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CO_2 chemisorption behavior of coordination-derived phenolate sorbents

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Abstract: CO_2 chemisorption via C-O bond formation is an efficient methodology in carbon capture especially using phenolate-based ionic liquids (ILs) as the sorbents to afford carbonate products. However, most of the current IL systems involved alkylphosphonium cations, leading to sides reaction via the ylide intermediate pathway. It is important to figure out the CO_2 chemisorption behaviour of phenolate-derived sorbents using inactive and easily accessible cation counterparts without active protons. Herein, phenolate-based systems were constructed via coordination between alkali metal cations with crown ethers to avoid the participation of active protons in CO_2 chemisorption. Reaction pathway study revealed that CO_2 uptake could be achieved by O–C bond formation to afford carbonate. CO_2 uptake capacity and reaction enthalpy were significantly influenced by the coordination effect, alkali metal types, and alkyl groups on the benzene ring.

Greenhouse gas (GHG) emissions have brought serious negative impacts on the environment (e.g. global warming) and the sustainable development of the economy.[1] Among the GHGs, including carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and fluorinated gases, CO_2 is the most abundant, accounting for nearly 75% of global GHG impact.[1b, 1c, 2] CO_2 capture from flue gas by engineered chemical reactions represents a distinct category of technologies to alleviate the environmental stress arising from the utilization of fossil fuels,[3] which requires relatively less land and water compared with other natural approaches including bioenergy with carbon capture and storage, afforestation and reforestation, and enhanced weathering of minerals.[4] To date, mainly two classes of chemisorption approaches capable of achieving efficient CO_2 chemisorption have been demonstrated and extensively investigated taking advantage of the chemical reaction between basic functionalities with CO_2.[3a, 5] First, homogeneous systems such as aqueous solutions of amines, alkali metal hydroxide salts and carbonate salts have acted as the workhorse of industrial CO_2 scrubbing, which could bind CO_2 strongly, but their volatility and toxicity are incompatible with large-scale deployment, as well as their inherent drawbacks including poor thermal stability, corrosion, and high energy demand for regeneration.[6] Second, heterogeneous nanoporous materials-supported amine functionalities could address the volatility issues, but tend to have slower sorption kinetics, and their optimum performance requires the maintenance of a high surface area over multiple cycles and preventing water condensation in the pores.[1a, 3c, 7]

In the past 15 years, ionic liquids (ILs) composed of cation and anion moieties have emerged as potential candidates for CO_2 capture, separation, and conversion combining the best attributes of liquid and solid sorbents, that is, low volatility, good thermal stability, high CO_2 capacity, good CO_2 selectivity, and fast carbon capture kinetics.[2b, 5, 8] Therefore, the design and synthesis of functionalized ILs for highly efficient CO_2 chemisorption has become a hot topic.[2b] In this respect, mainly two kinds of task-specific ionic liquids (TSILs) have been demonstrated, that is, amino-based ILs and superbase-derived ILs, which can absorb CO_2 through chemical interaction between basic groups and CO_2 via the formation of C–O, C–N, and C–C bonds, affording carbonate and carbamate products.[9] For example, using commercial phenol as the starting material, TSILs towards CO_2 chemisorption could be afforded, which were composed of phenolate anions coupled with superbase-derived cations[10] or phosphonium cations with long alkyl chains.[11] In addition, physiochemical properties of the phenolate-based TSILs could be tuned by introducing various substituent groups on different positions of the benzene rings or heteroatoms within the aromatic rings, leading to tuned CO_2 chemisorption behaviors.[12] For example, fluoro-phenolate-containing ILs exhibited fairly low viscosity and fast CO_2 sorption kinetics.[12b] Reaction enthalpy of the phenolate anion with CO_2 were significantly influenced by the electronic properties of the substituents on the benzene ring, which was reflected by the CO_2 uptake capacity trend.[12a, 13] Notably, besides the carbonate formation pathway via nucleophilic attack of the oxygen anion to the electron-deficient

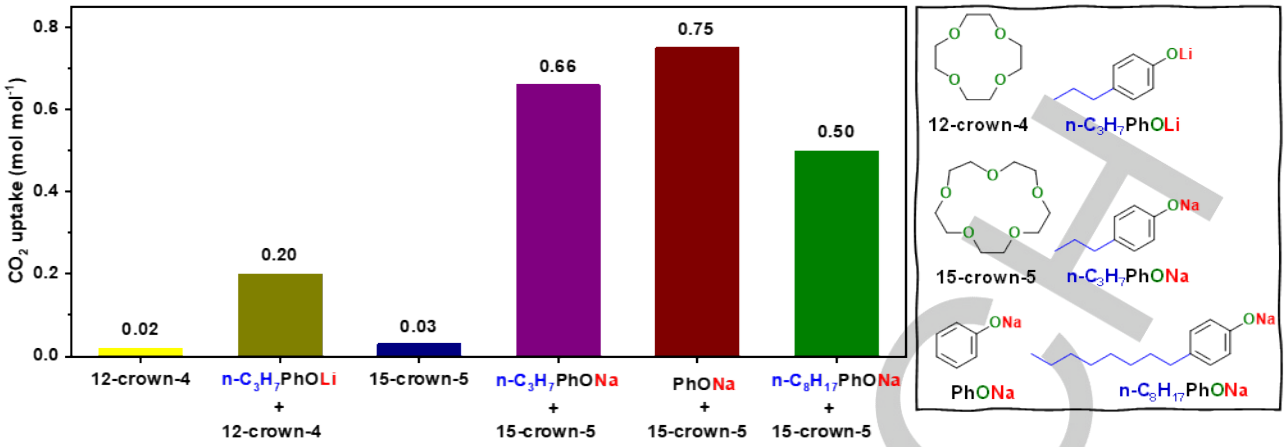

Figure 1. CO_2 chemisorption by phenolate-based sorbents composed of phenolate alkali metal salts and crown ethers (298 K, CO_2 pressure 1 bar).

carbon center in CO_2 molecule,[10-12] the work from Schneider's group demonstrated that for phenolate-based TSILs paired with alkylphosphonium cation, the oxygen atom of phenolate associated strongly with phosphonium cations and was able to deprotonate the cation to form an ylide with an affordable barrier, which could also participate in the subsequent reaction with CO_2 to form carboxylates.[14] Considering the efficient and wide applications of the phenolate-based systems in CO_2 chemisorption, it is important to figure out the CO_2 chemisorption behaviour of phenolate-derived sorbents using inactive and easily accessible cation counterparts without active protons being involved.

In this work, phenolate-based systems towards CO_2 chemisorption were constructed taking advantage of the coordination effect between alkali metal cations with crown ethers (Figure 1). Participation of active protons in the chemical reaction procedure with CO_2 could be avoided with Li^+ or Na^+ as the "bare" cations. Studies on CO_2 chemisorption behaviour revealed that CO_2 uptake could be achieved by O–C bond construction, affording carbonate as the product upon phenolate-CO_2 complex formation, as revealed by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy characterization. CO_2 uptake capacities were significantly influenced by the alkali metal-involved cations and alkyl groups being introduced on the benzene ring. Theoretical calculations proved that reaction enthalpy upon CO_2 chemisorption in the Na^+-containing system was higher than the Li^+-involved one, and it decreased by introducing alkyl substituents on the benzene ring. The results obtained herein will offer more insights into the CO_2 chemisorption behaviour of phenolate-based systems, and an alternative approach to afford efficient and stable liquid sorbents towards the separation of small gas molecules.

As previously reported, for chemical sorbents composed of basic anions and cations containing active C–H bonds, side reactions were observed during the CO_2 chemisorption processes. For example, a competing cation-CO_2 reaction channel was shown for ILs with basic azolides and alkylphosphonium cations, in which the azolide could catalyze the deprotonation of the acidic proton on the α-C of the alkylphosphonium, leading to the generation of an ylide being trapped by CO_2.[15] Imidazolium cations can also be unstable, with the acidic C_2 carbon being deprotonated by basic moieties.[16] The oxygen atom of phenolate could associate with the alkylphosphonium cations and promote its deprotonation, leading to the formation of ylides.[14] In order to avoid the influence brought on by the C–H bonds from the cations, alternative approaches should be deployed towards the construction of liquid ionic pairs composed of basic anions coupled with bare and stable cations. Crown ethers are cyclic chemical compounds consisting of several ether units, which can strongly bind certain cations to form stable complexes.[17] This offers new opportunities to design liquid phenolate-based sorbents with stable cations formed by the coordination of crown ethers with alkali metal cations. As an initial assessment, 4-n-propylphenol was taken as the starting material to afford the corresponding phenolate salts (denoted as n-C_3H_7PhOM) upon reacting with an alkali metal hydride, i.e. n-C_3H_7PhOLi and n-C_3H_7PhONa (Figure 1). The liquid sorbents were formed by simply mixing the n-C_3H_7PhOM with fitting crown ethers, herein n-C_3H_7PhOLi with 12-crown-4 and n-C_3H_7PhONa with 15-crown-5 to take advantage of the best coordination effect.[18] Then, the CO_2 uptake performance of the afforded sorbents was accessed at 298 K and 1 bar CO_2 pressure, and the results were shown in Figure 1. For the pure 12-crown-4 with only physical interaction with CO_2, a low CO_2 uptake capacity of 0.02 mol mol^{-1} was obtained. While the liquid sorbents formed by the coordination of 12-crown-4 with n-C_3H_7PhOLi exhibited increased CO_2 uptake capacity of 0.20 mol mol^{-1} phenolate salt. In addition, 15-crown-5 could afford a CO_2 uptake capacity of 0.03 mol mol^{-1}, and the CO_2 chemisorption performance was significantly increased to 0.66 mol mol^{-1} by the n-C_3H_7PhONa+15-crown-5 system. These results indicated that without the possible side reactions of ylide formation as that observed in ILs containing alkylphosphonium cations,[14] phenolate anions still possessed the ability to chemically bind CO_2, and the CO_2 uptake capacity was greatly influenced by the corresponding alkali metal cations, with n-C_3H_7PhONa more preferred than n-C_3H_7PhOLi. Other phenolate salts with Na^+ were also synthesized and used for CO_2 chemisorption after coordinating with 15-crown-5. PhONa+15-crown-5 with no alkyl group on the benzene ring showed a CO_2 uptake capacity of 0.75 mol mol^{-1}, higher than that achieved by n-C_3H_7PhONa with the n-propyl group at the para-position on the benzene ring. Further increasing the alkyl chain length to n-octyl group led to a CO_2 uptake capacity of 0.5 mol mol^{-1}. With 15-crown-5-coordinated Na^+ as the cation, CO_2 uptake capacity of the phenolate anion decreased in the following order: PhO^- > n-$C_3H_7PhO^-$ > n-$C_8H_{17}PhO^-$. Notably, the CO_2 uptake capacity achieved by the phenolate-based systems developed herein (up to 0.75 mol mol^{-1}) (Figure 1) was higher than that obtained using alkali metal chelated amines, i.e., [Li(DEA)][Tf_2N] with CO_2 uptake capacity of 0.52 mol mol^{-1} at 40 °C and 1 bar,[19] but still inferior compared with the bifunctional alkali metal chelated ILs, i.e., [$Na(DGA)_2$][Im] (1.23 mol mol^{-1} at 60 °C) and [$Na(MDEA)_2$][Pyra] (0.75 mol mol^{-1} at 80 °C) (Table S1).[20] This is caused by the different CO_2 reaction pathway and could be used to further improve the CO_2 chemisorption behavior. Although increasing the alkyl chain length on the phenolate anion somewhat led to decreased CO_2 uptake capacity, they still

owned advantages in at least two aspects. (1) During the long-term utilization of

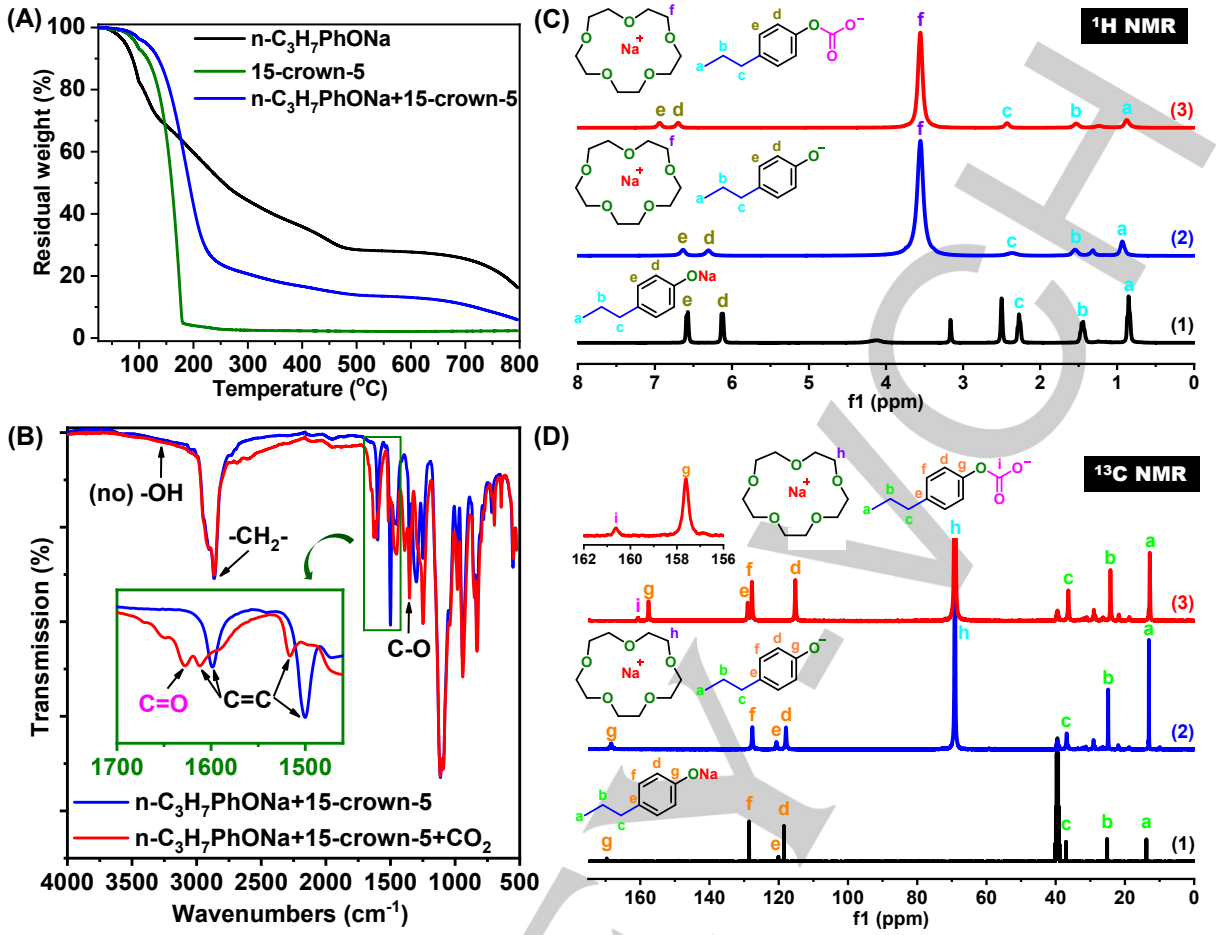

Figure 2. Characterization of the n-C_3H_7PhONa+15-crown-5 system before and after CO_2 chemisorption. (A) TGA result obtained under N_2 atmosphere with a ramping rate of 5 °C min^{-1}. (B) FTIR spectra. (C) ^{1}H NMR and (D) ^{13}C NMR spectra collected in d_6-DMSO of (1) n-C_3H_7PhONa, (2) n-C_3H_7PhONa+15-crown-5 mixture, and (3) n-C_3H_7PhONa+15-crown-5 + CO_2 mixture.

phenolate-based sorbents, oxidation of phenol to quinone is one of the possible reasons for the decreased CO_2 uptake performance,[21] with the latter having no capability to react with CO_2. While introducing substituted groups to the para-position of the -OH group on the benzene ring could inhibit such transformation and increase the stability of the phenolate-based sorbents. (2) For PhONa+15-crown-5 system, in order to get the liquid phase with relatively small viscosity, excess amount of 15-crown-5 was required (molar ratio of PhONa : 15-crown-5 as 1:5). Comparatively, after introducing alkyl chains on the benzene rings, the added amount of 15-crown-5 was significantly decreased, with molar ratio of 1:2 for both n-C_3H_7PhONa + 15-crown-5 and C_8H_{17}PhONa + 15-crown-5. In addition, the diminished CO_2 uptake capacity may be caused by the high steric hindrance endowed by introducing long alkyl chains, which influenced the coordination of the formed carbonate anion with the crown ether-surrounded alkali metal cations and excluded CO_2 molecules from the systems, as shown by the optimized structures after CO_2 chemisorption from theoretical calculation part.

Thermogravimetric analysis (TGA) results showed that the thermal stability of the n-C_3H_7PhONa+15-crown-5 mixture was clearly superior to the two starting materials benefiting from the coordination effect (Figure 2A). n-C_3H_7PhONa+15-crown-5 system before and after CO_2 chemisorption was characterized by FTIR and liquid NMR to determine the products of the phenolate-CO_2 complexes. FTIR spectra (Figure 2B) of n-C_3H_7PhONa+15-crown-5 system exhibited no signal of hydroxyl groups around 3300 cm^{-1}. Characteristic peaks for methylene groups located at 2865 cm^{-1}, which showed no variation after CO_2 capture, indicated that the n-propyl group was stable during the CO_2 uptake process. The C–O bond in the phenolate skeleton was clearly shown at 1354 cm^{-1}. Notably, after CO_2 capture, the peaks being assigned to the C=C stretch in the benzene ring blue-shifted from 1500 and 1600 cm^{-1} to 1517 and 1612 cm^{-1}, respectively, after binding with CO_2. A new peak appeared at 1629 cm^{-1}, belonging to the carbonyl group of the phenolate-CO_2 complex, which was consistent with the previously reported phenolate-based chemical sorbents for CO_2 uptake.[12a, 13] As there is no active C–H bond in the cation of the n-C_3H_7PhONa+15-crown-5 system, the product upon CO_2 capture should be carbonate. Notably, in the FTIR spectra of PhONa+15-crown-5 and n-C_8H_{17}PhONa+15-crown-5 systems before and after CO_2 chemisorption, a new peak located at 1629 cm^{-1} also appeared upon the carbonate formation (Figures S1 and S2). The structural change of the sorbents was further verified by NMR. In the ^{1}H NMR spectra (Figure 2C), compared with the n-C_3H_7PhONa salt, in which the chemical shifts of the protons on the benzene ring were 6.13 (peak d) and 6.58 ppm (peak e), these protons exhibited a downfield shift to 6.30 (peak d) and 6.63 ppm (peak e) due to the influence from the

coordination of Na^+ with 15-crown-5 and altered electronic interaction between the oxygen anion and Na^+.[22] Notably, after introducing CO_2, these protons shifted farther downfield to 6.71

Table 1. M–O bond length and reaction energy/enthalpy of phenolate-based absorbents obtained from theoretical calculation.

Entry	Absorbents[a]	M-O bond length (M=Li, Na) (Å)[b]	Reaction Energy (kJ/mol)[c]	Reaction Enthalpy (kJ/mol)[c]
1	n-C_3H_7PhOLi	1.61	-42.41	-36.27
2	n-C_3H_7PhONa	1.98	-56.35	-49.54
3	n-C_3H_7PhOLi+12-crown-4	1.80	-30.85	-25.54
4	n-C_3H_7PhONa+15-crown-5	2.22	-38.19	-30.87
5	PhONa+15-crown-5	2.16	-74.45	-69.39
6	n-C_8H_{17}-PhONa+15-crown -5	2.23	-37.96	-30.32

[a] Structures are shown in Figure 1. [b] Bond length measured in the optimized structures (Figure S4). [c] The calculations were carried out at B3LYP/6-311+G(d) level of theory with Grimme's D3 dispersion. Reaction energy and enthalpy of the absorbents with equimolar CO_2 capacity were collected and reaction shcemes were shown in Figure S5.

(peak d) and 6.94 ppm (peak e), respectively, owing to the electron-withdrawing effect of the formed carbonate species. Notably, the ^{13}C NMR spectra of n-C_3H_7PhONa+15-crown-5 exhibited significant differences before and after CO_2 uptake (Figure 2D). Besides the shift of the carbon signals of the benzene ring, a new peak located at 166.5 ppm showed up being assigned to the carbonyl group of the formed carbonate moieties, which was also consistent with what we previously obtained in CO_2 capture using phenolate-based ILs.[12a, 13] Therefore, the CO_2 chemisorption herein was achieved via the formation of carbonate from the reaction between phenolate anions with CO_2 (C-O bond formation), which is also reported in other phenolate-related absorbents including phenolic ILs with phosphonium cations,[12a] ILs with hydroxylate-containing pyridine rings,[13] phenolic ILs with various F atoms on the benzene ring,[12b] and bifunctional ILs with phenolate anion coupled with hydroxylalkylimidazolium cations.[23] A recyclability study was conducted with CO_2 desorption being performed at 55 °C under N_2 flow. The CO_2 uptake capacity could be maintained well within five successive sorption–desorption cycles using the n-C_3H_7PhONa+15-crown-5 system (Figure S3).

Theoretical calculations were conducted to figure out the influence of alkyl groups on the benzene, alkali metal cations, and the coordination effect on the CO_2 chemisorption behaviour of the phenolate-based systems (Table 1). For the optimized structures of the pure phenolate salts n-C_3H_7PhOM (M= Li, Na), the M–O distance in n-C_3H_7PhOLi was 1.61 Å, which was shorter than that in n-C_3H_7PhONa (1.98 Å), indicating that insertion of CO_2 into the less strong O-Na was more preferred. This was verified by the lower reaction energy/enthalpy of n-C_3H_7PhONa in CO_2 chemisorption compared with that of n-C_3H_7PhOLi (entry 1 vs. 2). Upon coordination with 12-crown-4, the O-Li distance increased to 1.80 Å in the n-C_3H_7PhOLi+12-crown-4 mixture (entry 1 vs. 3), and the same phenomenon was observed in the case of n-C_3H_7PhONa+15-crown-5, with the O–Na distance being increased to 2.22 Å upon coordination (entry 2 vs. 4). After coordination, the former with Li^+ center showed inferior reaction enthalpy (−25.54 kJ/mol) than the later one with Na^+ center (−30.87 kJ/mol), which was in consistency with the CO_2 uptake capacity variation (Figure 1). For sodium phenolate with different alkyl chains on the para-position of the benzene ring, the O–Na distances showed no significant change after coordination with 15-crown-5 (entries 4–6). However, the PhONa + 15-crown-5 system exhibited the lowest reaction enthalpy (−69.39 kJ/mol) compared with the other two systems with alkyl chain substitutes on the benzene ring (entries 4–6). Correspondingly, PhONa + 15-crown-5 system also achieved the highest CO_2 uptake capacity among these three (Figure 1). Therefore, for coordination-derived phenolate sorbents, the following CO_2 chemisorption behaviour could be concluded in terms of reaction enthalpy: (1) compared with the original phenolate salts, coordination with crown ethers led to decreased reaction enthalpies both for those with Li^+ and Na^+ cations (entry 1 vs. 3 and 2 vs. 4); (2) enthalpies of the Na^+-containing systems were higher than the corresponding Li^+-involved ones both in the pure phenolate salts and the liquids upon coordinating with crown ethers (entry 1 vs. 2 and 3 vs. 4); and (3) reaction enthalpy decreased upon introducing alkyl substituents on the benzene rings of the phenolates (entries 4–6). Optimized structures of n-C_3H_7PhONa+15-crown-5 system before and after reacting with CO_2 demonstrated that the Na^+ cation coordinated with the two oxygen atoms derived from CO_2 in the final carbonate product with similar Na–O distances (Figure 3). The optimized structures of PhONa+15-crown-5 and n-C_8H_{17}PhONa+15-crown-5 after reacting with CO_2 were shown in Figure S6. Notably, although some previous works studied the influence of cations in ILs on the behavior of CO_2 chemisorption, for example, introducing CO_2-philic alkyl chains (e.g., poly(ethylene glycol) moieties[24] or fluorinated structures[25]) led to enhanced CO_2 uptake. However, there is still lack of study focusing on the regulation of reaction enthalpy with CO_2 via the coordination effect from the coupled cations. The trend observed in this work may supply an alternative way to regulate the CO_2 chemisorption behavior, including the controlling over the energy requirement in CO_2 desorption, via metal-ion coordination. Similar strategies have been reported in solid absorbents composed of metal organic frameworks (MOFs) and polyamines.[1d, 1e]

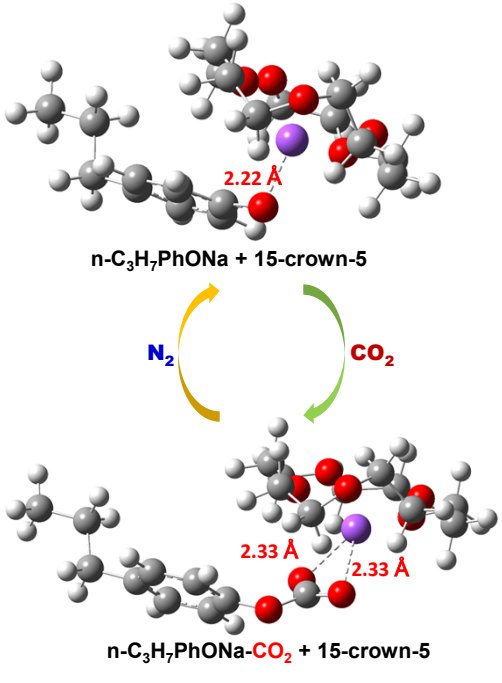

Figure 3. Optimized structures of n-C_3H_7PhONa+15-crown-5 before and after reacting with CO_2.

In summary, in order to understand the CO_2 chemisorption behaviour of phenolate-based systems and avoid the influence of cations, liquid sorbents composed of phenolate anion and alkali metal cations coordinated by crown ethers were constructed and used for CO_2 uptake. Carbonate formation upon reacting with CO_2 was detected and characterized by FTIR and liquid NMR. Experimental results together with theoretical calculations demonstrated the influence of substituted alkyl groups on the benzene ring, types of alkali metal cations, and the coordination with crown ethers on the CO_2 chemisorption behaviour. These findings will supply guidance and more opportunities for the future design of controllable and stable basic sorbents towards efficient capture and separation of small gas molecules.

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Keywords: carbon dioxide • chemisorption • crown ether • phenolate sorbents• coordination effect

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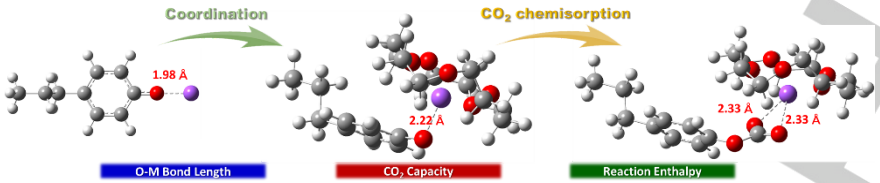

CO_2 chemisorption behavior of a phenolate-based system was studied taking advantage of the coordination between alkali metal cations with crown ethers, and regulation over CO_2 uptake capacity and reaction enthalpy was achieved by tuning the coordination effect, alkali metal types, and alkyl substituents.

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