Supporting information

Revealing how molten salts promote CO₂ capture on CaO

via impedance study and sorption kinetics simulation

Liang Huang¹, Chunming Xu², Rongzheng Ren², Qianwen Zheng¹, Zhenhua Wang²,

Benoît Louis³, Qiang Wang^{1,*}

¹College of Environmental Science and Engineering, Beijing Forestry University, 35 Qinghua East Road, Haidian District, Beijing 100083, P. R. China ²Beijing Key laboratory for chemical power source and green catalysis, school of chemistry and chemical engineering, Beijing Institute of Technology, Beijing, 100081, P. R. China

³Laboratoire de Synthèse, Réactivité Organiques et Catalyse, Institut de Chimie, UMR 7177, Université de Strasbourg, 1 rue Blaise Pascal, 67000 Strasbourg, France

Corresponding author:

Professor Qiang Wang,

College of Environmental Science and Engineering, Beijing Forestry University, 35

Qinghua East Road, Haidian District, Beijing 100083, P. R. China

E-mail: <u>qiang.wang.ox@gmail.com</u>; <u>qiangwang@bjfu.edu.cn</u>

Tel: +86 13699130626

Experimental Section

Sorbents preparation

Various types of alkali metal molten salts including chloride salts (LiCl, NaCl, and KCl), nitrate salts (LiNO₃, NaNO₃, and KNO₃), and sulfate salts (Li₂SO₄, Na₂SO₄, and K₂SO₄) were doped on commercial CaO (Xilong Scientific) via a wet impregnation method. All alkali metal salts were purchased from Sinopharm Chemical Rengent Co. Ltd. For each preparation, appropriate amounts of alkali metal salts were dissolved in 20 mL deionized water and then 2.80 g CaO was added to the solution with continuous stirring at room temperature. The resulting mixtures were dried in an oven at 120 °C overnight. Dried powders were ground in a mortar, then calcined at 750 °C for 5 h in air. The loadings of each molten salt were controlled at 10 mol%.

Characterization of sorbents

Ex-situ XRD patterns of samples were recorded on a Shimadzu XRD-7000s instrument in reflection mode with Cu K α radiation. The accelerating voltage was set at 40 kV with 30 mA current ($\lambda = 1.542$ Å) at 0.1° s⁻¹ from 5° to 65°. The morphology of samples was characterized by SEM analysis (SU8010, Hitachi) with an accelerating voltage of 5.0 kV. Powder samples were spread on carbon tape adhered to an SEM stage. Before observation, the samples were sputter coated with a thin gold layer to prevent charging and to improve the image quality. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were calculated using an SSA–7000 analyzer (Builder), measurements were performed using nitrogen adsorption at –196 °C. Prior to the analysis, ~0.1 g of sorbent was degassed at 110 °C for 4 h.

Ionic conductivity of CaO based sorbents were studied using electrochemical impedance spectroscopy (EIS) experiments and cyclic voltammetry (CV). These measurements were performed using a CHI660e electrochemical workstation (CH

Instruments Company, Shanghai, China). For each adsorbents, 0.1 g of sample powder was tableted to wafer under 15 Mpa pressure, then coated with silver paste on both sides and sticked with silver wire, before testing the sample wafer was heated to 750 °C at 5 °C min⁻¹. The equipment schematic was showed in figure S1, both ends of the sample wafer was connected with electrodes, the testing was conducted in a tube furnace to guarantee the calcination in an oxygen atmosphere, CHI660e Electrochemical Workstation and Personal Computer was used to analyze the electrical signals. Impedance spectra were obtained by applying an AC potential of amplitude 5 mV and varying the frequency from 1 Hz to 100 kHz at 600 °C under O₂ atmosphere. The conductivities were converted from the bulk resistance and the dimensions of the sample based on $\sigma = L/RA$, where σ is the oxygen ion conductivity, R is the bulk resistance, L and A is the thickness and sectional area of the pellets.¹ Bulk resistance, R was obtained from the Nyquist plots using Zsimdemo software, Cyclic voltammetry was tested at a scan rate of 100 mV/s from -1 V to 1V at 600 °C under O₂ atmosphere.



Figure S1. Diagram of electrochemical test system

Sorption experiments

Thermogravimetric sorption of CO₂ on alkali metal carbonate-promoted CaO was measured on a TGA analyzer (Q50 TA Instrument). Sorbents were first calcined in a Muffle furnace at a temperature of 750 °C for 5 h before the samples were transferred to the TGA analyzer. To avoid the error caused by the atmosphere, all samples were tested immediately after the first calcination; the sorbents were then further calcined in situ at 750 °C for 1 h in N₂ before the sorption runs were initiated. CO₂ sorption experiments were carried out at temperatures ranging from 400 °C to 700 °C under a constant flow of CO₂ (40 ml min⁻¹) and at ambient pressure (1 bar). The CO₂ capture capacity of a sample was defined as the amount of CO₂ adsorbed by 1 g of sorbent (mmol g⁻¹) after 1 h of reaction with CO₂ under the above conditions.



Figure S2. XRD patterns of (a) as-synthesized and (b) calcined 10 mol% $(Li-K)_2CO_3/CaO; (Li-K)_2SO_4/CaO; and (Li-K)Cl/CaO (\alpha, \beta, \gamma). (\blacksquare) Ca(OH)_2, (\heartsuit) CaO, (\clubsuit) alkali carbonate, (\bullet) alkali sulphate, (★) alkali chloride.$

The XRD patterns in Figure S2 (a) revealed that for all the alkali metal coated sample prepared by the wet impregnation method, the CaO phase changed to $Ca(OH)_2$ (JCPDS-04-0733) due to the presence of H₂O during preparation. Alkali metal salts was coexist and dispersed in Ca(OH)₂, the crystal structures of alkali metal salts were not

changed by the reaction with CaO and the generation of $Ca(OH)_2$, and no more production detected. Upon calcination at 750 °C in atmosphere for 5 h, the reflections assigned to $Ca(OH)_2$ disappeared and were replaced by crystalline CaO. Moreover, no other impurities were visible except alkali metal salts during the calcination process, implying a one-stage decomposition mechanism, no further reaction between CaO and alkali metal salts occurred. This XRD analysis shows a quite similar trends for these 3 lithium potassium salts, indicate that the different CO_2 uptake capacity was not due to the crystal structure of these sorbents.



Figure S3. FE-SEM images of (a) CaO; (b) 10 mol% (Li–K)Cl/CaO; (c) 10 mol% (Li–K)₂SO₄/CaO and (d) 10 mol% (Li–K)₂CO₃/CaO.

The morphologies and microstructures of CaO and coated CaO were studied by FE-SEM imaging, as displayed in Figure S3 (a-d). It is clear that the CaO grains (Figure S3a) were packed densely with small particles of smooth surfaces and an average size

of 500 nm. When stirred in a mixed alkali metal salts solution and reacted with H_2O , the CaO particles became more porous, and many pores and channels extending to the interior of the particles were created. 10 mol% (Li–K)Cl/CaO, 10 mol% (Li–K)₂SO₄/CaO and 10 mol% (Li-K)₂CO₃/CaO (Figure S3b-d) was assembled by small grains with rough surfaces and a less intertwined pore network, which likely facilitated CO₂ sorption, corresponding to the improvements of hydration. From the comparison of these FE-SEM images, it is found that the grain diameters of 3 modified CaO are similar in shape, the difference is that grain diameter for (Li–K)₂CO₃/CaO is a little smaller than the others, which corresponded well with the N₂ sorption results (Table S1). Considering that there are no futher reaction between the components, this little differentiation was resulting from the preparation process.



Figure S4. (a) N_2 adsorption-desorption isotherms for alkali metal salts; pore distribution of (b) (Li–K)Cl/CaO; (c) (Li–K)₂SO₄/CaO and (d) (Li–K)₂CO₃/CaO.

Typical BET isotherms of sorbents are presented in Figure S4a. A sharp capillary

condensation step at relatively high pressures of $P/P_0 > 0.45$ was evident in all the modified CaO. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, this adsorption–desorption isotherm showed characteristics of type-IV with a pronounced hysteresis loop, which clearly suggested its mesoporosity.² Figure S4b-d show the pore size distribution of coated CaO, the pore size peak was between 2 nm-40 nm, corresponded to the mesopores. Compared (Li-K)₂CO₃/CaO with (Li-K)Cl/CaO and (Li-K)₂SO₄/CaO, it exhibited a little increase in specific surface area and mesopore volume (Table S1) duo to its smaller grain diameters as show in SEM image, which lead to a substancial pore size distribution in 7-10 nm.

 Table S1. BET special surface area, BJH pore size and BJH pore volume for each sorbents.

sorbents	BET SSA (m ²	BJH Pore size (Å)	BJH Pore volume (cm ³
	g ⁻¹)		g ⁻¹)
(Li-K)Cl/CaO	4.28	116.6	0.035
(Li-K) ₂ CO ₃ /CaO	23.88	79.1	0.145
(Li-K) ₂ SO ₄ /CaO	6.600	105.8	0.045

Cyclic voltammetry (CV) test was conducted to explore the conductivity of each samples. Figure S5 exhibits the CV curves of bare CaO and coated CaO. Apparently, neat CaO and (Li-K)Cl/CaO show no current change between -1 and 1V, however, at the same condition, CV curve for (Li-K)₂SO₄/CaO and (Li-K)₂CO₃/CaO indicate a correlative current change along with voltage altering, indicates that (Li-K)₂SO₄/CaO and (Li-K)₂CO₃/CaO were conductive, possibly due to ionic conduction.s



Figure S5. Cyclic voltammetry curve of (a) CaO; (b) (Li–K)Cl/CaO; (c) (Li–K)2SO4/CaO and (d) (Li–K)2CO3/CaO.



Figure S6. Experimental and predicted CO₂ sorption curves for CaO and 10 mol% alkali metal salts coated CaO samples. (\Box) (Li–K)₂SO₄/CaO, (\circ) (Li–K)₂CO₃/CaO, (∇) hydrated CaO, and (\diamond) (Li–K)Cl/CaO.

To understand the detailed reaction process for CO_2 capture on neat and promoted CaO samples, the dynamic variations during the reaction of the particles with CO_2 were further examined by fitting to the well accepted double exponential model (Figure S6) as reported for other sorbents.^{3, 4} The double exponential model is:

$$y = Aexp(-k_1t) + Bexp(-k_2t) + C$$
(5)

We assume that there were two different sorption processes occur in the whole sorption process, which is an initial fast reaction controlled stage followed by a much slower state diffusion stage which was generally accepted. The FR stage is due to the surface gas-solid reaction of CO₂ with CaO, during which a thin layer of CaCO₃ formed in short periods. The following SD stage required the diffusion of CO₃²⁻ and O²⁻ ions through the previously formed carbonate layer. In equation 5, y represents the CO_2 uptake amount of sorbents in the form of millimoles per gram, t is the sorption time in minute, k_1 and k_2 are the kinetic parameters in the surface chemical reaction and bulk diffusion process, respectively. Constants A and B are the coefficient of each process that controls the whole CO_2 sorption process, and C was the y value when t tending to infinity indicates the maximum sorption capacity. The kinetic parameters obtained from the fitting are presented in Table S2, including the R^2 values. As represented by the high R^2 values, sufficiently good fitting could be obtained for all the sorption curves. In general, these results demonstrate that k_1 values (direct CO₂ chemisorption in CaO particle surfaces) are more than one order of magnitude higher than k_2 values (CO₂ chemisorption kinetically controlled by diffusion processes), this is a typical behavior observed for the CO₂ capture process in CaO sorbents at high temperatures, thus, denote that the diffusion process was the limiting process. When alkali metal salts was coated on CaO, the k values presented the following tendency. For (Li-K)Cl/CaO, both k_1 and k_2 value was much smaller than hydrated CaO, indicated that chemisorption and

diffusion process kinetically obstructed, because of its insoluble liquid layer covering the active sites. While for (Li-K)₂CO₃/CaO and (Li-K)₂SO₄/CaO, k_1 value was a little higher compared with hydrated CaO, demonstrated that the presence of carbonate/sulfate salts facilitate the carbonate formation over the particle surface. For (Li-K)Cl/CaO and hydrated CaO which didn't show O²⁻ transmittance capacity, *A* is larger than *B*, shows that diffusion stage have great influence on the overall CO₂ sorption process. By changing the coating mixtures to (Li-K)₂CO₃ and (Li-K)₂SO₄, *B* became larger than *A*, demonstrated that diffusion stage was no longer a limiting factor, chemisorption process with fast reaction rate contribute more to the total uptake capacity.

C R^2 $k_1(min^{-1})$ $k_2(min^{-1})$ В sorbents A 0.799 (Li-K)Cl/CaO 0.017 -0.438 -3.007 3.506 0.999 Hydrated CaO 1.443 0.032 -2.481 -4.755 7.050 0.997 (Li-K)₂CO₃/CaO 1.615 0.043 -8.136 -4.020 10.581 0.991 (Li-K)₂SO₄/CaO 0.033 -9.079 -4.384 0.989 1.681 11.461

Table S2. Fitted kinetic parameters for CO₂ sorption on hydrated CaO and coated CaO.

Notes and references

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