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CO_2 adsorption over modified AC samples: A new methodology for determining selectivity

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ABSTRACT

Activated carbon (AC) based adsorbents having high and stable CO_2 adsorption capacity with enhanced CO_2 selectivity in presence of CH_4 were developed. Alkali modified AC samples were prepared, their CO_2 adsorption capacities were measured, a new methodology for selective adsorption capacity determination under multi-component gas mixture flow was developed, and the results were analyzed to determine the preparation procedure yielding optimum adsorbent design. Two groups of adsorbents were prepared by K_2CO_3 impregnation on air and HNO_3 oxidized forms of a commercial AC followed by calcination at various temperatures. The resulting adsorbents were named according to calcination temperatures as AC*x*K-calT. The highest CO_2 adsorption capacity was measured on AC3K-300 sample as 110 mg/g adsorbent at 1000 mbar CO_2 and 25 °C. CO_2 adsorption was confirmed reversible, whereas CH_4 adsorption was found partially irreversible. The highest mass based CO_2:CH_4 selectivity, ca. 3.7, was achieved over AC2K-200 at 25 °C for the 50%CO_2-50%CH_4 mixture. AC2K-200 was further tested at higher total pressures, for 0–5000 mbar pressure range, at 25 °C. CO_2 adsorption capacity was measured as 197 mg/g adsorbent at 5000 mbar CO_2. Among Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models, D-R was found to be the most successful one explaining CO_2 adsorption behavior of AC samples.

1. Introduction

Presently 85% of the total energy requirement of the world is supplied by fossil fuel based power production plants (coal, oil, gas), which are responsible for 40% of CO_2 emission into the atmosphere. Since anthropogenic production and atmospheric accumulation of CO_2 is the main reason for global warming and climate change, its capture, sequestration and utilization (CCS & U) is one of the most challenging issues of environmental sustainability. As CCS is an expensive process, cost effective CCS options need to be developed and proliferated [1].

CO_2 emission mitigation in power plants can be accomplished through post-combustion, pre-combustion and oxyfuel-combustion [2]. Among the available capturing methods involved in all those technologies, adsorption has been considered as the most promising owing to its low energy requirement led by the exothermicity of the process, cost advantage and ease of applicability over a relatively wide range of temperatures and CO_2 partial pressures. An efficient adsorbent must have high adsorption capacity, selectivity towards CO_2, fast adsorption and desorption kinetics, good physical and chemical stability, and regenerability by modest pressure and temperature to minimize operational energy costs [3].

Current potential adsorbent materials for CO_2 capture are carbon materials such as carbon molecular sieves, carbon nanotubes, and activated carbons (ACs), zeolites and metal organic frameworks [4]. AC is the most preferred adsorbent in industries due to its low cost, high surface area, high porosity, adequate mechanical strength after repeated adsorption and desorption cycles and high CO_2 adsorption capacity at ambient pressure and temperature.

ACs originate from different carbonaceous materials like bituminous coal, petroleum/coal tar pitch, nutshell, coconut husk, wood and lignite, and are activated with different procedures, such as CO_2 activation, steam (physical) activation or chemical activation via oxygenation, nitrogenation, hydrogenation, etc. agents. Depending on the origin and preparation method, adsorption capacity is highly affected by the surface chemistry and pore structure [5].

Various basic groups are incorporated on AC aiming to increase the CO_2 adsorption capacity via enhancing CO_2 affinity [6]. Introduction of Lewis bases onto AC surfaces may increase the capture performance due to mildly acidic nature of CO_2. There are several ways of increasing the basicity of AC including removal/neutralization of the acidic

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Nomenclature

b	Langmuir equilibrium canstant ($mmHg^{-1}$)
calT	Calcination temperature (°C)
E	Characteristic energy of the system (J/mol)
k	Fruendlich model parameter
m	Mass of adsorbant (g)
n	Fruendlich model parameter
P	Pressure of adsorbate (mmHg)
P_s	Saturation pressure (mmHg)
P_T	Total pressure (Torr)
P_1	Partial pressure at time t_1 (Torr)
P_2	Partial pressure at time t_2 (Torr)
$P_2^{'}$	Maximum partial pressure signal value obtained in adsorption test (Torr)
P_1^{*}	Normalized partial pressure at time t_1
P_2^{*}	Normalized partial pressure at time t_2
Q	Adsorbed amount (mmol/g adsorbent)
Q_m	Theoretical monolayer adsorption capacity (mmol/g adsorbent)
R	Universal gas constant (R = 8.314 J/mol K)
t_1	Initial time (min)
t_2	Time at partial pressure signals stabilized (min)
$t_2^{'}$	Time at maximum partial pressure signal value obtained in adsorption test (min)
T	Temperature (K)
ν	Volumetric flow rate (ml/min)
V_{raw}	Raw adsorbed volume (ml)
W	Adsorbed amount (cc/g)
W_0	Micropore capacity (cc/g)
x	Mass of adsorbate (g)

Subscripts

b	Blank test
X_n	Gas species n

functionalities through introduction of oxygen containing surface groups, and replacing acidic groups with proper basic ones having nitrogen functionalities [7,8]. Ammonia treatment is considered to be an effective way of adding nitrogen functionalities to AC surface. The studies [9–11] showed that ammonia addition integrated with a thermal treatment considerably enhanced CO_2 uptake of the AC based adsorbents.

Another prominent method to enhance the CO_2 adsorption capacity is promoting the AC surface through chemical impregnation of alkali species. Improved CO_2 adsorption capacities were reported upon NaOH, MgO, CaO and Na_2CO_3 impregnation for carbon based adsorbents [12–14]. Caglayan and Aksoylu [14] reported the enhancement of CO_2 adsorption capacities of air oxidized and nitric acid oxidized AC samples impregnated with Na_2CO_3 by 15 and 16 folds, respectively, compared to their pristine forms. Somy et al. [15] reported a 25% increase in CO_2 adsorption capacity upon impregnation of Cr_2O and Fe_2O_3 followed promotion by Zn^{2+}. Guo et al. [16] reported a novel PEI-K_2CO_3/AC sorbent with a retained CO_2 capture capacity of 3.42 mmol CO_2/g after 5-cycle-adsorption-desorption tests. In another study [17], cation (K, Li, Ca, Mg) impregnated AC based sorbents were reported to show higher adsorption capacities than the raw AC.

Selective CO_2 removal from a gas mixture is required in different industrial purposes [18–23], such as the removal of CO_2 contamination from natural gas to produce LNG, and separation of CO_2 from the other gases in the flue gas of a power plant. Hence, studies in literature focus on effective adsorbent design for selective CO_2 adsorption from flue gas, and determination of CO_2/CH_4 and CO_2/N_2 selectivities of the adsorbents. Shen et al. [20] reported the adsorption capacities of 1.918 mol/kg for CO_2 and 0.270 mol/kg for N_2 at 30 °C and 100 kPa on pitch based AC beads. Gil and co-workers [21] reported the mole based CO_2/CH_4 selectivity of 4.26 on AC prepared from Novolac phenol-formaldehyde resins and olive stones. Lopes et al. [22] provided the adsorption capacity sequence as $H_2O > CO_2 > CH_4 > CO > N_2 > H_2$ on activated carbon extrudates for the pure gases in a steam methane reforming off-gas. Guo et al. [23] reported the capture capacity of 64.75 mg CO_2/g adsorbent for pure CO_2, 38.58 mg/g for binary mixture of N_2-CO_2 (99:1), and 64.74 mg/g ternary mixture of N_2-CO_2-H_2O (97:1:2) on K_2CO_3/AC.

The purpose of the current study is to design and develop AC-based adsorbents having both high and stable CO_2 adsorption capacity, and ability to adsorb CO_2 selectively from CO_2-CH_4 mixture. In this context, a new methodology for the determination of selective CO_2 adsorption capacity of the AC-based adsorbents under multicomponent gas mixture flow was developed and elucidated. The methodology utilizes gravimetric analyzer-mass spectrometer data and enables adsorption capacity and isotherm model constant calculation for each species under binary, ternary or multicomponent flows. Air and HNO_3 oxidized AC adsorbent series, AC2K-calT and AC3K-calT respectively, were prepared by K_2CO_3 impregnation followed by calcination at various temperatures. The adsorbent samples were characterized by SEM-EDX in order to analyze their microstructural properties and alkali dispersion on their surface, and tested for their adsorption and selective adsorption performances via using gravimetric analyzer-mass spectrometer measurement system.

2. Experimental

2.1. Adsorbent preparation and characterization

The modified AC based adsorbents used in this study were prepared via different oxidative, alkali and thermal treatments applied on a commercial AC (NORIT ROX 0.8). In preparation of AC1, AC pellets were crushed and sieved into 354–250 μm (45–60 mesh) particle size (AC0) first. Then, 20 g AC0 was treated with 2 N HCl solution under total reflux for 12 h to remove some ash and sulfur content. In order to remove the remaining HCl from the AC surface, the samples were washed with deionized (DI) water under total reflux for an additional 6 h. Finally, the slurry was dried at 115 °C overnight.

AC2 was prepared by oxidizing 10 g AC1 in a quartz down flow reactor in a tube furnace under the flow of 10 ml/min O_2–190 ml/min N_2 mixture for 10 h at 450 °C. Heating the AC up to the oxidation temperature and cooling down to the 25 °C processes were done under the flow of 150 ml/min N_2 [14]. AC3 was prepared by oxidizing 10 g AC1 in 5 N HNO_3 solution under total reflux for 3 h followed by rinsing the sample with boiling DI water till the solution had a homogeneous appearance. Finally, the obtained sample was dried at 115 °C overnight.

AC2K and AC3K adsorbents were prepared by incipient-to-wetness impregnation of 10 wt.% K_2CO_3 solution on 2 g of AC2 and AC3, respectively. AC2K and AC3K samples were subjected to calcination at different temperatures under 5% O_2-95% N_2 gas mixture for 2 h. The resulting adsorbents were named according to calcination temperatures as AC*x*K-calT (Table 1).

The microstructural properties of the samples were analyzed by SEM, and the metal dispersion on their surface was measured by SEM-EDX (Energy Dispersive X-Ray). The tests were conducted at a Philips XL 30 ESEM-FEG system, having a maximum resolution of 2 nm. Secondary electron (SE) images were obtained for modified AC adsorbents. The analyses were performed at the Advanced Technologies Research and Development Center of Boğaziçi University.

X-ray photoelectron spectroscopy (XPS) analysis was performed to characterize the surface species on the adsorbents. XPS spectra were