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Effective hydrogenation of CO_2 to formate catalyzed by ionic liquid modified acetate-Cu†

Jinling Hu,‡ Jia Liu, ‡ Chenfei Yao, Lei Zhou, Youting Wu,* Zhibing Zhang* and Xingbang Hu *

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Hydrogenation of CO_2 is challenging, especially when non-precious metals are used as catalysts. Herein, we report an effective hydrogenation of CO_2 to formate catalyzed by imidazole ionic liquid modified acetate-Cu. The catalytic ability of acetate-Cu was greatly enhanced by ionic liquid modification. The highest turnover number could reach 2005, which is 12.2 times higher than that of unmodified acetate-Cu. Besides, the ionic liquid modified acetate-Cu is easy to be recycled.

Introduction

Carbon dioxide (CO_2) is a common greenhouse gas and its emission is gradually increasing. On the other hand, artificial CO_2 conversion could produce highly valuable chemicals, which provides a chance to reduce CO_2 emission. Hydrogenation of CO_2 is becoming an important way to produce acids, esters, aldehydes, alcohols and even hydrocarbons. Of them, formic acid is an important chemical raw material, which can be used as an antiseptic, a pesticide as well as a material for tanning leather.[1] Moreover, formic acid is widely employed in synthetic chemistry as an acid, reductant, carbon source and hydrogen storage material.[2] Among these reported methods for the synthesis of formic acid, catalytic hydrogenation of CO_2 is an excellent choice because of the ready availability and low cost of CO_2,[3,4] and the excellent atom-economy of CO_2 reduction employing hydrogen. However, the activation of CO_2 is difficult due to the thermodynamic stability and kinetic inertness of the CO_2 molecule.[5]

Catalytic reduction of CO_2 with hydrogen has been widely reported using a series of metals since the pioneering work of Inoue *et al.*[6] Research studies have shown that noble metal catalysts exhibit higher activity for CO_2 hydrogenation (such as Ru,[7–18] Rh,[19–21] and Ir[1,22–27]). For example, the TON values of CO_2 hydrogenation in the presence of phosphaamidine based Rh(I)/Ru(II) complexes, Ru PNP-pincer and Ir(III)-pincer complexes are 4720, 706 500, and 3 500 000, respectively. Usually, metal-catalyzed CO_2 hydrogenation involves two steps: the splitting of H_2 by the metal center to produce a metal hydride compound, and the insertion of CO_2 into the metal hydride to produce formate.[28–31] Noble metals can efficiently activate H_2 and the noble metal based metal-hydride compound is more stable, both of which are beneficial for the CO_2 hydrogenation. However, the rarity and high cost of noble metals limit their practical applications. Though the first-row transition metals are cheaper, Earth abundant and less toxic, their catalytic activity is much low, such as iron,[32–35] cobalt,[36–40] nickel and copper.[41–44]

Copper acetate ($Cu(OAc)_2$), a commercially available cheap compound, has been reported for its ability to catalyze the hydrogenation of CO_2 to formate with a low TON (165).[42] In fact, even when a ligand with stronger electron donating ability is used, the TONs of copper based catalysts are still not high, such as a TON of 500 for the hydrogenation of CO_2 to formate catalyzed by triphosphine-ligated copper.[43] Bertrand and us developed a cyclic (alkyl)(amino)carbene copper[45] and found that a TON of 1881 can be achieved using cyclic(alkyl)(amino)carbene copper as the catalyst.[44] Though the catalytic ability of copper has been obviously enhanced, the synthesis of cyclic(alkyl)(amino)carbene is not easy, which makes this kind of catalyst expensive. Until now, it has been quite challenging to obtain easily accessed copper catalysts for the hydrogenation of CO_2 to formate.

Ionic liquid (IL) modifications are well-known as a method to make catalysts recyclable because their solubility can be adjusted by using different cation–anion combinations.[46–49] We earlier reported the structure–reactivity relationships of acetylacetone-Fe and metalloporphyrin by theoretical calculations,[50,51] which suggested a way to control the reactivity of organometallic compounds for oxidation reactions. Herein, for the first time, we found that IL modification can greatly enhance the catalytic activity of $Cu(OAc)_2$ for the hydrogenation of CO_2 to formate. The highest TON of this simple copper catalyst is up to 2005.

School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China. E-mail: huxb@nju.edu.cn, ytwu@nju.edu.cn, zbzhang@nju.edu.cn; Fax: +86 2583 336599; Tel: +86 2583 596665

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‡ These authors contributed equally.

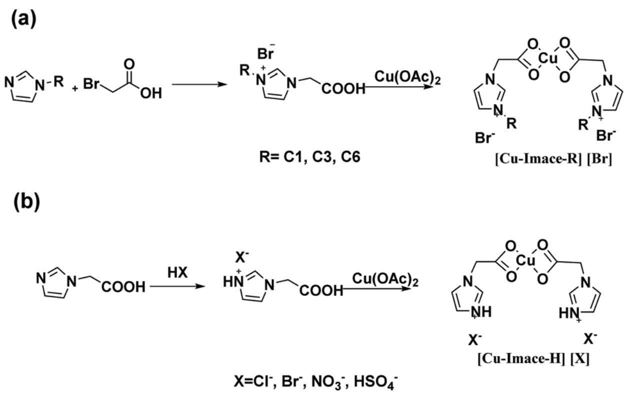
Results and discussion

Our research began with the exploration of catalysts containing different metal centers with acetate or acetylacetonate as ligands (Table 1, entries 1–10). Obviously, copper-based catalysts are more reactive than others. The TON values of $Cu(OAc)_2$ and $Cu(acac)_2$ are at least 3 times higher than those of other catalysts investigated here. After modification by ILs (Scheme 1), both the catalytic activities of $Cu(OAc)_2$ and $Cu(acac)_2$ are improved (Table 1, entries 1, 8 and 11–19). In particular, for $Cu(OAc)_2$, the influence of IL modifications is more remarkable. Further research studies were performed to synthesize $Cu(OAc)_2$ supported by imidazole ILs with different anions and R carbon lengths. Changing the carbon length of imidazole influences the TON slightly. As the carbon length increases from 1 to 6, the TON of the catalysts decreases from 420 to 352 (Table 1, entries 12–14). However, alkyl substitution on the N atom of imidazole is important for enhancing the reactivity. Changing the methyl of [Cu-Imace-C1][Br] by H results in an obvious decrease of TON from 420 to 194 (Table 1, entries 12 and 15). Changing the anion is another method to control the reactivity of these IL supported catalysts. The TON values of catalysts with different anions follow the order: [Cu-Imace-H][HSO_4] > [Cu-Imace-H][Br] > [Cu-Imace-H][Cl] > [Cu-Imace-H][NO_3] ≫ [Cu-Imace-H][BF_4]. A quite small TON was obtained for [Cu-Imace-H][BF_4] because it almost cannot be dissolved in the solvent.

Table 1 Hydrogenation of CO_2 with different catalysts[a]

Entry	Catalyst	TON[b]
1	$Cu(OAc)_2{\cdot}H_2O$	68
2	$Zn(OAc)_2$	2
3	$Fe(OAc)_2$	2
4	$Pd(OAc)_2$	20
5	$Co(OAc)_2$	<1
6	AgOAc	19
7	$Cu(OAc)_2{\cdot}H_2O/PPh_3$	32
8	$Cu(acac)_2$	97
9	$Co(acac)_2$	8
10	$Mn(acac)_3$	4
11	[Cu-ace-mim][Cl]	164
12	[Cu-Imace-C1][Br]	420
13	[Cu-Imace-C3][Br]	393
14	[Cu-Imace-C6][Br]	352
15	[Cu-Imace-H][Br]	194
16	[Cu-Imace-H][BF_4]	21
17	[Cu-Imace-H][Cl]	162
18	[Cu-Imace-H][NO_3]	122
19	[Cu-Imace-H][HSO_4]	235

[a] Reaction conditions: Catalysts (0.02 mmol), DBU (20 mmol), THF (5.0 mL), CO_2 (2 MPa), and H_2 (2 MPa), 100 °C, 21 h. [b] TON = mol formate/mol catalyst, calculated from the formate ^1H NMR integration relative to an internal standard of isopropanol.



Scheme 1 Synthesis of the catalysts.

The diversity in the reactivity of catalysts with different cations and anions should be induced by the influence of IL modification on the electrical structure of the center metal. Copper(II) has a single electron, which provides a chance to observe the influence of a ligand on its electrical structure by electron paramagnetic resonance (EPR). Based on the results of EPR (Fig. 1), it is quite clear that IL modification changes the electrical structure of copper(II) obviously. The electron arrangement around the copper of different catalysts supported by [Cu-Imace-R][Br] (R = C1, C3 or C6) is similar to each other (Fig. 1a). However, this is not the case for catalysts supported by ILs with different anions (Fig. 1b). The paramagnetic resonance varies greatly when the anion of the catalyst is changed.

To further understand the influence of IL modification on the electron structures, all the catalysts were fully optimized

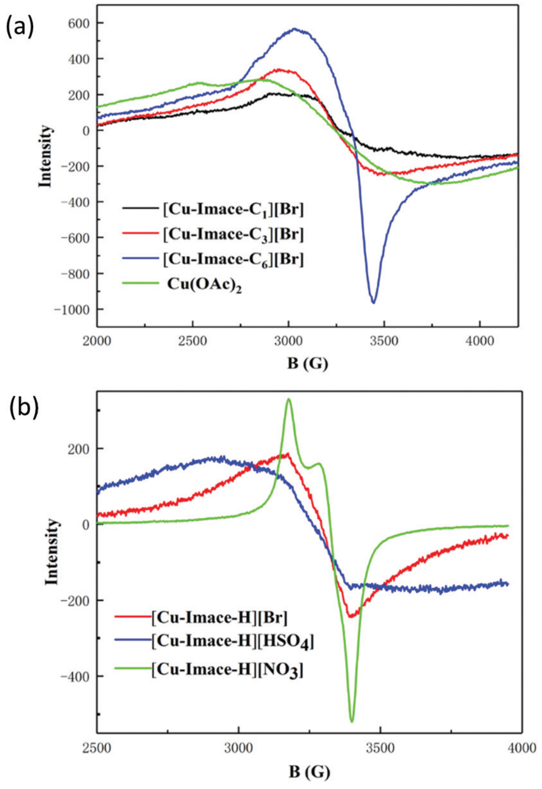


Fig. 1 (a) EPR of catalysts with different cations. (b) EPR of catalysts with different anions.

with the UM06-2X/6-311+G*/LANL2DZ method. Both the high and low spin states were taken into consideration and it was found that the low spin state catalysts were more stable. It is interesting to note that one of the anions of the IL modified catalysts binds with the copper center with a distance ranging from 1.942 to 2.457 Å (Fig. 2). In agreement with the EPR results (Fig. 1), the spin densities carried by copper of [Cu-Imace-R][Br] (R = C1, C3 or C6) are similar to each other, whereas those of [Cu-Imace-H][X] are quite different (Table 2). It should be the result of anions coordinating with copper. According to the frontier orbital theory,[52] the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is a useful structural parameter to predict the reactivity of a catalyst. A smaller gap between the HOMO–LUMO means a more reactive compound. Theoretical calculation results revealed that the HOMO–LUMO gaps of all IL modified catalysts are smaller than that of unmodified $Cu(OAc)_2$ (Table 2). In particular, [Cu-Imace-R][Br] (R = C1 and C3) has the smallest HOMO–LUMO gaps which correspond to the most reactive catalysts in the experiments (Table 1).

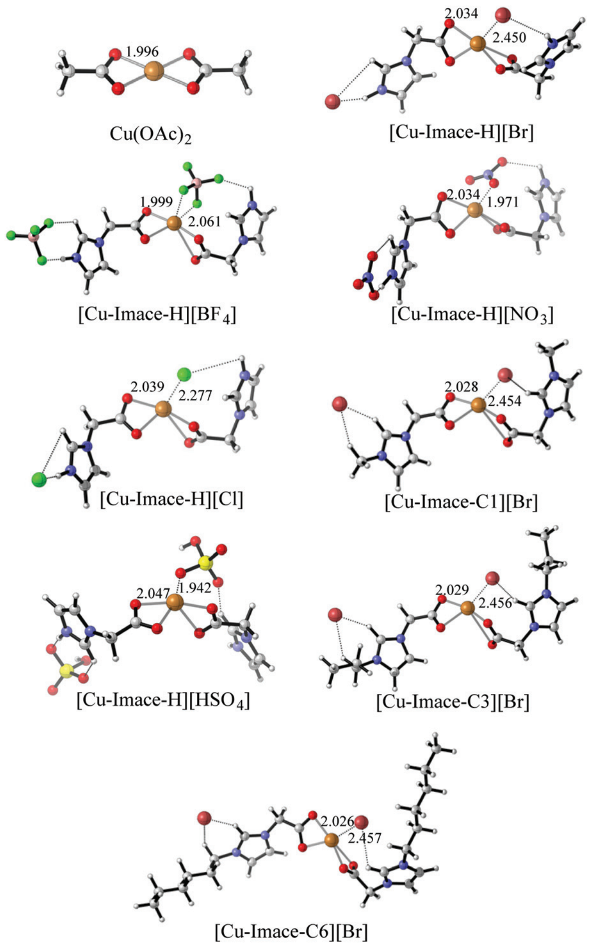


Fig. 2 The optimized structures of catalysts calculated by the UM06-2X/6-311+G*/LANL2DZ method. The shown values are bond lengths in Å.

Table 2 Some important structural parameters of catalysts

	Q_{Cu}[a]	SD_{Cu}[b]	Gap[c]
$Cu(OAc)_2$	1.247	0.637	9.815
[Cu-Imace-C1][Br]	1.281	0.660	4.638
[Cu-Imace-C3][Br]	1.315	0.663	4.753
[Cu-Imace-C6][Br]	1.327	0.664	4.849
[Cu-Imace-H][Br]	1.278	0.664	4.802
[Cu-Imace-H][Cl]	1.306	0.671	6.008
[Cu-Imace-H][BF_4]	1.473	0.726	8.350
[Cu-Imace-H][NO_3]	1.398	0.693	7.281
[Cu-Imace-H][HSO_4]	1.423	0.718	7.662

[a] The charge carried by copper. [b] The spin density carried by copper. [c] The HOMO–LUMO gap (in eV) of the catalysts.

The CO_2 hydrogenation to formic acid is thermodynamically unfavorable. Usually, organic or inorganic bases are used to react with formic acid,[7–44] which can move the unfavorable reaction towards the formation of formate. An organic base can also bind with copper(II),[42] thus, changing the reactivity of these IL modification catalysts (Table 3). The use of more basic TMG and TBD results in a lower TON (Table 3, entries 4 and 5). These results indicate that the catalytic activity is not strongly associated with the pKa of the added base.[43] Reactions using LUT or TEA gave quite low TONs. It may be the result of steric hindrance which makes the binding between LUT or TEA and the copper center difficult. Hence, the coordination of the organic base is important for the hydrogenation of CO_2 catalyzed by IL supported acetate-Cu.

According to the results listed in Table 1, [Cu-Imace-C1][Br] is the best choice from the viewpoint of reactivity. This catalyst was therefore used for further optimized experiments. With the increase of reaction temperature, the catalytic activity also improved. However, once the temperature was higher than 120 °C, the TON decreased, which is induced by the decomposition of the catalyst (Table 4, entries 1–3). Through thermogravimetric analysis (Fig. 3), it is found that the catalyst has no significant mass loss below 200 °C, which indicates that the catalyst itself is very stable at the reaction temperature. Thus, the catalyst decomposition may be attributed to the presence of reduction gas H_2 at higher temperature. A higher reaction pressure and longer reaction time are also beneficial for the

Table 3 Hydrogenation of carbon dioxide with different bases

Entry	Base[a]	TON
1	LUT	<1
2	DBN	108
3	TEA	<1
4	TMG	43
5	TBD	164
6	DMAP	20

[a] Base: DBU (1,8-diazabicyclo [5.4.0] undec-7-ene), LUT (2,6-lutidine), DBN (1,5-diazabicyclo [4.3.0] non-5-ene), TEA (triethylamine), TMG (*N*,*N*,*N*′,*N*′-tetramethyl-guanidine), TBD (1,5,7-triazabicyclo [4.4.0] dec-5-ene), and DMAP (4-dimethylaminopyridine)

Table 4 Hydrogenation of carbon dioxide under different reaction conditions[a]

Entry	Solvent	T (°C)	P (MPa)	Time (h)	TON	Con.[e]/%
1	THF	80	4	21	86	8.6
2	THF	100	4	21	420	42.0
3	THF	120	4	21	210	21.0
4	CH_3CN	100	4	21	320	32.0
5	CH_3OH	100	4	21	<1	<0.1
6	DME	100	4	21	287	28.7
7	Toluene	100	4	21	103	10.3
8	H_2O	100	4	21	2	0.2
9	THF	100	2	21	76	7.6
10	THF	100	6	21	704	70.4
11[b]	THF	100	6	48	2005	50.1
12[b,c]	THF	100	6	48	1987	49.7
13[b,d]	THF	100	6	48	1635	40.9

[a] Reaction conditions: [Cu-Imace-C1][Br] (0.02 mmol) and DBU (20 mmol). The amount of DBU is 20 mmol. [b] [Cu-Imace-C1][Br] (0.005 mmol). [c] The second run of the catalyst. [d] The third run of the catalyst. [e] Molar ratio of the product and initial DBU determined by ^1H NMR.

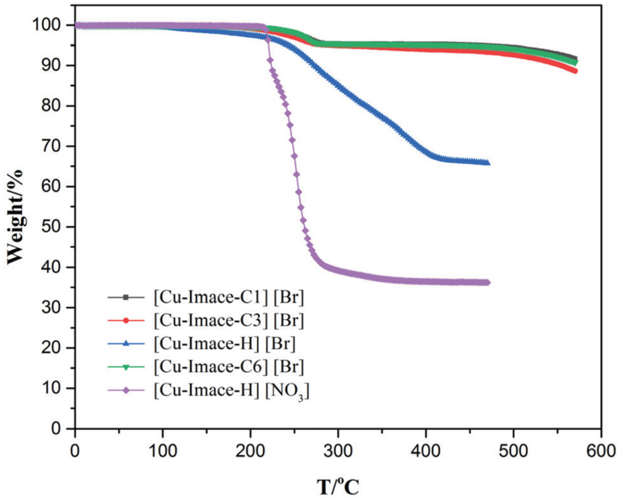


Fig. 3 TGA curves of catalysts.

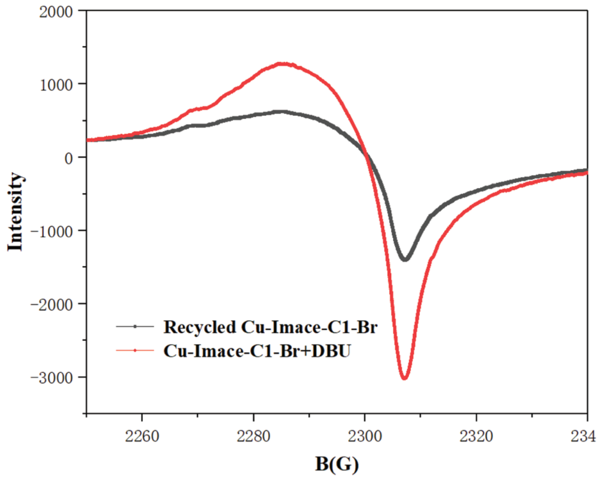


Fig. 4 EPR spectrum of the catalyst with DBU.

formation of formate. Different solvents were used in the reaction (Table 4, entries 4–10). The results suggest that protic solvents are not suitable for this reaction. Acetonitrile was earlier chosen as the solvent in the catalytic system of $LCu(MeCN)PF_6$ and an excellent result was obtained.[43] However, acetonitrile weakened the reactivity of the catalyst in our research. Using THF as solvent, a TON up to 2005 can be achieved in the presence of only 0.005 mmol of [Cu-Imace-C1][Br] (Table 4, entry 13). This TON value is far higher than that using $Cu(OAc)_2$ (TON = 165)[53] and it is also higher than that using triphosphine-ligated copper (TON = 500)[43] and cyclic(alkyl)(amino) carbene copper (TON = 1881) as catalysts.[44] In the catalyst recycling experiment, the reactivity of the catalyst decreases about 18% after three cycles (Table 4, entries 11–13). EPR results of the recycled catalyst and the new one indicate that there is no change in both the oxidation state and coordination mode of the catalyst during the reaction (Fig. 4).

As for the mechanism of this reaction, previous reports proposed a hydrogenation mechanism that involved a copper hydride generation and CO_2 insertion into the Cu–H bond.[28–31,42,54–58] To verify whether the catalytic system works according to the above-mentioned mechanism, the reactor containing the catalyst, DBU and THF was first filled with H_2 for 2 hours and then H_2 was released before it was filled with CO_2 for further reaction. Formate was obtained as the final product. Mixtures of the first step were characterized by EPR (Fig. S11†). Compared with the reference,[59] the hyperfine coupling of the EPR indicated that a copper hydride was formed in the reaction.

Conclusions

In summary, we have developed a kind of copper catalyst modified with an ionic liquid, which was efficient at the hydrogenation of CO_2. The catalyst was based on copper acetate, which is cheap and easy to obtain. The synthesis of the catalyst is simple and environment friendly. Modification by an imidazole ionic liquid can greatly enhance the catalytic reactivity of copper acetate. A TON up to 2005 can be achieved, which is obviously higher than these reported data of copper based catalysts.[42–44] The IL modification method should be applicable for other catalysts to enhance their reactivity.

Experimental

General consideration

All solvents and organic bases were dried and degassed using standard procedures. Reagents of analytical grade were obtained from commercial suppliers and used without any purification (commercially available catalysts: $Cu(OAc)_2·H_2O$, $Zn(OAc)_2$, $Fe(OAc)_2$, $Pd(OAc)_2$, $Co(OAc)_2$, AgOAc, $Cu(acac)_2$, Co $(acac)_2$, $Mn(acac)_3$, 2-bromoacetic acid and

N-methylimidazole). NMR spectra were recorded on a Bruker AV 400 spectrometer. FT-IR spectra were recorded on a Nicolet-360 infrared spectrometer. H_2 (99.999 vt%) and CO_2 (99.99 vt%) were purchased from Nanjing Tianze Gas Center, Nanjing.

Preparation of catalysts

The IL modified copper acetate ([Cu-Imace-H][X]) and copper acetylacetonate ([Cu-ace-min][Cl]) were synthesized using a similar procedure reported by us.[60,61] [Cu-Imace-R][Br] was synthesized using the processes presented in Scheme 1. The preparation of [Cu-Imace-C1][Br] was taken as an example. First, 8.2 g *N*-methylimidazole was reacted with 13.9 g 2-bromoacetic acid in 30 mL acetonitrile under reflux for 48 h. The reaction mixture was evaporated under reduced pressure at 60 °C, and a white powder was obtained. Water was used to recrystallize the powder, and pure [Imace-C1][Br] was obtained. In the next step, 2.21 g [Imace-C1][Br] was reacted with 1.99 g $Cu(OAc)_2{\cdot}H_2O$ in 50 mL water at 100 °C. The generated acetic acid was removed using water vapor. Another 50 mL of water was continuously added into the reaction system until the reaction was completed. A white power was obtained and water was used to recrystallize the powder to produce pure [Cu-Imace-C1][Br].

[Cu-ace-mim][Cl] was synthesized using a similar procedure reported by us.[60]

CO_2 hydrogenation catalyzed by different catalysts

All the catalytic reactions were carried out in an autoclave. In a typical catalytic reaction, a 50 mL stainless autoclave was charged with the catalyst dissolved in dry THF (5 mL) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 3.04 g, 20 mmol). The reactor was pressurized with 40 bar of a $1:1$ $H_2:CO_2$ mixture at room temperature and then heated and stirred at 100 °C for 21 hours. After the reactor was cooled to room temperature and vented, the mixture was dried under vacuum. The dried mixture was redissolved in 3 mL water and 0.2 g isopropanol was added as an internal standard. A volume of 100 μL aliquot was diluted in 450 μL D_2O and ^1H NMR spectroscopy was used to estimate the yield of formate.

Conflicts of interest

There is no conflict to declare.

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