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Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm
Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

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COMMUNICATION

Self-Enhancement of CO Reversible Absorption Accompanied by Phase Transition in Protic Chlorocuprate Ionic Liquids for Effective CO Separation from N_2 †

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An efficient strategy for the high-capacity capture of CO is reported, and a phase change in protic chlorocuprate ionic liquids (PCILs) from liquid to solid is found during CO absorption. The highest CO capacity is 0.96 mol_{CO}/mol_{IL}, being at least 150 times higher than that in [BMIM][PF_6]. Both absorption and membrane permeation reveal that the PCILs are potential in the selective separation of CO from N_2.

Carbon monoxide (CO) is a highly toxic gas that is completely forbidden to be emitted to the air. On the other hand, CO is widely used as material in the chemical industry (such as the famous Fischer-Tropsch synthesis, hydroformylation and carbonylation reaction, etc.) and there are a huge amount of CO generated in the industrial processes involving combustion and partial oxidation of carbon. Hence, the CO removal, recovery and storage are becoming of great concern.[1,2] Since the solubilities of CO in both polar and nonpolar solvents are extremely low,[3] unlike the treatment of acid gases (such as CO_2, SO_2, or H_2S), the widely used organic or inorganic absorbents can not work well for the separation of CO due to its neutral characteristic.[2] Until today, it is still a big challenge to control the CO emission by absorption.[1] As an alternative method, the oxidation of CO to CO_2 have been widely investigated.[4] However, this method usually requires noble metal based catalysts, and CO_2 itself is a greenhouse gas that is limited to be released to the air.[2]

Ionic liquids (ILs) have been proposed as promising green materials owing to their unique properties, such as wide liquid range, no measurable vapour pressure, tunable structure and high thermal stability.[5] It has been known that many acid gases (such as CO_2,[6] SO_2,[7] H_2S,[8] or NO[9]) have remarkable solubilities in various ILs. ILs have been thought as green solvents for the removal of these gases. However, the solubilities of CO in these known ILs are rather small.[10,11] For examples, the solubilities of CO in 37 different ILs range from 0.66×10^{-3} to 4.20×10^{-3} mol_{CO}/mol_{IL} at 22 °C and 1 bar.[11a] Even at greatly elevated pressures, the CO solubilities are still quite low in the well-known ILs (0.040 mol_{CO}/mol_{IL} in [BMIM][PF_6] at 91 bar and 20 °C,[11b,11c] 0.022 mol_{CO}/mol_{IL} in [BMIM][CH_3SO_4] at 89 bar and 20 °C,[11d] 0.026 mol_{CO}/mol_{IL} in [BMIM][BF_4] at 35 bar and 25 °C[11e]). Recent research found that the CO solubility in carbanion-functionalized IL (up to 0.046 mol_{CO}/mol_{IL} at 1 bar and 25 °C) is almost 10 times higher than that in the typical ILs (such as [Bmim][PF_6], [Bmim][CF_3COO], and [Bmim][BF_4] etc.).[12] As far as we know, this value represents the highest CO loading in ILs up to now.

CO can coordinate with transition metals through CO-to-metal σ-donation.[1,13] On this basis, ammonia-cuprous chloride aqueous solution and its modified versions have been developed and applied for CO capture.[14] However, the chemical processes using these absorbents suffer from high pollution and consumption, which does not fulfill the requirements for green chemistry. Hence, some environmentally friendly transition metal materials were developed for the seperation of CO, such as soft nanoporous crystal,[1] metal organic frameworks (MOFs),[13] alkyl-imidazolium cuprate ILs,[15] membranes,[16a-16e] and nano-gold[17]. Among these, alkyl-imidazolium cuprate ILs, as a kind of ionic liquid-transition metal hybrid materials, show improved solubilities (up to 0.156 mol_{CO}/mol_{IL} at 30 °C and 8 bar) for CO in comparison with the typical ILs (such as [BMIM][PF_6], [BMIM][CH_3SO_4], and [BMIM][BF_4] etc.).[11,15] However, the absorption capacity of these imidazolium chlorocuprate ILs is still not good enougth for industry application. Matsuda and Kitagawa et al. revealed that the structure change of a nanoporous material could bring the self-accelerating adsorption of CO to further improve the absorption capacity. However, extremely low temperature (120 K) was required for the self-accelerating adsorption.[1] Herein, we report a self-enhancement of CO adsorption at room temperature, which is accompanied by a phase transition from liquid to solid during CO absorption in protic chlorocuprate ILs (PCILs). Furthermore,

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization of PCILs, preparation of SILM and gas measurement apparatus. See DOI: 10.1039/x0xx00000x

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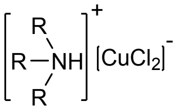
DOI: 10.1039/C9CC00089F

the supported ionic liquid membrane (SILM) impregnated with [TEA][$CuCl_2$] is tested to show good CO permeability and CO/N_2 ideal permselectivity.

The structures of PCILs are presented in Scheme 1. They can be easily synthesized by the atom-economic reaction between CuCl and trialkylamine hydrochloride (see ESI for synthesis and characterization details). [TMA][$CuCl_2$] is solid at room temperature and can not be used as absorbent. [TEA][$CuCl_2$] and [TPA][$CuCl_2$] are liquid at room temperature and have high decomposition temperature (>220 °C). At 30 °C, their viscosties are 77.9 and 214.1 mPa·s respectively (see ESI, Table S1), which are significantly lower than most task-specific ILs for the gas absorption.[2]



Scheme 1 The structure of PCILs. R=methyl, [TMA][$CuCl_2$]; R=ethyl, [TEA][$CuCl_2$]; R=propyl, [TPA][$CuCl_2$].

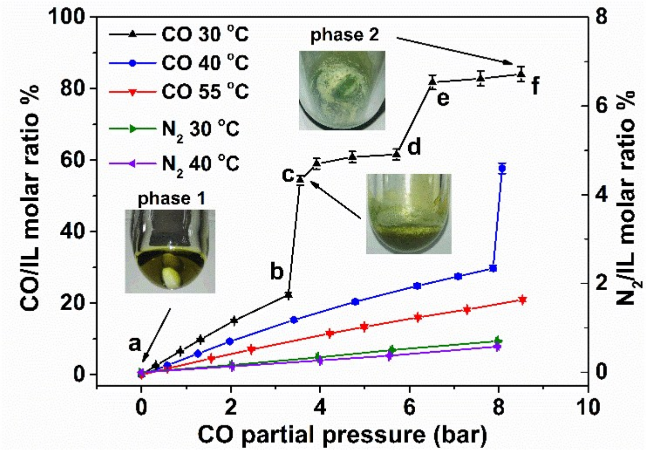


Fig. 1. Solubility of CO (left axis) and N_2 (right axis) in [TEA][$CuCl_2$] under different CO pressures and temperatures.

With the use of similar apparatus that we set up for measuring the gas solubility in ILs,[7d,8b-8e] the CO solubilities in [TEA][$CuCl_2$] were determined at different temperatures and CO pressures (Fig. 1). At 30 °C and 1 bar, a solubility of 0.078 mol_{CO}/mol_{IL} was obtained. This data is obviously higher than those obtained in other ILs at similar temperature and pressure, including classical ILs (0.66×10^{-3} to 4.20×10^{-3} mol_{CO}/mol_{IL} at 22 °C and 1 bar),[11,12] carbanion-functionalized IL (0.046 mol_{CO}/mol_{IL} at 1 bar and 25 °C), [12] and alkyl-imidazolium cuprate ILs (0.17×10^{-3} to 0.020 mol_{CO}/mol_{IL} at 30 °C and 1 bar)[12,15]. For all of the known ILs, the CO solubility increases slowly with the increasing CO pressure.[11,15] This is the same for the curve from point a to b of CO absorption in [TEA][$CuCl_2$] (Fig. 1). A quite interesting self-enhancing absorption was observed from point b to c at 30 °C. A small pressure elevation (0.265 bar) results in a transition in the CO absorption capacity (0.32 mol_{CO}/mol_{IL}) and the solubility at point c can arrive at 0.54 mol_{CO}/mol_{IL}. At the same time, [TEA][$CuCl_2$] changes from pure liquid to liquid-solid mixture (see ESI, Fig. S10). From point c to d, the curve increases slowly. The second accelerating absorption happens from d to e, and [TEA][$CuCl_2$] becomes almost solid. Being benefited from the two transitions on the absorption process, the CO absorption capacity is raised to 0.84 mol_{CO}/mol_{IL} at 8.5 bar and 30 °C. For the absorption in [TPA][$CuCl_2$], similar self-enhancing absorption of CO was also observed and the highest CO absorption capacity is 0.96 mol_{CO}/mol_{IL} (see ESI, Fig. S8). This data is 6 times higher than that in 1-hexyl-3-methylimidazolium chlorocuprate (0.156 mol_{CO}/mol_{IL} at 30 °C and 8 bar),[15a] and at least 150 times higher than that in the well-known [BMIM][PF_6] IL (6.3×10^{-3} mol_{CO}/mol_{IL} at 20 °C and 12 bar).[11b]

Even though CO absorption has been widely investigated in different ILs (including classical ILs, carbanion-functionalized IL, and alkyl-imidazolium cuprate ILs) under elevated pressures, no such phase transition and self-enhancement of CO absorption were observed.[10,11c-11e,12,15c,15d] The self-accelerating CO sorption reported by Matsuda and Kitagawa et al. was induced by the structure change of nanopores in a crystalline material at extremely low temperature (120 K).[1] Obviously, the situation in these PCILs is different. To find out more details about the phase transition and CO self-enhancing absorption in [TEA][$CuCl_2$], the fourier transform infrared spectra (FTIR), nuclear magnetic resonance (NMR), and density functional theory (DFT) calculations were investigated.

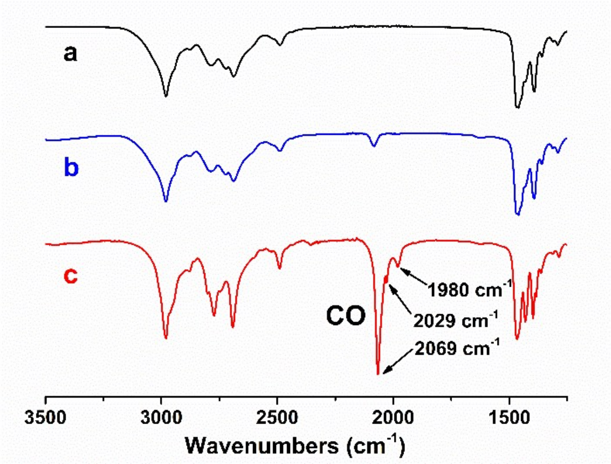


Fig. 2. FTIR spectra of (a) fresh [TEA][$CuCl_2$]; (b) [TEA][$CuCl_2$] absorbing CO at 30 °C and 1 bar; (c) [TEA][$CuCl_2$] absorbing CO at 30 °C and 8.5 bar.

The FTIR spectra before and after the absorption were presented in Fig. 2. [TEA][$CuCl_2$] absorbing CO at 30 °C and 1 bar results in a new peak at 2082 cm^{-1} which can be assigned to the stretching vibration mode of CO interacting with Cu^+ sites.[1,15d] Correspondingly, a peak at 170.0 ppm appears in the ^{13}C-NMR of [TEA][$CuCl_2$] after absorbing CO (see ESI, Fig. S9). Both the data in FTIR and NMR spectra clearly show the capture of CO in [TEA][$CuCl_2$]. For the solid obtained at point f of Fig. 1 ([TEA][$CuCl_2$] absorbing CO at 30 °C and 8.5 bar), a quite strong absorbance of CO was observed at 2069 cm^{-1}, indicating the existence of a large amount of CO. In particular,

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two new peaks appear at 2029 and 1980 cm^{-1} that can be assigned to the CO stretching vibration of $Cu(CO)_2^+$ and $Cu(CO)_3^+$.[15e,15f] This is obviously different from previous researches using compounds containing Cu^+ or Cu^{2+} as absorbents, in which only one peak of Cu(CO) was observed under a series of pressure.[1,15*d*] It is worth noticing that $Cu(CO)_2^+$ and $Cu(CO)_3^+$ carry twice and three times of CO comparing with $Cu(CO)^+$.

Theoretical calculations were further performed to investigate the structures of [TEA][Cl], [TEA][$CuCl_2$] and [TEA][$CuCl_2$] binding one to three CO (Fig. 3) (see ESI for calculation details). The calculated binding energy between [TEA][$CuCl_2$] and CO is -18.5 and -30.3 kJ/mol for 1:1 and 1:2 ([TEA][$CuCl_2$]:CO) absorption respectively, which are close to our experimental data obtained from the reaction equilibrium thermodynamic model (see ESI for details, Table S5). The calculated Cu-C_{CO} distance in [TEA][$Cu(CO)Cl_2$] is 1.915 Å, being quite close to that in the crystal of [$Cu_2(CO)(tmpn)_2PhCO_2$](BPh_4)[18]. It is very interesting to find that the binding of CO can weaken one of the Cu-Cl bond in $[CuCl_2]^-$ (Cu-Cl bond length increases from 2.215 to 3.342 Å). The Cl-H bond length becomes shorter and shorter at the same time (from 2.228 to 2.101 Å). The structures of [TEA][$Cu(CO)_2Cl_2$] and [TEA][$Cu(CO)_3Cl_2$] look more like the complexes of [TEA][Cl] and $Cu(CO)_nCl$ (n=2 and 3). The formation of [TEA][Cl] (solid) should be responsible for the phase change during CO absorption. Although $Cu(CO)_nCl$ is not stable, the formation of solid [TEA][Cl] can enwrap the complex $Cu(CO)_nCl$ and stabilize it to some extend. Increasing temperature is unfavourable for the stabilization of $Cu(CO)_nCl$ and the formation of solid. Hence, we can observe that there is no phase change and self-enhancing CO absorption at 55 °C and this phenomenon was delayed at 40 °C (Fig. 1).

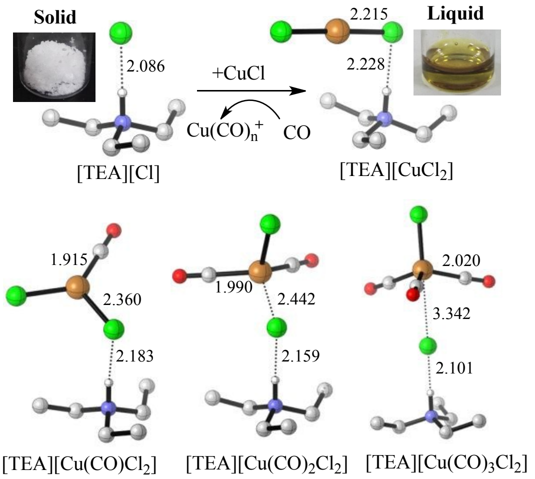

Fig. 3. The optimized structures of [TEA][Cl], [TEA][$CuCl_2$] and [TEA][$CuCl_2$] binding one to three CO. The shown values are bond lengths in Å. The actual pictures of [TEA][Cl] and [TEA][$CuCl_2$] are also shown. All hydrogen atoms of C-H are omitted for clarity. C grey, N blue, O red, Cl green, Cu brown.

Desorption or release efficiency is critical for an ideal CO absorbent or storage material. When the CO-saturated sample obtained at 30 °C and 30 bar (1.10 mol_{CO}/mol_{IL}) was kept under static condition, it needs about 3000 mins to release 95% CO (see ESI, Fig. S11a). Stirring the sample at room temperature can obviously accelerate the speed of CO releasing. The reason may be that the stirring can destroy the shell formed by solid [TEA][Cl]. The special structure of the CO-saturated [TEA][$CuCl_2$] may offer many methods to control the CO releasing speed. Among the methods investigated here, adding DMSO is the most effective one, which can release about 95% CO in 1 min (see ESI, Fig. S11d). However, this method is not recommended because it makes the recycling of [TEA][$CuCl_2$] quite difficult. Both heating and using microwave are effective methods to release CO, and the desorption can be finished in 3-5 mins (see ESI, Figs. S11b and S11c).

To testify the recyclability of PCILs for CO absorption, the multiple cycles of CO absorption/desorption were performed in both [TEA][$CuCl_2$] and [TPA][$CuCl_2$] (see ESI, Fig. S12). In each cycle, CO was absorbed at 30 °C and 8 bar, and desorbed at 80 °C and 0.1 kPa. In 5-cycle experiments, the PCILs were reused without obvious loss of absorption and desorption efficiency. In addition, there was also no obvious change in the FTIR and NMR spectra between the fresh and regenerated PCILs (see ESI, Figs. S13 and S14), indicating that [TEA][$CuCl_2$] and [TPA][$CuCl_2$] are stable during the recycling.

Because CO is the isoelectronic analogue of N_2 and they have similar molecular volume, the separation of CO from N_2 is quite difficult and full of challenge.[1] The high solubility of CO in these PCILs offer an important chance to achieve selective separation of CO from N_2. Both absorption and membrane separation were considered. The solubility of N_2 in [TEA][$CuCl_2$] at different temperatures and N_2 pressures (Fig. 1) were measured and the selectivities of CO/N_2 were calculated (ESI, Table S3). The selectivities $S_{0.9/0.9}$ (defined as the ratio of CO solubility at 0.9 bar to. N_2 solubility at 0.9 bar, similar definitions hereinafter), $S_{4.0/4.0}$ and $S_{7.0/7.0}$ are up to 94.1, 176.3 and 134.2 respectively at 30 ^oC, and the separation factor $F_{0.1/0.9}$ (defined as $S_{0.1/0.9}$/(0.1 bar/0.9 bar)) is 102.4, which shows great potential in the practical application of separating CO from N_2 through absorption process.

The remarkable solubility of CO in [TEA][$CuCl_2$] also offers us an additional opportunity to enhance the efficiency of selective membrane separation of CO from N_2. Herein, using the apparatus in our previous work for the SILMs preparation and gas permeation measurement (see ESI for details), the permeabilities of CO and N_2 as well as the ideal CO/N_2 selectivity in [TEA][$CuCl_2$] SILMs at 40 ^oC were determined (see ESI, Fig. S15). The CO permeability decreases from 178.3 to 88.2 barrers when the CO partial pressure increases from 0.05 to 0.5 bar, which is a typical feature of facilitated transport mechanism.[16*f*-16*h*] Nevertheless, the permeability of CO shows a growing trend when the CO partial pressure exceeds 0.5 bar.The CO permeability is up to 170.5 barrers when the CO partial pressure is 1.5 bar, being superior to that (37.3 barrers) in alkyl-imidazolium cuprate ILs under the same CO transmembrane pressure.[16*a*,16*b*] The permeability of N_2 in [TEA][$CuCl_2$] is 6.9 barrers, and the calculated CO/N_2 selectivity arrives at 25.1 when the CO partial pressure is 1.5 bar, which is almost 10 times higher compared to other SILMs used for the

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separation of CO and N_2 (see the comparison in ESI, Table S4).[16a,16c-16e]

In summary, we developed an efficient method for the high efficient and reversible capture of CO. During the absorption of CO in the PCILs at elevated pressures, a phase change from liquid to solid happens. As a result, up to 0.96 mol_{CO}/mol_{IL} absorption capacity was obtained, which is at least 150 times higher than that in the well-known [BMIM][PF_6] IL.[11b] The CO releases from the PCILs can be well controlled by pressure swing, temperature swing, stirring, solvent addition, or microwave radiation (releasing time: 1 to 3000 mins). These new PCILs can be easily reused without obvious loss of absorption and desorption efficiency. Compared to the well known COSORB absorbent, PCILs possess the advantage of low viscosity, large absorption capacity and organic solvent-free. In addition, these new PCILs show also great potential in the selective membrane separation of CO from N_2 that may offer a better alternative to the current methods.

Acknowledgement

This work was supported by National Natural Science Foundation of China (No.21576129, 21676134, and 21878141).

Conflicts of interest

We have no conflicts of interest to declare.

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