

Extrapolation of the Clausius-Clapeyron plot for estimating the CO₂ adsorption capacities of zeolites at moderate temperature conditions

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Abstract—CO₂ adsorption capacity of zeolite 13X and Na⁺-chabazite at 473 K was estimated by extrapolating the CO₂ adsorption isotherm data measured in the temperature range of 298 to 373 K by employing the Clausius-Clapeyron equation, and compared with those by gravimetric measurements using a TGA unit and by the breakthrough curves obtained using a gas mixture (CO₂ 30% in N₂ balance) in a fixed bed adsorption unit. All three methods produced comparable CO₂ adsorption capacities, and justified the suggested experimental approach of the extrapolation procedure using the low temperature isotherm data for estimating gas adsorption capacity at high temperature conditions.

Keywords: Zeolites, CO₂ Adsorption, Clausius-Clapeyron Equation, TGA, Breakthrough

INTRODUCTION

Current global climate disorder is believed to be largely attributed to the CO₂ emissions and accumulations in the atmosphere from the combustion of fossil fuels for power generation, and significant effort has been made to develop carbon capture and storage (CCS) technologies to reduce the global warming caused by rise in the CO₂ level in the atmosphere. While the large-scale separation of CO₂ from power plant post-combustion exhaust is handled by liquid amine-based sorption [1], CO₂ capture by solid materials such as zeolites [2], carbons [3], alumina [4], and metal-organic frameworks (MOFs) [5] based on adsorption processes at room temperature conditions is being actively investigated.

Considerable interest in CO₂ capture in a precombustion mode has also been made over the last ten years. Reducing greenhouse gas emissions under the conditions of high thermal efficiency is important in designing future power plants [6], and the integrated gasification combined cycle (IGCC) in which pre-combustion capture of high concentration CO₂ is taking place under moderate to high temperature conditions is being considered. Zeolite 13X is one of the dry adsorbents considered for IGCC, showing stable CO₂ capture performance at 363–473 K [7,8], and chabazite (CHA) type zeolites were also reported promising [9–11]; CHA has a relatively higher Si/Al ratio (approximately 2.4) than 13X [12], which can lead to higher CO₂ capture selectivity. To evaluate the performance of a given adsorbent for the pre-combustion application, we need to measure CO₂ capture capacity at around 473 K.

For CO₂ adsorption capacity measurement of a given adsorbent, adsorption isotherm obtained using a standard volumetric unit is the most common method used among the volumetric, gravimet-

ric, and breakthrough techniques available. For a volumetric unit, typical surface area measuring equipment is employed after changing the adsorbate from N₂ to CO₂, whereas gravimetric measurement is conducted by thermogravimetric analysis (TGA) in a flow system. Finally, a fixed bed flow system using a suitable gas mixture is used for the CO₂ gas breakthrough measurement. Various research groups have been estimating CO₂ adsorption capacity of a given adsorbent using one of these approaches, but no one has yet systematically compared the closeness of the values obtained by different measuring devices. Obviously, these values have to be sufficiently close enough, since we are measuring a thermodynamic quantity under given set of experimental conditions. More importantly, it will be useful if one can estimate the gas adsorption capacity of an adsorbent at a more challenging moderate to high temperature conditions using a commonly available static volumetric unit rather than employing a flow system.

In this study, the validity of extrapolating the adsorption isotherm data measured in the range of 298 to 373 K using a volumetric adsorption unit to estimate the adsorption capacity of zeolites at high temperature of 473 K was demonstrated; the maximum temperature attainable by a common volumetric adsorption unit is limited to ca. 373 K. Both zeolite 13 X and CHA were tested as an adsorbent to demonstrate the general applicability of the proposed method.

EXPERIMENTAL

1. Zeolite Synthesis and Characterization

Commercial zeolite 13X was purchased from Sigma-Aldrich, while K⁺-chabazite was hydrothermally synthesized, ion-exchanged to Na⁺ form (NaCHA), and conditioned at 373 K overnight in the laboratory [13]. The XRD (Rigaku) patterns of the zeolite samples were confirmed using Cu K α (λ =1.54 Å) radiation, and the N₂ adsorption-desorption isotherms (BELsorp-mini, BEL, Japan) were measured at 77 K. The specific surface areas of the samples were calculated using the BET (Brunauer-Emmett-Teller) method. Chemi-

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^{*}This article is dedicated to Prof. Seong Ihl Woo on the occasion of his retirement from KAIST in 2016.

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cal composition of the zeolite samples was examined with a Hitachi S-4300 electron microscope equipped with an energy dispersive X-ray spectroscopy.

2. CO₂ Adsorption Measurements

The CO₂ sorption isotherms at static condition was obtained by means of a Belsorp(II)-mini at temperature from 298 to 373 K. Prior

to the uptakes test, samples were heated at 573 K under in vacuum ($P=10^{-3}$ Torr) for 12 h.

As shown in the supplementary information (see Scheme S1), the zeolite sample was loaded into an alumina sample pan and the adsorption run was carried out using high purity CO₂ (99.999%) with helium (ultra-high purity, U-Sung) as the purge gas in the pre-

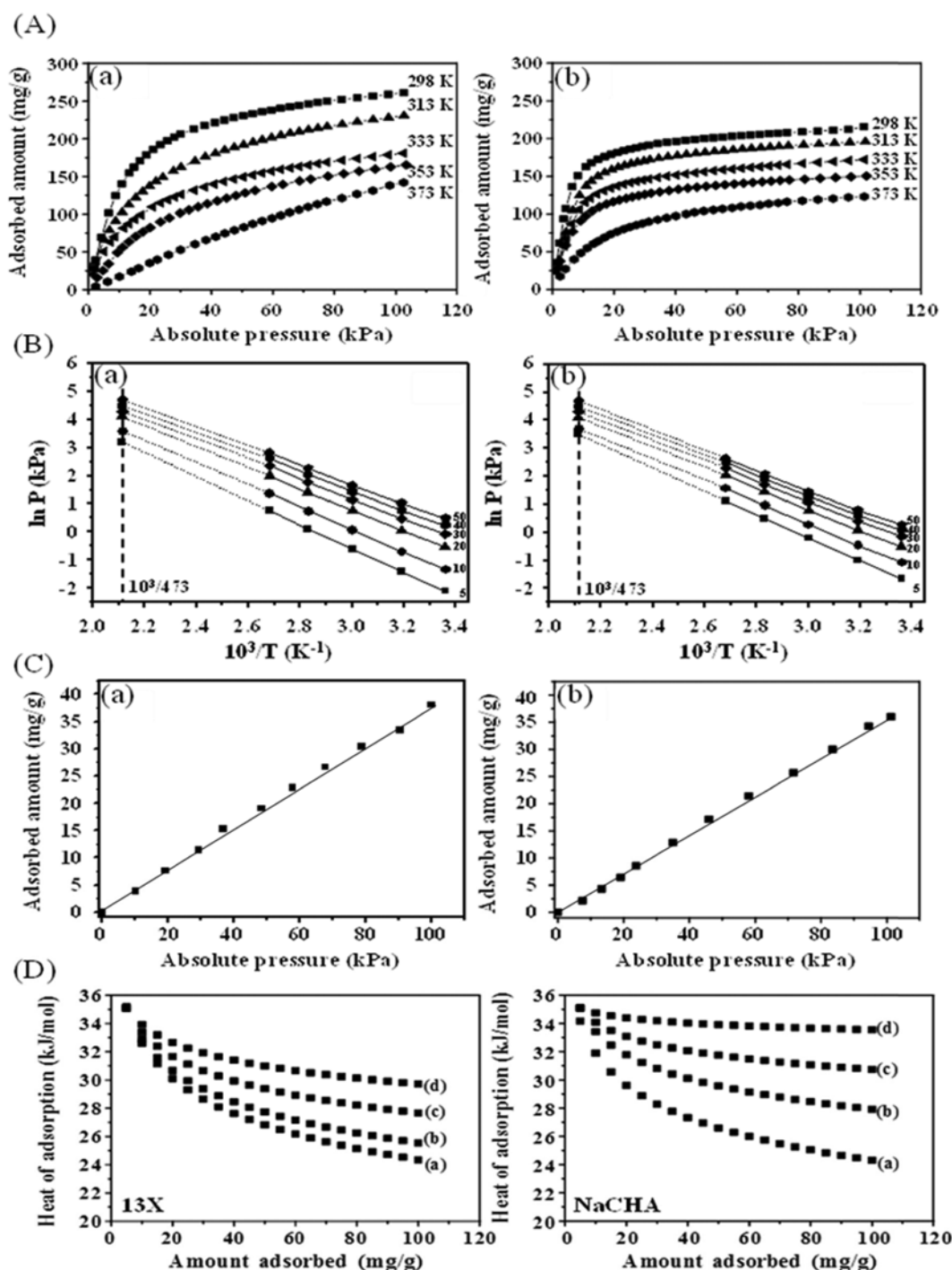


Fig. 1. (A) CO₂ adsorption isotherms of (a) 13X and (b) NaCHA at 1 bar; (B) adsorption isosteres in a temperature range from 298 to 373 K on (a) 13X and (b) NaCHA with extrapolation to 473 K; (C) adsorption isotherms of (a) 13X and (b) NaCHA at 473 K generated using the data in Fig. 1(B) via extrapolation; (D) heat of CO₂ adsorption on 13X and NaCHA at (a) 298-313 K, (b) 313-333 K, (c) 333-353 K and (d) 353-373 K.

Table 1. Physicochemical properties and CO₂ adsorption capacities of Na⁺ form zeolites

Sample	Type	Si/Al	Surface area (m ² /g)	CO ₂ adsorption capacity (mg CO ₂ /g-adsorbent)						
				Volumetric equipment ^a					CAL ^b	TGA ^c
				298 K	313 K	333 K	353 K	373 K	473 K	473 K
NaCHA	CHA	2.3	520	215	195	172	150	125	36	33
13X	FAU	1.4	804	260	230	180	165	141	38	36

^aBy a volumetric instrument (BELsorpII-mini, BEL, Japan)^bCO₂ adsorption capacity at 473 K estimated using the Clausius-Clapeyron equation employing the adsorption data in the range of 298-373 K^cBy TGA^dBy custom-made breakthrough apparatus using a gas mixture of 30 vol% CO₂ with N₂ balance

treatment and desorption step. A feed flow rate of 30 mL/min to the sample chamber was controlled with an MFC. All samples were pretreated at 573 K for 2 h before the CO₂ adsorption test, and desorption step was carried out at 623 K.

Break-through measurements (see Scheme S2) involved using a tubular adsorption column within a tube furnace, which is made of stainless steel with a total length of 350 mm (12.7 mm diameter and 1 mm wall thickness). Gas flow rates were monitored by mass flow controllers installed upstream of the adsorption bed. A back-pressure controller between the adsorption bed and the product exit was installed to maintain constant adsorption pressure in the bed, and adsorption pressure in column was monitored with a pressure gauge. The relative amounts of the gases passing through the column were monitored by using a mass spectrometer (Hiden Analytical HPR20). 0.5 g of pre-treated zeolite samples was placed inside the column, and the gas mixture was fed into the column at a flow rate of 100 mL/min.

RESULTS AND DISCUSSION

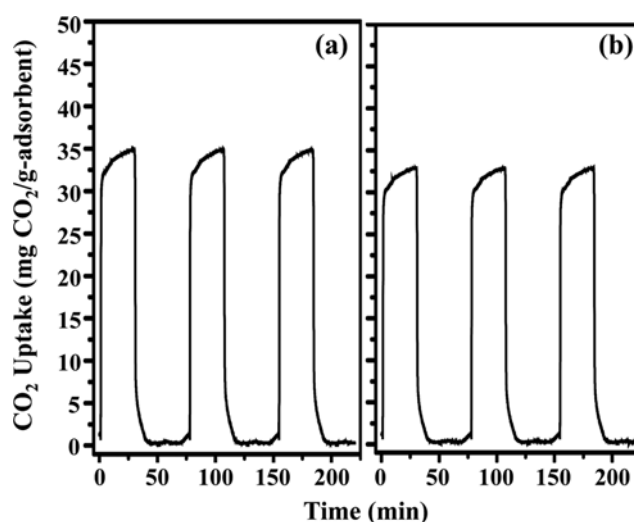
Physicochemical properties of NaCHA and the commercial Zeolite 13X are summarized in Table 1, which confirmed high quality of the zeolite products. Fig. S1 shows the N₂ adsorption-desorption isotherm and XRD pattern of NaCHA prepared in our laboratory.

Fig. 1(A) shows the CO₂ adsorption isotherms of 13X and NaCHA measured in the range from 298 to 373 K, which are in close agreement with the published data [7-11]. The adsorbed amount of CO₂ decreases with temperature in both cases due to exothermic nature of the adsorption process. The experimental adsorption data were then fitted to the Langmuir-Freundlich equation (Eq. (1)), where Q is the moles CO₂ adsorbed, P is the equilibrium pressure, Q_m is the moles CO₂ adsorbed at saturation, and finally B and t are the isotherm parameters.

$$Q = \frac{Q_m B P^{1/t}}{1 + B P^{1/t}} \quad (1)$$

The heat of adsorption was estimated by applying the Clausius-Clapeyron equation (Eq. (2)) as a function of surface coverage, where ΔH_{ads} is the heat of adsorption, P is pressure, R is the gas constant, and T denotes the adsorption temperature.

$$\ln \frac{P_1}{P_2} = -\frac{\Delta H_{ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

**Fig. 2. Recycle runs of CO₂ adsorption-desorption on (a) 13X and (b) NaCHA at 1 bar, 473 K.**

From the linear extrapolation of the Clausius-Clapeyron plot in Fig. 1(B), we can extract a set of pressure vs. surface coverage data at 473 K including the surface coverage at 1 bar condition, which corresponds to the expected adsorption capacity at 1 bar (Fig. 1(C)). As shown in Fig. 1(D), the heat of adsorption calculated at zero surface coverage produced virtually the same asymptotic values (ca. 35 kJ/mol for both NaCHA and 13X) irrespective of adsorption temperature. In addition, the average heat of adsorption increased with the adsorption temperature, which implies that only a fraction (see Fig. 2) of the adsorption sites with increasingly higher heat of adsorption are responsible for the adsorption taking place at increasingly high temperatures.

Fig. 2 shows cyclic CO₂ adsorption (at 473 K)/desorption (at 623 K) runs over the same zeolites using a gravimetric unit using a high purity CO₂ (99.999%). CO₂ adsorption measurements were performed using a TGA (SCINCO thermal gravimeter S-1000) connected to a flow panel for the CO₂ adsorption-desorption measurement (See Scheme S1). The CO₂ adsorption capacity estimated using the lower temperature adsorption isotherms from the volumetric unit produced ca. 10% higher adsorption capacities (36 and 38 mg/g-adsorbent for NaCHA and 13X, respectively) than those obtained by direct measurements using a TGA unit (33 and 36 mg/g-adsorbent for NaCHA and 13X, respectively), which is very rea-

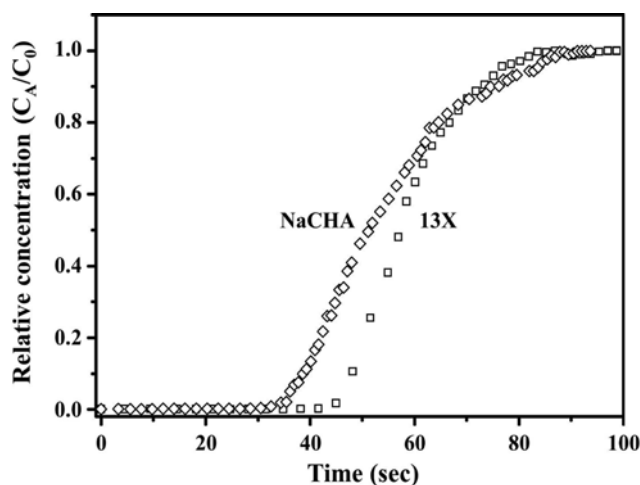


Fig. 3. Breakthrough curves of NaCHA and 13X at 1 bar, 473 K.

sonable considering that the pretreatment conditions for zeolite adsorbents before adsorption runs in TGA unit are less rigorous than that implemented for a high vacuum volumetric equipment.

The CO₂ adsorption capacities of 13X and NaCHA at 473 K were also measured by integrating their respective breakthrough curves obtained (Fig. 3) using a home-made breakthrough equipment employing a gas mixture (CO₂ 30% and N₂ 70%) (See Scheme S2). Again 13X exhibited slightly higher CO₂ capture capacity (34 mg/g-adsorbent) than by NaCHA (31 mg/g-adsorbent).

CONCLUSION

CO₂ adsorption capacities over zeolite 13X and Na⁺-chabazite were estimated in three different ways. At high temperature CO₂ adsorption at 473 K, gravimetric measurement using a TGA unit was the most convenient to operate, which estimated the adsorption capacities somewhat higher than those obtained by integrating the breakthrough curves obtained using a gas mixture in a fixed bed adsorption unit. Extrapolation of the CO₂ adsorption isotherm data obtained using a standard volumetric unit in the tem-

perature range of 298 to 373 K proved to be accurate enough estimation of the adsorption capacities under the given conditions.

ACKNOWLEDGEMENT

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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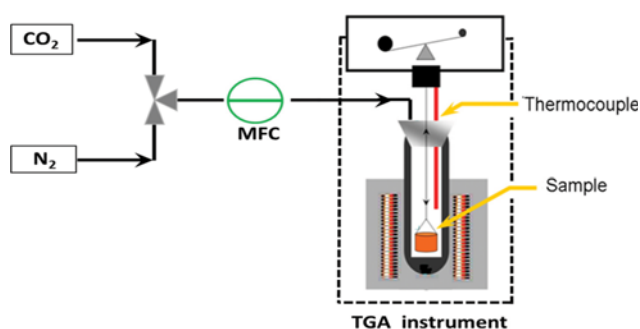
Supporting Information

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Scheme S1. Schematic diagram of the modified TGA adsorption unit used.

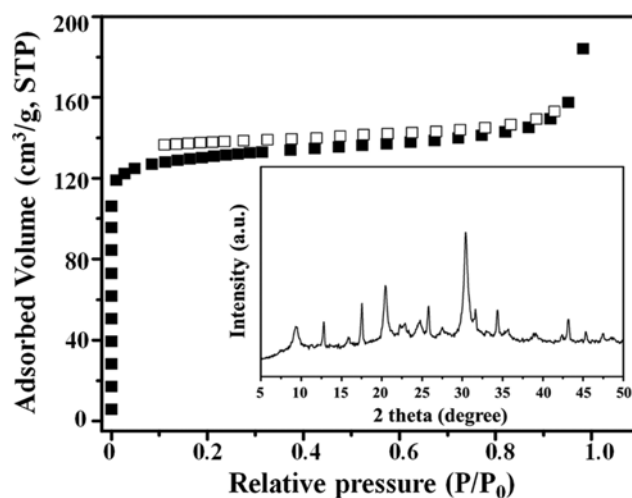
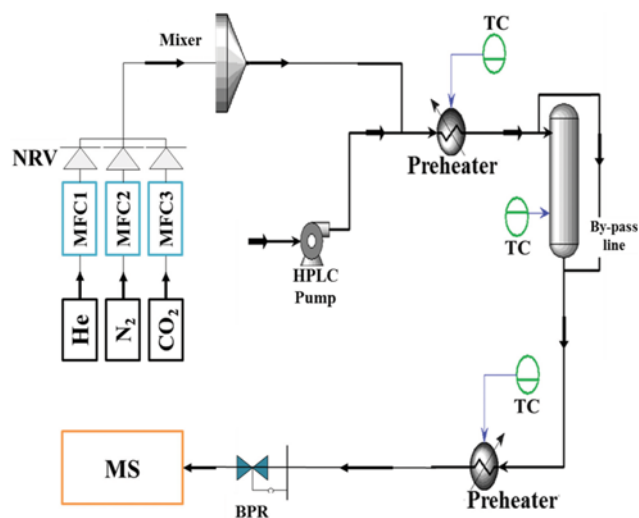


Fig. S1. N₂ adsorption-desorption isotherm of NaCHA zeolite at 77 K. The inset shows XRD pattern.



Scheme S2. Schematic diagram of the breakthrough experimental unit used.

BPR. Back pressure regulator NRV. Non return valve
MFC. Mass flow controller TC. Temperature controller
MS. Mass spectrometer