
$Cu(OAc)_2$+en (1/1)	10	*This paper*
$[Fe(BF_4)_2]\cdot 6H_2O$/ PPh_3 (no amine)	825	*Science, **2011**, 333, 1733*
$[Fe(BF_4)_2]\cdot 6H_2O$/ $2PPh_3$ (no amine)	1942	*Science, **2011**, 333, 1733*
$RuCl_2(PPh_3)_3$	905	*Angew. Chem. Int. Ed,* **2008**, 47, 3962
$Fe_3(CO)_{12}$ UV light	292	*Angew. Chem. Int. Ed*., **2010**, 49, 8993
$RuBr_3\cdot xH_2O$	1475	*ChemSusChem,* **2008**, 1, 751
$[RuCl_2(Benzene)]_2$/40 PPh_3	505	*Tetrah. Lett., **2009**, 50, 1603*