Supplementary Material (ESI) for Green Chemistry

Simple and recyclable ionic liquid based system for the selective decomposition of formic acid to hydrogen and carbon dioxide

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Supporting Information

Table of all experiments

entry	ionic liquid	Conversion formic acid [%]	(H_2) [%]	(CO_2) [%]	(CO) [%]	Yield H_2 (%)
1.1 [a]	[EMIM][NTf_2]	71	33	26	0.0	71
1.2	[EMIM][NTf_2]	4.9	4.1	3.5	0.0	4.9
2.1 [a]	[EMIM][$MeP(OMe)O_2$]	73	29	22	0.4	72
2.2	[EMIM][$MeP(OMe)O_2$]	83	32	26	0.2	83
2.3	[EMIM][$MeP(OMe)O_2$]	100	38	30	0.3	100
3.1 [a]	[EMIM][$HP(OMe)O_2$]	68	25	20	2.5	62
3.2	[EMIM][$HP(OMe)O_2$]	64	27	22	0.7	63
3.3	[EMIM][$HP(OMe)O_2$]	100	36	29	0.6	98
3.4	[EMIM][$HP(OMe)O_2$]	72	32	27	0.4	71
4.1 [a]	[EMIM][OTf]	9.1	6.8	4.9	0.0	9.1
4.2	[EMIM][OTf]	4.7	3.8	3.4	0.0	4.7
5 [a]	[EMIM][PF_6]	26	5.2	4.0	9.6	9.1
6.1 [a]	[EMIM][OAc]	59	27	16	0.0	59
6.2	[EMIM][OAc]	86	33	25	0.0	86
7.1 [a]	[EMMIM][OAc]	91	32	25	0.0	91
7.2	[EMMIM][OAc]	100	34	28	0.0	100
7.3	[EMMIM][OAc]	100	38	30	0.0	100
7.4	[EMMIM][OAc]	100	37	31	0.0	100
7.5	[EMMIM][OAc]	-	-	-	-	-
7.6	[EMMIM][OAc]	-	-	-	-	-
7.7	[EMMIM][OAc]	97	39	38	0.0	97
7.8	[EMMIM][OAc]	100	35	29	0.0	100
7.9	[EMMIM][OAc]	100	34	27	0.0	100
7.10	[EMMIM][OAc]	100	33	26	0.0	100
8.1 [a]	[EMIM][$EtSO_4$]	11	7.2	5.2	0.5	10
8.2	[EMIM][$EtSO_4$]	2.9	1.7	1.8	0.7	2.0
9.1 [a]	[EMIM][$OcSO_4$]	94	31	25	0.4	93
9.2	[EMIM][$OcSO_4$]	89	33	26	0.0	89
9.3	[EMIM][$OcSO_4$]	100	39	32	0.2	100
9.4	[EMIM][$OcSO_4$]	100	37	31	0.0	100
9.5	[EMIM][$OcSO_4$]	-	-	-	-	-
9.6	[EMIM][$OcSO_4$]	-	-	-	-	-
9.7	[EMIM][$OcSO_4$]	5.6	6.5	6.1	0.0	5.6
10.1 [a]	[EMIM][DCA]	10	2.9	9.2	3.9	4.3
10.2	[EMIM][DCA]	13	3.4	13	4.9	5.3

Reaction conditions: addition of 0.5 g formic acid before each run; reaction time 22-70 h, temperature 80°C; [a)] initial experiment: ionic liquid 3.00 g, $RuCl_3$ 2.1 mg (10.1 µmol), sodium formiate 68 mg (1mmol), formic acid 0.46 g (10 mmol); reaction time 84 h, temperature 80 °C;

Further experimental information

General reaction procedure

The reactions were carried out in steel autoclaves with a glass inlet and a total volume of 28 mL. The ionic liquid (3.0 g), formic acid (0.46 g), sodium formate (0.068 g) and the catalyst (10.1 µmol Ruthenium) were charged into the reactor. The system was purged with nitrogen and then pressurized to 12 bar. Then, the reactor was placed in a heating block and heated at the desired temperature. The reaction progress was monitored by a digital manometer. Conversion and TOF were calculated from the pressure values and the GC analysis data. For the recycling experiments, after cooling and venting, formic acid (0.50 g) was added to the reaction mixture. Then the reactor was newly purged with nitrogen and finally pressurized with 12 bar nitrogen. The reaction was re-started by switching on the heating.

Mercury poisoning experiments

The mercury poisoning experiments were conducted by variation of a standard recycling experiment. To a reaction mixture, which proved to be active in the previous run, 0.50 g formic acid and 0.30 g mercury (Hg:Ru = 150:1) were added. Then the reactor was closed and pressurized with 12 bar nitrogen and the mixture stirred at rt for 2 h. Finally the reaction was started by heating the reactor to 80°C. The recorded pressure and GC analysis showed no influence of the added mercury.

TEM sample preparation

A small droplet of the reaction mixture was placed on a carbon-film coated copper grid and then carefully rinsed with 3 ml isopropyl alcohol to remove the ionic liquid. The remaining amount of ionic liquid was checked by light microscopy. The grid was dried for 24 hours and then placed for analysis in a Philips CM 300 UT high resolution transmission electron microscope.