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Thermodynamics of Adsorption of Carbon Dioxide on Various Aerogels

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ABSTRACT

Excess CO$_2$ adsorption isotherms on silica, resorcinol-formaldehyde, carbon, and wheat starch aerogels at 308 K, 318 K, and 328 K and at pressures up to 35 bar were measured using a volumetric method. Total or absolute adsorption isotherms were calculated from experimentally obtained excess adsorption isotherms using the pore volume of each adsorbent. It was found that silica aerogel with the BET surface area of 1158 m^2 g^{-1} had a maximum absolute uptake of 14 mmol g^{-1} and resorcinol-formaldehyde aerogel (RFA-19) with the BET surface area of 620 m^2 g^{-1} had a maximum uptake of 13 mmol g^{-1} at 308 K and 35 bar. CO$_2$ adsorption isotherms for silica, resorcinol-formaldehyde, and wheat starch aerogels were well represented with the Langmuir model whereas isotherms for carbon aerogel were fitted with the Freundlich model. It was also found that the excess uptake correlated well with the mesopore surface area of each aerogel at various pressures. The isosteric heat of adorption for each aerogel was also determined from the variation of pressure with temperature at a constant excess uptake. Among all aerogels, wheat starch aerogel had the highest value of −32.1 kJ mol^{-1} and carbon aerogel had the lowest value of −17.7 kJ mol^{-1}. Adsorption capacities of aerogels determined were comparable with other classes of adsorbents and presents an opportunity for further investigation of aerogels as potential materials for carbon capture especially at high pressures.

1. Introduction

Global warming is leading to destabilization of marine ecosystems, increase in sea-levels, and acidification of oceans. The major cause of global warming is the greenhouse gas, carbon dioxide (CO$_2$), which is primarily produced by the combustion of fossil fuels and its capture is important to prevent the increase of concentration of CO$_2$ in the atmosphere [1–3]. In addition to capturing carbon dioxide for sequestration, carbon capture is also of interest to natural gas industries because approximately 40% of the natural gas reserves are unexploited due to high CO$_2$ content and the costs associated with separating CO$_2$ [4,5]. Therefore, there is a need for development of high performance and cost effective carbon capture technologies. Several techniques such as absorption, cryogenic distillation, membrane separation, and adsorption are being investigated for carbon capture. Adsorption is advantageous as it is cost-effective, applicable for a wide range of temperatures and pressures, and requires low energy for regeneration of adsorbent [3,6,7].

A wide variety of adsorbents have been investigated for carbon capture by chemisorption and physisorption at different temperatures and pressures [6–8]. These include chemical sorbents such as metal oxides [9,10] and various porous physical sorbents such as activated carbon [11,12], zeolites [13], metal-organic frameworks (MOFs) [14]

and aerogels [15]. A major disadvantage in using chemical sorbents is difficult regeneration of the sorbent [6,7], therefore, many studies are focused on physical sorbents. For instance, Siriwardane et al. [16] determined adsorption isotherms of CO$_2$ on activated carbon and zeolite at 298 K and pressures up to 20 bar. At lower pressures, Zeolite 13X had a higher adsorption capacity compared to activated carbon, however, activated carbon had greater adsorption capacities at high pressures. Maximum adsorption capacity was 8.5 mmol g^{-1} at 20 bar for activated carbon compared to 5.2 mmol g^{-1} for Zeolite 13X. In addition, Cavenati et al. [17] measured high pressure CO$_2$ adsorption isotherms on Zeolite 13X at different temperatures and found that adsorption capacity increased with increasing pressure with a maximum adsorption capacity of 7.4 mmol g^{-1} at 298 K and 32 bar. Higher capacities at high pressures were found to be dependent on the surface area of the materials because activated carbon had higher surface area (897 m^2 g^{-1}) then zeolite 13X (506 m^2 g^{-1}). Moreover, Millward and Yaghi [14] investigated different MOFs and determined maximum CO$_2$ adsorption capacity of 35 mmol g^{-1} for MOF-177 at 298 K and 42 bar.

Aerogels may also be used as adsorbents for carbon capture due to their large surface areas and tunable properties. Both inorganic and organic aerogels are being investigated in many laboratories around the world for a wide variety of applications including thermal insulation and drug delivery [15,18]. A number of studies on adsorption of CO$_2$ on

Table 1
Summary of Studies on Carbon Dioxide Adsorption on Aerogels.

Aerogel	Feed Composition	Temperature (K)	Pressure (bar)	Maximum Capacity (mmol g⁻¹)	Reference
Amino-functionalized silica aerogel (5.2 wt% N)	100% CO_2	298	0.025	0.523	[15]
Amine-modified silica aerogel	10% CO_2, 10% H_2O in N_2	298	1	6.97	[18]
Carbon aerogel (from melamine-formaldehyde resin)	100% CO_2	298	1	2.2	[19]
Carbon aerogel (from chitosan and polybenzoxazine)	100% CO_2	298	1	5.72	[21]
	100% CO_2	273	1	6.70	
	100% CO_2	298	2	6.25	
Amine-hybrid silica aerogel	1% CO_2 in N_2	298	1	5.55	[23]
80 wt% Tetraethylenepentamine loaded silica aerogel	100% CO_2	348	1	6.10	[24]
Silica aerogel	100% CO_2	298	1	3.3	[25]
Chitosan-(20%) graphene oxide aerogel	100% CO_2	298	1	4.15	[26]

different native and modified aerogels have also been reported. Some studies reported adsorption capacity at a single temperature and pressure [15,19] while others determined adsorption isotherms showing the relationship between the amounts of CO_2 adsorbed and pressures at a constant temperature [20,21]. Adsorption isotherms are necessary not only for design and modeling of adsorption systems but also for evaluating properties such as heats of adsorption [22]. Silica aerogel and amine-modified silica aerogels had CO_2 adsorption capacities in the range of 3.30–6.97 mmol g⁻¹ at 298 K and 1 bar [18,23–25]. Similarly, carbon aerogels synthesized from different organic precursors had CO_2 adsorption capacities in the range of 2.20–6.70 mmol g⁻¹ at 298 K and 1 bar [19,21,26]. Table 1 provides a summary of studies on aerogels along with their maximum CO_2 adsorption capacity. There is no systematic study in the literature on the effect of pore properties such as pore size, pore volume, and surface area of different aerogels on CO_2 adsorption. There are also no studies on organic aerogels and CO_2 adsorption on aerogels at high pressures.

In this study, silica aerogel, two resorcinol-formaldehyde aerogels with different pore sizes, carbon aerogel, and wheat starch aerogel were synthesized and excess adsorption isotherms of CO_2 on these aerogels were measured at 308 K, 318 K, and 328 K and at pressures up to 35 bar using a volumetric method. The absolute (total) adsorption isotherms were also calculated from excess adsorption isotherms. Isotherms were fitted with Langmuir and Freundlich models and isosteric heats of adsorption were also calculated.

2. Experimental

2.1. Materials and Synthesis of Aerogels

Resorcinol (99%), sodium carbonate (99.99%), and ethanol (99.9%) were purchased from Merck. Formaldehyde (36%) was purchased from Lachema. Tetraethylorthosilicate (TEOS) (98.0%) and ammonium hydroxide (2.0 M in ethanol) were purchased from Sigma Aldrich, and hydrochloric acid (37%) was purchased from Riedel-de Haen. Wheat Starch was purchased from Kenton (Turkey). Chemicals were used as-received. Water was distilled and deionized. Carbon dioxide (99.998%), nitrogen (99.99%), and helium (99.999%) were purchased from Air Liquide.

2.1.1. Silica Aerogel

Tetraethylorthosilicate, distilled water, and ethanol were mixed in the presence of acid catalyst (HCl in ethanol) for 30 min. Then base catalyst, ammonia solution in ethanol, was added and the mixture was stirred for 1 minute. The molar ratios of the chemicals, TEOS:ethanol:H_2O:HCl:NH_4OH were 1:1.01:2.97:0.0022:0.0089. Solution was then transferred into a mold and left for 30–40 minutes until gel was formed. Gel was then put into a solution (50% water and 50% ethanol) and placed in the oven at 50 °C for 24 hours. Solvent exchange with pure ethanol was then carried out to obtain alcogel. Alcogel was dried using supercritical CO_2 for extraction of the solvent

in the Applied Separations SFE unit which consists of a high pressure extraction vessel (500 mL) in an oven, a pump, a carbon dioxide cylinder, a cooler, a rotameter and a control unit for controlling the temperature of the extractor and the expansion valve. Drying was performed at 40 °C and 100 bar with a CO_2 flow rate of 1.5 L/min for 8 hours. After the extraction was over, the vessel was slowly depressurized at 40 °C and aerogels were obtained.

2.1.2. Resorcinol-Formaldehyde Aerogel

Resorcinol-formaldehyde aerogels (RFAs) were synthesized based on the procedure described by Pekala [27]. Two different types of RFAs were synthesized based on their pore sizes. One had a pore size of 19 nm and another had a pore size of 7 nm. For the preparation of RFAs, resorcinol was first dissolved in water and alkaline catalyst sodium carbonate was then added to the solution. Resulting mixture was stirred for 10 minutes and then formaldehyde was added. For the RFA with pore size of 19 nm (RFA-19), resorcinol to formaldehyde ratio of 0.5, resorcinol to alkali catalyst ratio of 200, and resorcinol to water ratio of 0.02 was used. For the RFA with pore size of 7 nm (RFA-7), resorcinol to formaldehyde ratio of 0.5, resorcinol to alkali catalyst ratio of 50, and resorcinol to water ratio of 0.08 was used. The mixture was then poured into a sealed container. The solutions were cured at room temperature for 24 hours, for another 24 hours at 50 °C, and for 72 hours at 90 °C. Resulting gels were taken out of their molds and placed in acetone. Solvent exchange with pure acetone was carried out to obtain acetogels. Acetogels were dried using supercritical CO_2 for extraction of the solvent at 50 °C and 138 bar with a CO_2 flow rate of 1.5 L/min for 8 hours. After the extraction was over, the vessel was slowly depressurized at 50 °C and aerogels were obtained.

2.1.3. Carbon Aerogel

Carbon aerogel was prepared via pyrolysis (carbonization) of RFA-19 at 1000 °C in flowing N_2 (100 ml min⁻¹) for 6 hours.

2.1.4. Wheat Starch Aerogel

Wheat starch aerogel was synthesized according to the method described by De Marco et al. [28]. A homogenous starch solution with 5 wt% wheat starch was prepared in distilled water and then gelatinized at 110 °C. The hydrogel was poured into molds and placed in the fridge for retrogradation at 4 °C for 72 hours. Alcogel was obtained by replacing water in the pores with ethanol at room temperature. Increasing ethanol concentration (30%, 50%, 70%, 90% and two times 100% v/v) were used for solvent exchange and each exchange lasted for 24 hours. Alcogels were then dried using supercritical CO_2 for extraction of the solvent at 40 °C and 100 bar with a CO_2 flow rate of 1.5 L/min for 8 hours. After the extraction was over, the vessel was slowly depressurized at 40 °C and aerogels were collected.

2.2. Material Characterization and CO_2 Adsorption Measurements

The Brunauer-Emmett-Teller (BET) surface area (SA), pore size, and