

Equimolar CO Capture by Cuprous-Based Quaternary Deep Eutectic Solvents

Shu-Xian Zhu,[†] Zhang-Min Li,[†] Wen-Qiang Gong, Zi-Teng Gao, Hua Guan, Ming-Shuai Sun, Yan Zhou,^{*} and Duan-Jian Tao^{*}



Cite This: *Ind. Eng. Chem. Res.* 2023, 62, 2937–2943



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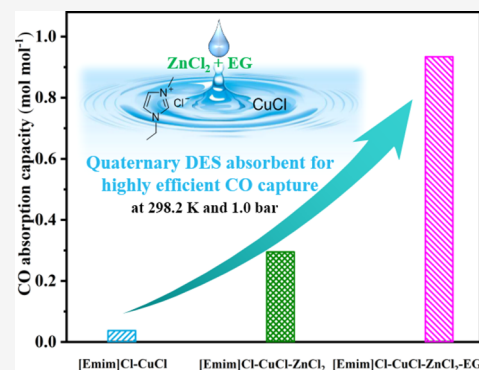


Article Recommendations



Supporting Information

ABSTRACT: Because of inefficient π -complexation of Cu^+ sites, the CO solubilities of current available cuprous-based liquid absorbents are still unsatisfied and far away from equimolar CO capture. Herein, a novel cuprous-based quaternary deep eutectic solvent (DES) was prepared and employed as a superior absorbent for equimolar CO capture. It is found that the cuprous-based quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG showed a record CO uptake capacity (0.934 mol/mol, almost equimolar CO capture) and good ideal selectivities for CO/N₂, CO/CO₂, and CO/H₂ at 1.0 bar and 298.2 K, which is by far the best liquid absorbent for efficient absorption of CO. The results of spectroscopic characterizations reveal that ZnCl₂ and EG could weaken the Cu–Cl bond to have a significant red-shift, contributing to strengthen the Cu⁺ species interacting with more CO and thereby boosting CO capacity. Additionally, the CO absorption process was completely reversible, further demonstrating the good reusability of [Emim]Cl-CuCl-ZnCl₂-EG. The cuprous-based quaternary DES thus shows good potential for efficient and selective absorption of CO.



INTRODUCTION

As a toxic gaseous pollutant, carbon monoxide (CO) is mainly generated and emitted from various tail gases such as syngas, waste gas from yellow phosphorus tails, and blast furnace.^{1,2} The traditional method for CO elimination is through the burning of the bulk of CO or being oxidized into CO₂ catalytically by noble metals. However, this treatment suffers from the drawback of a huge emission of CO₂, which has a negative impact on the environment.^{3,4} On the other hand, CO is widely used as a basic raw material for producing bulk chemicals including acetic acid, methanol, and amide.^{5,6} Thus, it is greatly significant to explore the recovery and utilization of CO from many tail gases.

Being a type of advanced solvents, ionic liquids exhibit a variety of unique properties such as tunable designability, high dissolvability, and negligible volatility.^{7–11} So far, many ILs have been reported and employed for CO absorption.^{12–18} For example, Ohlin et al.¹² used a common IL [Bmim][Tf₂N] to reach a very low CO absorption capacity of 1.25×10^{-3} mol/mol at 303.2 K and 1.0 bar. Tao et al.¹⁵ designed a kind of carbanion-based ILs for reversibly capturing CO with a capacity of 0.046 mol/mol at 298.2 K and 1.0 bar. After that, Liu et al.¹⁷ prepared the cuprous-based IL [EimH]-[CuCl₂] for CO absorption and the CO uptake capacity was 0.118 mol/mol at 1.0 bar and 303.2 K. Above progresses show that such low solubilities of CO in those ILs had been achieved so far compared with common acidic gases CO₂ and SO₂. The

development of novel absorbents for CO capture with a large uptake capacity is still challenging.

Deep eutectic solvents (DESs) containing many cations and/or anions species are analogous to ILs, which are prepared by the simple complexation of H-bonding acceptors with an H-bonding donor (e.g., polyol, amine, amide) or metal halide salt.^{19–22} In addition to having similar good properties to ILs, DESs also exhibit many promising characteristics over ILs, such as facile preparation, effortless purification, and lower costs. Recently, Tao et al.²³ have developed a cuprous-based DES [BimH]Cl-CuCl-1.0ZnCl₂ for efficiently capturing CO at high temperatures (>333 K). ZnCl₂ can activate CuCl in [BimH]Cl-CuCl-1.0ZnCl₂ to achieve a CO solubility of 0.075 mol/mol even at 353.2 K. This implies that screening and finding other DESs composed of CuCl and ZnCl₂ would have the potential for achieving a very large CO uptake capacity (i.e., ~1 mol/mol).

Herein, a novel cuprous-based quaternary DES was prepared by mixing 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), cuprous chloride (CuCl), zinc chloride (ZnCl₂), and ethylene

Received: December 25, 2022

Revised: January 19, 2023

Accepted: January 24, 2023

Published: February 1, 2023



glycol (EG) at an equal molar ratio. In comparison with the protic imidazolium IL [BimH]Cl, the cuprous-based quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG showed an outstanding thermal stability and had the ability to reversibly capture CO with a capacity as high as 0.934 mol/mol and displayed ultrahigh ideal selectivity for CO/N₂, CO/CO₂, and CO/H₂. Several characterizations further demonstrated that ZnCl₂ and EG played essential roles in strengthening the Cu⁺ species interacting with CO, leading to such excellent CO uptake capacity and outstanding ideal selectivity. In particular, the recyclability of the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG was also investigated in CO absorption and desorption cycles.

EXPERIMENTAL SECTION

Materials. 1-Ethyl-3-methylimidazolium chloride ([Emim]Cl, 99%), zinc chloride (ZnCl₂, 98%), anhydrous cuprous chloride (CuCl, 99.9%), and ethylene glycol (EG, 99.8%) were obtained from Shanghai Aladdin. The specifications of these chemicals including the CAS number, molecular weight, formula, and important impurities are also listed in Table S1 in the Supporting Information. Pure gas N₂, H₂, CO, and CO₂ (≥99.99%) were purchased from Jiangxi Huate Special Gas Co., Ltd. Other chemicals were directly used without any additional treatment.

Preparation of Cuprous-Based DESs. The cuprous-based quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG, cuprous-based ternary DES [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl (Table 1) were prepared by a simple mixing procedure.

Table 1. Cuprous-Based DESs with Different Components

DES	mole ratio			
	[Emim]Cl	CuCl	ZnCl ₂	EG
[Emim]Cl-CuCl	1	1		
[Emim]Cl-CuCl-ZnCl ₂	1	1	1	
[Emim]Cl-CuCl-ZnCl ₂ -EG	1	1	1	1

In a typical run, the raw materials [Emim]Cl, CuCl, ZnCl₂, and EG were charged at an equal molar ratio into a 25 mL glass flask in sequence. Then, the above mixture was stirred at room temperature for 1 h under N₂ protection. In the end, a quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG was obtained. The preparation of ternary DES [Emim]Cl-CuCl-ZnCl₂ and binary DES [Emim]Cl-CuCl were the same as the procedure of quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG, only excepting the use of raw materials EG and ZnCl₂, respectively.

Characterization of Cuprous-Based DESs. The measurement of a Karl Fisher titration was carried out to test the water content of these three DESs, and the water content was found to be less than 0.05%. The instruments cone-plate viscometer (Brookfield DV II + Pro) and Anton Paar DMA 4500 automatic densitometer were used to measure the viscosities and densities of cuprous-based DESs, respectively. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS SUPRA, using Al K α as the radiation source. Raman spectra were performed on a LabRAM HR spectrometer. Fourier-transform infrared (FTIR) spectra were carried out using a Nicolet 6700 spectrometer. Thermogravimetric analysis was measured using a PerkinElmer Diamond TG/DTA analyzer. Differential scanning calorimetry (DSC) analysis was recorded on a Netzsch DSC 200F3 analyzer.

Determination of CO Solubility. According to our previous work,^{17,24,25} the measurement of CO solubility was determined using a pressure drop method, which is conducted on an apparatus equipped with a dual chamber (Figure S1, Supporting Information). More details are presented in the Supporting Information. Triplicate measurements were performed to calculate an average value of CO solubility in the DES.

RESULTS AND DISCUSSION

Physical Properties of DESs. Since the density and viscosity of the fluid profoundly affect the mass transfer and diffusion rate of the gas in the solvent medium, these two physical properties of cuprous-based DESs were systematically examined. Figure 1 shows the density of the prepared cuprous-

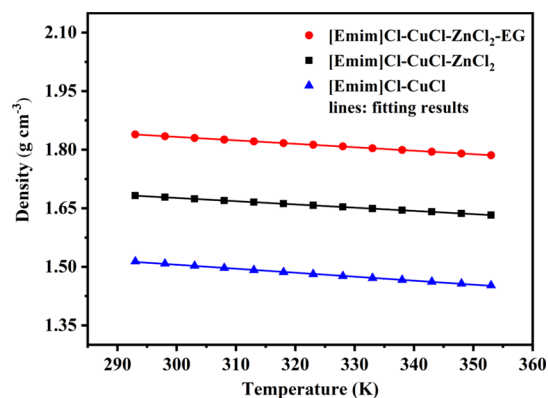


Figure 1. Densities of [Emim]Cl-CuCl, [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl-ZnCl₂-EG at different temperatures.

based DESs at the temperature range of 293.2–353.2 K. It is found that the density values of these three DESs were located between 1.40 and 1.90 g·cm⁻³ within the tested range of temperature, and a linear decrease was found for the density values as temperature increases. Also, Figure 2 shows the

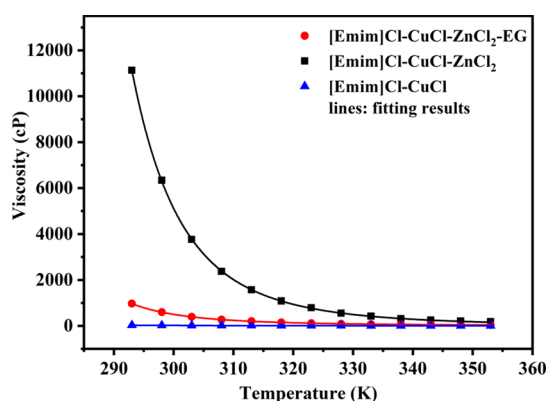


Figure 2. Viscosities of [Emim]Cl-CuCl, [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl-ZnCl₂-EG at different temperatures.

viscosity values of cuprous-based DESs at the same temperature range. The viscosity values of [Emim]Cl-CuCl and [Emim]Cl-CuCl-ZnCl₂-EG were 30 cP and 631 cP at 298.2 K, respectively, but the viscosity of [Emim]Cl-CuCl-ZnCl₂ was as high as 6343 cP at 298.2 K. This shows that the binary DES [Emim]Cl-CuCl and quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG would have relatively good fluidity for the absorption of

Table 2. Summary of CO Capture Capacities of Different Absorbents

absorbents	temperature (K)	pressure (bar)	CO absorption capacity		ref.
			mol/mol	mmol/g	
[Emim]Cl-CuCl	298.2	1.0	0.038	0.153	this work
[Emim]Cl-CuCl-ZnCl ₂	298.2	1.0	0.295	0.772	this work
[Emim]Cl-CuCl-ZnCl ₂ -EG	298.2	1.0	0.934	2.217	this work
[Emim]Cl-CuCl-ZnCl ₂ -EG	303.2	1.0	0.741	1.759	this work
[Emim]Cl-CuCl-EG	298.2	1.0	0.073	0.256	this work
[Emim]Cl-ZnCl ₂ -EG	298.2	1.0	0.001	0.002	this work
[EimH][OAc]-0.6CuOAc	293.2	1.0	0.450	1.107	18
[HDEEA][Cl] + CuCl + EG (1:1:4)	293.2	1.0	0.203	0.645	26
[EimH][CuCl ₂]	293.2	1.0	0.157	0.068	17
[P ₄₄₄₈][Pen]	298.2	1.0	0.046		15
CuCl/[Hmim]Cl	303.2	1.0	0.020		14
[TEA][CuCl ₂]	303.2	1.0	0.078		16
[Bmim][Tf ₂ N]	303.2	1.0	0.0015		12
[BimH]Cl-CuCl-1.0ZnCl ₂	353.2	1.0	0.075		23

CO. Moreover, as shown in Figure S2 (Supporting Information), the amount of EG in [Emim]Cl-CuCl-ZnCl₂- x EG ($x = 0.2, 0.4, 0.6, 0.8,$ and 1.0) had a significant effect on their viscosities. With the largest addition amount of EG among these five quaternary DESs, [Emim]Cl-CuCl-ZnCl₂-EG exhibited the lowest viscosity value of 631 cP. In addition, the density and viscosity values were regressed by linear eq 1 and nonlinear Vogel–Fulcher–Tamman (VFT) eq 2, respectively. The fitted parameters are summarized in Table S2 in the Supporting Information.

$$\rho / (\text{g cm}^{-3}) = A_1 + A_2 T / K \quad (1)$$

$$\eta = \eta_0 \times \exp(A_3 / (T - T_0)) \quad (2)$$

The thermal stability of cuprous-based DESs is also essential to the absorption of CO. The thermogravimetric curves are shown in Figure S3 in the Supporting Information. It is indicated that the starting temperatures of weight loss for [Emim]Cl-CuCl, [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl-ZnCl₂-EG were 510, 610, and 400 K, respectively. The ternary DES [Emim]Cl-CuCl-ZnCl₂ showed the best thermal stability. Also, the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG could be stable enough for the absorption and desorption of CO in the temperature range of this work. In addition, the melting temperatures of EG and [Emim]Cl-CuCl were found to be 262 and 217 K, respectively (Figures S4 and S5, Supporting Information). The glass transition temperatures of ternary DES [Emim]Cl-CuCl-ZnCl₂ and quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG were further detected at 229 and 243 K (Figures S6 and S7, Supporting Information), confirming that these two DESs like ionic liquids possess such typical thermal behavior.

CO Absorption Performance. To evaluate the CO uptake capacity of as-prepared DESs, the solubilities of CO in three cuprous-based DESs were examined at 298.2 K. The results are listed in Table 2. Surprisingly, the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG exhibited a record CO uptake capacity of 0.934 mol/mol at 298.2 K and 1.0 bar, which is significantly larger than those of [Emim]Cl-ZnCl₂-EG (0.001 mol/mol), [Emim]Cl-CuCl-ZnCl₂ (0.295 mol/mol), [Emim]Cl-CuCl-EG (0.073 mol/mol), and [Emim]Cl-CuCl (0.038 mol/mol). These results show that CuCl is the active component responsible for CO absorption. The absence of ZnCl₂ and or EG in [Emim]Cl-CuCl-ZnCl₂-EG decreased the

CO uptake capacities. It is demonstrated that ZnCl₂ and EG play important roles in the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG for promoting efficient absorption of CO. Moreover, Figure S8 (Supporting Information) shows the absorption kinetics of CO in these three cuprous-based DESs at 298.2 K and 1.0 bar. It is found that [Emim]Cl-CuCl shows the fastest CO absorption rate value of 20 min at 298.2 K and 1.0 bar, probably due to its smallest viscosity value of 30 cP (Figure 2). On the contrary, [Emim]Cl-CuCl-ZnCl₂-EG exhibited the slowest CO absorption rate to achieve such an ultrahigh CO uptake capacity, in which the equilibrium time required is at least 100 min. This suggests that the π -complexation between CO and Cu⁺ species in [Emim]Cl-CuCl-ZnCl₂-EG is relatively slow, requiring enough and long contact time. In addition, the CO uptake capacities and rates of [Emim]Cl-CuCl and [Emim]Cl-CuCl-ZnCl₂-EG were compared with those of reported ILs and DESs such as [Bmim][Tf₂N], [P₄₄₄₈][Pen], [EimH][CuCl₂], [TEA]-[CuCl₂], [EimH][OAc]-0.6CuOAc, and [BimH]Cl-CuCl-1.0ZnCl₂.^{12,14–18,23,26} As seen from Table 2, the solubility of CO in [Emim]Cl-CuCl-ZnCl₂-EG at 298.2 K was 1–2 orders higher than the cases of all the current reported absorbents. The CO absorption equilibrium time of 20 min for binary DES [Emim]Cl-CuCl was comparable to that of the reported composite IL [EimH][OAc]-0.6CuOAc. The quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG had a similar CO uptake rate of 100 min compared with [BimH]Cl-CuCl-1.0ZnCl₂.

Subsequently, the impact of temperature and pressure on the CO uptake capacity in the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG was also investigated. The results are listed in Table 2. As the temperature increased to 303.2 K, the solubility of CO in [Emim]Cl-CuCl-ZnCl₂-EG decreased slightly to 0.741 mol/mol at 1.0 bar, showing that a low temperature is positive for the absorption of CO. This is consistent with many gas absorption processes using liquid solvents in the literature.^{27–29} Figure 3 shows the CO absorption isotherms of cuprous-based DESs at 298.2 K. It is indicated that the solubilities of CO in ternary DES [Emim]Cl-CuCl-ZnCl₂ and binary DES [Emim]Cl-CuCl increased linearly with an increase of CO partial pressure. The absorption of CO in these two DESs is a physical absorption behavior. However, the solubility of CO in quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG improved significantly from 0.049 to 0.675 mol/mol with an increase in the pressure from 0.4 to 0.8 bar at 298.2 K,

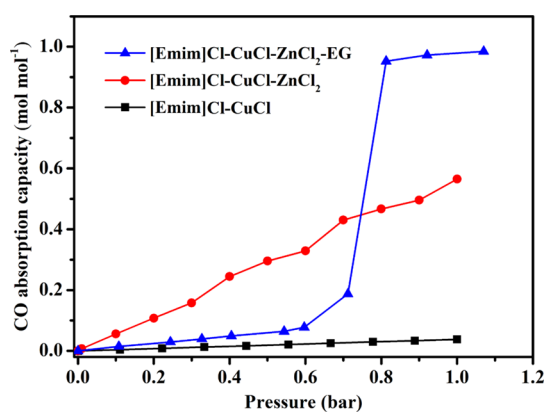


Figure 3. CO absorption isotherms of cuprous-based DESs at 298.2 K.

which strongly deviates from the linear growth. This shows that except for physical adsorption, a chemisorption interaction would take place between [Emim]Cl-CuCl-ZnCl₂-EG and CO, when the pressure increased to near 0.8 bar. The quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG could enable the Cu⁺ sites to coordinate with CO smoothly, thus making an obvious increase in CO absorption capacity. This finding is in good agreement with the self-enhancing CO absorption phenomenon in [TEA][CuCl₂] reported by Hu and co-workers.¹⁶

In the process of industry, CO is often accompanied with other competitive gases (e.g., N₂, H₂, and CO₂) and it is necessary to examine the capacity of these competing gases. Therefore, the absorption solubilities of pure N₂, CO₂, and H₂ in [Emim]Cl-CuCl-ZnCl₂-EG were measured using an intelligent gravimetric analyzer. The results are shown in Figure 4. It is found that the quaternary DES [Emim]Cl-CuCl-

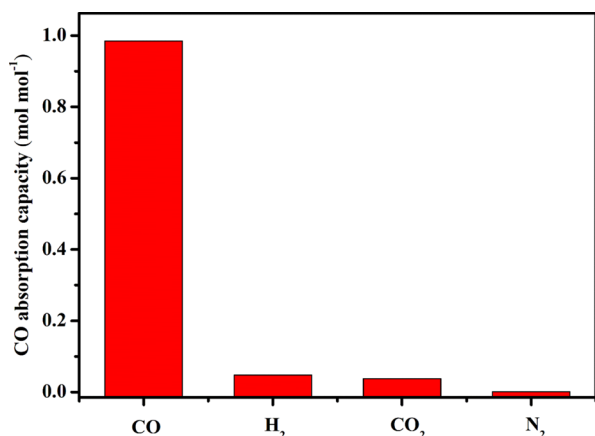


Figure 4. Absorption of CO, H₂, CO₂, and N₂ in [Emim]Cl-CuCl-ZnCl₂-EG at 298.2 K and 1.0 bar.

ZnCl₂-EG showed an extremely low capacity in the capture of pure N₂ or CO₂ or H₂ in comparison with efficient absorption of CO. The ideal absorption selectivities of CO₂/CO, H₂/CO, and N₂/CO were calculated to be 23, 18, and 943 at 298.2 K and 1.0 bar, respectively, indicating that [Emim]Cl-CuCl-ZnCl₂-EG is much better than many reported DESs or ILs in the literature.^{12–18,23,26,30,31} The quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG thus shows remarkable potential for selective absorption of CO from other competitive gases.

Mechanism of CO Absorption. To clarify ultrahigh CO absorption capacity, several characterizations of FTIR spectra, Raman spectra, and XPS spectra for cuprous-based DESs before and after CO capture were carried out. As seen in Figure 5, a new IR peak at 2105 cm⁻¹ was observed for

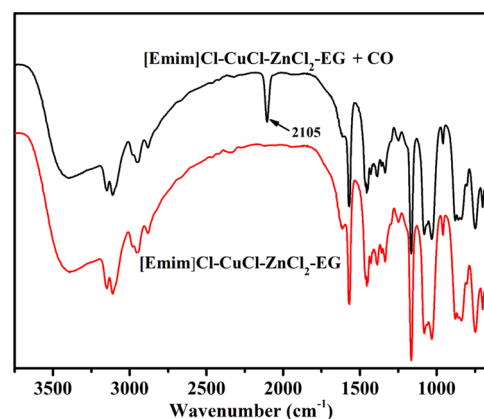


Figure 5. FTIR spectra of [Emim]Cl-CuCl-ZnCl₂-EG before and after CO absorption.

[Emim]Cl-CuCl-ZnCl₂-EG + CO, which belongs to the absorbed CO stretching vibration from the complex of Cu(CO)⁺ in the liquid phase. This observation can be verified by many previous studies,^{16–18} in which the Cu⁺ sites smoothly interacted with CO to form the complex of Cu(CO)⁺ through π complexation. Moreover, compared to the free CO (2143 cm⁻¹), the vibration frequency of captured CO from the complex of Cu(CO)⁺ in the liquid phase was obviously red-shifted, confirming the chemical interaction of [Emim]Cl-CuCl-ZnCl₂-EG with CO to form the complex of Cu(CO)⁺.^{16,18}

XPS characterization for CuCl, ZnCl₂, [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl-ZnCl₂-EG was carried out to obtain the detailed valence states of Cu and Zn elements (Figure 6). The binding energy characteristic of Cu 2p of CuCl is located at 932.5 eV. It is found that after adding ZnCl₂ alone or charging both ZnCl₂ and EG into fresh CuCl, the binding energies of Cu 2p in [Emim]Cl-CuCl-ZnCl₂ and [Emim]Cl-CuCl-ZnCl₂-EG slightly increased from 932.5 to 932.7 eV (Figure 6a). Accordingly, the binding energies of Zn 2p in [Emim]Cl-CuCl-ZnCl₂ and [Emim]Cl-CuCl-ZnCl₂-EG had an obvious decrease of 0.8 eV compared with fresh ZnCl₂. Their peaks were observed at 1022.6 eV (Figure 6b). These results clearly demonstrate that ZnCl₂ weakens the Cu–Cl bond of [Emim]Cl-CuCl-ZnCl₂-EG, and the electron deficiency of Cu⁺ species in [Emim]Cl-CuCl-ZnCl₂-EG could be more favorable for coordinating with CO through π complexation.^{32,33} This finding is in good agreement with the observation reported by Tao et al.^{17,23}

The boosting of ZnCl₂ and EG for efficient absorption of CO in [Emim]Cl-CuCl-ZnCl₂-EG was further characterized using the technology of Raman spectroscopy. It is shown in Figure 7 that a typical characteristic peak located at 297 cm⁻¹ in CuCl belonged to the stretching vibration of Cu–Cl.^{17,32} For comparison, the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG showed an obvious red-shift in the stretching vibration frequency of Cu–Cl at 282 cm⁻¹, whereas the binary DES [Emim]Cl-CuCl retained the characteristic peak at 294 cm⁻¹. Previous studies indicate that a red-shift of Raman spectra in

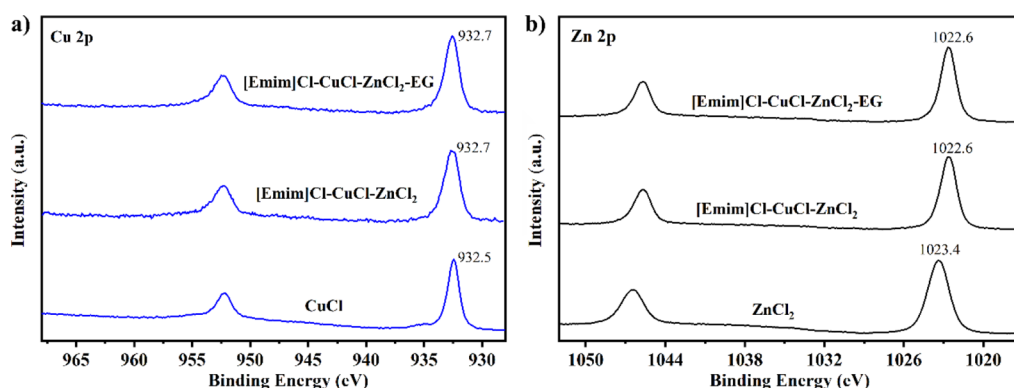


Figure 6. (a) XPS of Cu 2p in CuCl, [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl-ZnCl₂-EG. (b) XPS of Zn 2p in ZnCl₂, [Emim]Cl-CuCl-ZnCl₂, and [Emim]Cl-CuCl-ZnCl₂-EG.

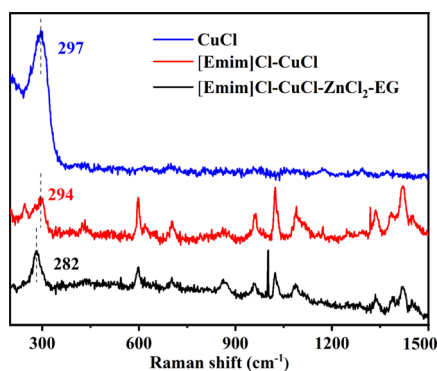


Figure 7. Raman spectra of CuCl, [Emim]Cl-CuCl, and [Emim]Cl-CuCl-ZnCl₂-EG.

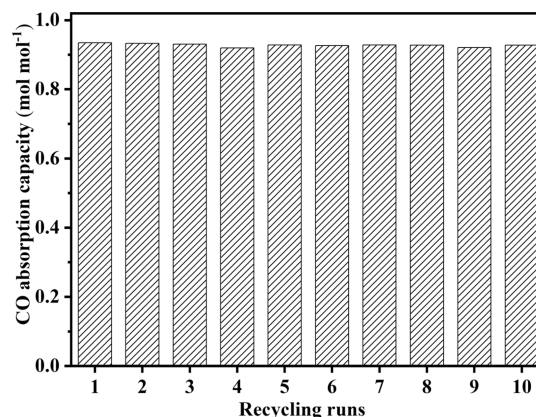


Figure 8. Reusability of [Emim]Cl-CuCl-ZnCl₂-EG in CO absorption-desorption cycles.

the Cu–Cl bond could increase the coordination number of Cu⁺ and thereby facilitate Cu⁺ coordinating with more ligand molecules.^{17,34} Thus, these results reliably verify that ZnCl₂ and EG can activate CuCl in [Emim]Cl-CuCl-ZnCl₂-EG and enable the Cu⁺ species to interact with more CO. As a result, a record CO uptake capacity of 0.934 mol/mol at 298.2 K and 1.0 bar was achieved.

Regeneration Performance. Ten consecutive experimental cycles for CO absorption-desorption were carried out to assess the recyclability and reusability of [Emim]Cl-CuCl-ZnCl₂-EG. After CO absorption, the CO-loaded [Emim]Cl-CuCl-ZnCl₂-EG was heated to 333.2 K under 0.10 bar for 20 min for regeneration. As shown in Figure 8, there is no obvious loss of CO uptake capacity during the whole absorption-desorption operation after 10 cycles, showing the highly reversible absorption of CO in [Emim]Cl-CuCl-ZnCl₂-EG. Furthermore, Figure 9 shows the FTIR spectra patterns of fresh and regenerated [Emim]Cl-CuCl-ZnCl₂-EG after 10 cycles. It is observed that the typical characteristic bands were wholly preserved, showing that [Emim]Cl-CuCl-ZnCl₂-EG is stable enough for capturing CO efficiently and reversibly.

CONCLUSIONS

Three cuprous-based DESs were prepared successfully and employed as excellent absorbents for CO capture. It is illustrated that the quaternary DES [Emim]Cl-CuCl-ZnCl₂-EG had an ultrahigh uptake capacity of 0.934 mol CO per mol of Cu⁺, as well as excellent ideal selectivities for CO/N₂ (943), CO/CO₂ (23), and CO/H₂ (18) were obtained at 298.2 K and 1.0 bar. The characterizations of FTIR spectra, Raman

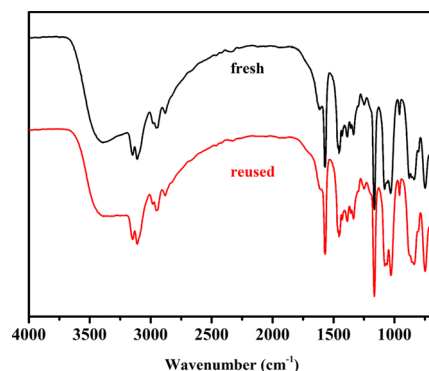


Figure 9. FTIR spectra of fresh and reused [Emim]Cl-CuCl-ZnCl₂-EG.

spectra, and XPS indicate that the obvious red-shift phenomenon of the Cu–Cl vibration caused by ZnCl₂ and EG could strengthen the interaction of Cu⁺ species with CO, resulting in the superior equimolar CO capacity. Additionally, [Emim]Cl-CuCl-ZnCl₂-EG also showed good recyclability in 10 cycles of reversible CO absorption and desorption. The cuprous-based quaternary DES shows very attractive application potential for selective absorption and recovery of CO from tail gas.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c04620>.

Apparatus and method for the determination of CO absorption (Figure S1); viscosity curves (Figure S2); thermogravimetric curves (Figure S3); DSC curves (Figures S4–S7); absorption rate of CO (Figure S8); specifications of the used chemicals (Table S1); and fitted parameters of viscosity and density (Table S2) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Yan Zhou – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China; orcid.org/0000-0003-0108-5061; Email: anitachow@jxnu.edu.cn

Duan-Jian Tao – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China; orcid.org/0000-0002-8835-0341; Email: djtao@jxnu.edu.cn

Authors

Shu-Xian Zhu – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Zhang-Min Li – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Wen-Qiang Gong – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Zi-Teng Gao – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Hua Guan – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Ming-Shuai Sun – National Engineering Research Center for Carbohydrate Synthesis, Key Laboratory of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China; orcid.org/0000-0002-5126-4159

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.iecr.2c04620>

Author Contributions

[†]S.-X.Z. and Z.-M.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundations of Jiangxi Province (20192ACBL20025) and the Key Lab of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, Jiangxi Normal University (KFSEMC-202209).

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