



Integrated basic treatment of activated carbon for enhanced CO₂ selectivity[☆]



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ABSTRACT

We attempted the use of three chemical agents viz nitric acid (**HN**), calcium nitrate (**CaN**) and calcium ethanoate (**CaEt**) to achieve enhanced CO₂ selective adsorption by activated carbon (AC). In dry phase treatment, microporous coconut shell-based carbon (**CS**) exhibits higher CO₂ capacity than coal-based. However, upon wet-phase pre-treatment, modified **CS** samples showed lesser CO₂ adsorption efficiency. Surface characterization with X-ray photoelectron spectroscopy confirms the presence of calcium and amine species on the samples with integrated treatment (**A-CaN**). These samples recorded the highest low-level CO₂ capture despite calcinated CaEt-doped samples (**C-CaEt**) showing the highest value for pure and high level CO₂ adsorption capacities. The slope and linearity values of isobaric desorption were used to estimate the proportion of CO₂ chemisorbed and heterogeneity of the adsorbents' surfaces respectively. Consequently, integrated basic impregnation provides the most efficient adsorbents for selective adsorption of both indoor and outdoor CO₂ levels.

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1. Introduction

Over the years, several preparation and modification approaches have been employed to enhance the efficiency of activated carbons in various applications (AC) [1,2]. With CO₂ popularly indicted to be responsible for anthropogenic global warming, its source-reduction and containment have sufficed as major ways to attenuate present change in climate [3–5]. CO₂ adsorption on porous materials, for effective capture and temporal storage has therefore become of interest. The use of AC prepared with different agents under various conditions has been reported [6–13]. Intrinsically, AC has high potential for adsorbing fluids by physisorption, by virtue of its extremely high surface area achieved by its intensely developed pore structure. However, the levels at which CO₂ is often present in our environment is much lower, i.e. about 0.04–0.3% (ranging from unpolluted to subway spaces) and 4–15% (flue gases of power stations) for indoor and outdoor, respectively [14,15], hence the selectivity of prepared or modified AC towards CO₂ in these trace and lower-major levels determines its applicability to environmental use. Many researchers have published works on the preparation of adsorbents with various

excellent capacities for pure CO₂ feed. However, to an environmentalist, such adsorbents are of no relevance, except their reported efficiencies quantitatively indicate their selectivity towards CO₂ in both indoor and outdoor levels.

The effect of dry phase pre-oxidation prior amination of AC has been experimented and found to promote CO₂ selectivity by chemisorption [16–21], even though the impregnation method often lead to reduction in pure CO₂ adsorption capacity due to blockage and distortion of micropores. HNO₃ is one of the mineral impregnants that have proven to be efficient wet oxidants in inducing large amount of surface oxygen functionalities (SOFs) on ACs [22–25]. However, it has not been investigated if such prowess is based on the acidity (H⁺) or the nitrate's oxidation potential. Also, no work has reported its use in incorporating SOFs that enhance amination by creating specific surface nitrogen functionalities (SNFs) with significant affinity towards Lewis acid gases such as CO₂.

We therefore attempt to modify commercially available AC by thermal treatment methods after wet pre-treatment, in order to enhance the selective adsorption of CO₂ for both indoor and outdoor levels. This was investigated and reported in current work.

2. Experimental

2.1. Materials

Commercially available coconut shell (WSC-470) and coal (WS-490) based AC, procured from Calgon Carbon Corporation, USA were used as starting materials. Specific surface area (*S_{BET}*) [26]

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and pore size distributions [27,28] were determined with the use of Belsorp II mini, supplied by BEL Japan, Inc. Ultimate analysis was carried out with an automatic elemental analyzer, Flash EA 1112 (CE) while K-Alpha (Thermo-electron) X-ray photoelectron spectrometer was employed to quantitatively identify the chemical functionalities present. Thermogravimetric analyzer (TGA) STA N-1000, acquired from SCINCO, Korea, was used to determine the ambient CO₂ capture capacity and also to carry out isobaric desorption of CO₂ laden adsorbents.

2.2. Methods

2.2.1. Sample pretreatment

As-received pellets, partially ground and characterized between 2 and 1 mm, were copiously washed with deionized water, filtered and dried at 120 °C for 24 h. Pre-cleaned granules were then cooled, bagged and name-tagged **CS** and **CL**, used as raw coconut shell-based and coal-based ACs (RACs), respectively.

Samples of 2 M HNO₃, 1 M, each of Ca(NO₃)₂ and Ca(CH₃COO)₂, were prepared and, respectively, referred to as **HN**, **CaN** and Ca(Et)₂ hereafter, in sample identification. A solution of 2 M HNO₃ was related to 1 M of Ca(NO₃)₂ to relatively obtain equal amount of moles of nitrate ($n\text{NO}_3^-$) in both agents, whilst $n\text{Ca}$ in Ca(NO₃)₂ and Ca(Et)₂ was also assumed equal. Table 1 summarizes sample pretreatment procedures employed.

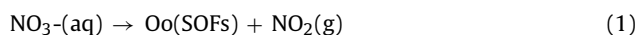
After pretreatment, the samples were copiously washed with deionized water and filtered under vacuum before drying at 120 °C for 12 h. They were retrieved, cooled in a electric desiccator prior thermal treatments at 800 °C.

2.2.2. Heat treatment of pre-treated samples

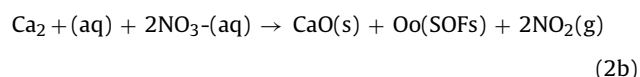
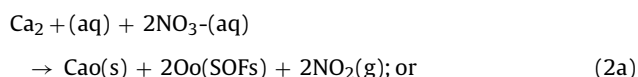
An amount of 15 g treated sample was introduced into quartz reactor, placed in a vertical furnace and ramped up to 800 °C at 6.5 °C/min under N₂ atmosphere. It was kept at this temperature for 2 h under NH₃ flow for amination (**A**) while the N₂ flow was unchanged for calcination (**C**). After the soaking period, the furnace cools to 100 °C. Further cooling to room temperature was carried out under N₂ flow.

Prepared adsorbents were then retrieved and outgassed at 120 °C under mild vacuum condition for 2 h. Cooling and preserving each sample then followed as described in Section 2.2.1. The envisaged reaction mechanisms that ensued in the treatment processes are expressed in Eqs. (1)–(3).

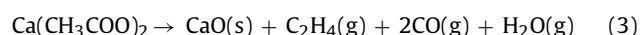
(i) Surface oxygen functionalities (SOFs) incorporation by HNO₃



(ii) Simultaneous impregnation of calcium and SOFs by Ca(NO₃)₂



(iii) Calcium impregnation with Ca(Et)₂ (calcination)



2.2.3. pH_{pzc}

In order to determine carbon's surface pH at point of zero charge, six solutions of 0.1 M KNO₃ with initial pH values (pH_i) of 2, 4, 6, 8, 10 and 12 were prepared with dropwise addition of 0.05 M solutions of HNO₃ and KOH, limiting the ionic content to H⁺, K⁺, OH[−] and NO₃[−] [29,30]. Aliquots of each pre-treated adsorbent was added to each solution and agitated for 24 h, before the final pH (pH_f) was measured.

A plot of pH_f against pH_i was made and the observed plateau along the pH_i axis represents the pH_{pzc}.

2.3. CO₂ adsorption test

The eventual test on the prepared adsorbents was the determination of CO₂ adsorption capacities, carried out with the aid of BelsorpII mini and TGA. At room temperature, the monosorp instrument enabled the measurement of absolute adsorption capacity (q_{abs}), i.e. from subnormal pressure of 0 to 1 atm as samples were outgassed to a vacuum state prior measurement, while the TGA was used to determine adsorption capacity at ambient pressure (q_{amb}). For environmental applicability, selectivity tests were carried out to determine the adsorption efficiency for high (10%) and low (0.3%) CO₂ levels. The matrices of the CO₂ feeds were conditioned to mimic outdoor and indoor air respectively. CO₂ isobaric desorption at 120 °C, was carried out on selected samples in order to estimate the rate and ease of CO₂ desorption.

3. Results and discussion

3.1. Textural examination

In order to determine changes in textural properties brought about by the surface treatments, the S_{BET} and porosity of test samples were assessed and reported in Table 2. Pretreatment brought about decrease in S_{BET} with varying degrees of pore modification with respect to the carbon precursor. Both carbon types showed similar depreciation in S_{BET} when pre-oxidized with HNO₃, as Ca(NO₃)₂ showed more etching effect than Ca(Et)₂ on **CL**. The reverse was observed with **CS**, as Ca(Et)₂ brought about the most significant deterioration in textural properties, although there was no evident changes in the average pore size ($Av.dp$) for all samples. It is opined that the differences in the effect of the solutions on the carbon types could be better understood with results of volatile (%V.C) and ash contents (%A.C) obtained from proximate analysis.

Table 1
Procedures for preparation of impregnants and pre-treatment.

RAC	Agent	Preparation of impregnant	Impregnation method	ID
RAC granules (CS, CL)	HNO ₃ (HN)	500 mL of 2 M HNO ₃ was prepared. Used after 1 h	100 mL of agent was added to 20 g of RAC. Agitation at 100 rpm for 3 h in a defrosted environment followed	HN-CS; HN-CL
	Ca(NO ₃) ₂ (CaN)	Dissolution in water and gentle stirring for 1 h. Make up to 500 mL mark while stirring. Use after 1 h		CaN-CS; CaN-CL
	Ca(Et) ₂ (CaEt)	Dissolution in water and gentle stirring for 2 h. Make up to 500 mL mark. Further 3 h stirring, filter and use at once	100 mL of agent was added to 20 g of AC in a pirex bottle and capped. It was agitated at 150 rpm for 5 h in a defrosted environment	CaEt-CS; CaEt-CL

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