Adsorption Equilibria of CO₂ and Small Hydrocarbons in AEI-, CHA-, STT-, and RRO-type Siliceous Zeolites

*Trong D. Pham, Raul F. Lobo**

Center for Catalytic Science and Technology, University of Delaware, Department of Chemical
and Biomolecular Engineering, Newark, DE, 19716, USA

*Corresponding author: Raul F. Lobo

Email: lobo@udel.edu

Phone: +1-302-831-1261

Fax: +1-302-831-1048

Graphic abstract

Abstract

AEI, CHA, and STT siliceous zeolites and RUB-41 (RRO) were prepared with low concentration of internal silanols and were characterized by X-ray diffraction, N₂ adsorption isotherms, electron microscopy, and ²⁹Si MAS NMR spectroscopy. Adsorption isotherms of methane, ethylene, ethane, propylene, propane, and CO₂ were measured volumetrically on siliceous zeolites AEI, CHA, RRO, and STT at various temperatures ranging from 273 K to 323 K up to a pressure of 101.3 kPa. The Clausius-Clapeyron equation was used to calculate the isosteric heats of adsorption. The amount adsorbed depends strongly on adsorbate polarizability in the low-pressure region, and on the adsorbent micropore volume in the high-pressure region. Adsorption entropy losses are independent of temperature and increase with increasing adsorption enthalpy. RRO showed the highest pure-component selectivity of CO₂ over CH₄, and potential for the separation of the natural gas mixtures; AEI, CHA, and RRO-type materials showed potential for the kinetic separation of propylene/propane.

Keywords: Adsorption, hydrocarbon, isotherm, siliceous, zeolites, separation

1. Introduction

Zeolite adsorbents play an important role in separation technology, industrial catalysis and pollution control [1-6]. Siliceous zeolites are hydrophobic and organophilic crystalline silica molecular sieves [7-9]. These materials can provide an energetically uniform and nonpolar environment for adsorption of relatively small gas molecules and hydrocarbons. These zeolites are also extremely stable to thermal and hydrothermal treatments [9, 10]. The siliceous zeolites have, in principle, no framework aluminum, but due to impurities in the synthesis reagents, small amounts of aluminum are often found in the samples leading to low rates of acid catalyzed reactions and slow polymerization of adsorbed olefins [11].

The separation of small olefins and paraffins, which currently relies on energy-intensive cryogenic distillation, is one of the most important separation processes in the petrochemical industry [11-13], and alternative technologies based on adsorption processes are being investigated [14]. Propane/propylene separation in 8-membered ring zeolites is based on the differences in relative diffusion rates [6, 13, 15], or kinetics of adsorption, and it is found that propylene adsorbs faster than propane. Small pore zeolites often have high selectivity for CO₂/CH₄ separation [16, 17], which may be valuable in natural gas purification. The materials have also received considerable attention for NO_x selective catalytic reduction (SCR) [18, 19] and the methanol-to-olefins reaction (MTO) [20, 21]. Understanding of hydrocarbon poisoning of SCR catalysts and the selectivity of ethylene/propylene in MTO reaction requires prior a better understanding of adsorption.

In this report, we investigate the adsorption of CO₂ and small hydrocarbons in a series of siliceous zeolites of framework types AEI, CHA, RRO, and STT prepared in fluoride media with low concentration of internal silanol groups [22]. These data are compared to adsorption of CO₂ and alkanes on silicalite (MFI) that has been widely investigated before [23-29]. We have investigated the zeolites AEI (space group *Cmcm*), containing a three-dimensional pore structure

related to the CHA structure type: it consists of double-six rings and small 8-membered ring windows (Figure 1) [30]. CHA has large ellipsoidal cavities with internal dimensions of about $0.67 \text{ nm} \times 1.00 \text{ nm}$, differing from AEI in that AEI has a pear-shaped cage [31, 32]. STT is unique in the sense that it contains two-dimensional arrays of cages with molecular access between the cages in the planes being restricted by seven ($2.5 \times 3.5 \text{ \AA}$) and nine ($3.8 \times 5.4 \text{ \AA}$) member-ring windows [33, 34]. RUB-41 (RRO) has a two-dimensional 8×10 -membered ring pore system (Figure 1). The pore aperture of RRO along the [100] direction is $6.5 \times 4 \text{ \AA}$ and along the [001] direction is $5 \times 2.7 \text{ \AA}$. Since its aperture is too narrow to allow the passage of any hydrocarbons, the pore along [001] has no influence on the adsorption kinetics. This phenomenon was observed in 2 dimensional ITW-type zeolites, consisting of one circular window ($3.8 \times 4.1 \text{ \AA}$) and one restricted window ($2.4 \times 5.3 \text{ \AA}$) [35]. We report a comparison of the adsorption capacities, enthalpies, and entropies of CO_2 , methane, ethylene, ethane, propylene and propane on these four zeolites. It was also found that AEI, CHA, and RRO materials are potential candidates for the kinetic separations of propylene and propane gas mixtures.

2. Experimental Section

2.1. Materials

Adsorbents:

Pure silica chabazites (CHA) and SSZ-23 (STT) were synthesized using the formula mentioned by Pham *et al* [36].

RUB-39 was prepared following the protocol reported by Wang *et al* [37]. Typically, 2.87 g of Cabosil M-5 and 8.8 g of dimethyldipropylammonium hydroxide solution (DMDPA-OH 40 wt%, Sachem Inc.) was added to 3.33 g of deionized (DI) water to give the solution with the following molar composition: 3 SiO_2 : 0.5 DMDP-OH : $10 \text{ H}_2\text{O}$. The mixture was stirred until a uniform gel was obtained, and then transferred into a Teflon-lined stainless steel autoclave (23 ml) and kept at

423 K with a 40 rpm rotating speed for 21 days (only 10 days with the presence of 5 %wt RRO seed). The solid product, RUB-39, was separated by filtration, washed with DI water three times, and dried at 353 K overnight. The as-synthesized RUB-39 was calcined in air in a tube furnace (Lindberg Blue M) by heating at a rate of 3 K/min at 773 K for 6 hours, and then heating to 853 K for another 4 hours. The condensation of silanol groups upon calcination leads to the formation of RUB-41 (RRO).

Synthesis of siliceous AEI: The first step consist in the synthesis of N,N-Diethyl-2,6-dimethylpiperidinium iodide (DEDMP-I) cation that was prepared following the procedure by Zones [38]. The iodide salt is converted to the hydroxide salt by exchanging with Bio-Rad AG1-X8 anion exchange resin overnight with the mass composition of 1 DEDMP-I: 3 resin: 5 H₂O. The resin-aqueous suspension was filtered, washed with DI water, and the filtrate concentrated using a rotovapor. The final OH-form concentration (12.9 %wt) was titrated by HCl using phenolphthalein as an indicator.

The second step consists of the preparation of AEI with a Si/Al=11. This sample was prepared using a procedure similar to that reported in ref [38]. A solution of 5 g of sodium silicate (PQ corp., 28.5% SiO₂, 8.9% Na₂O), 0.4 g of NaOH 1M, and 6 g of DI water was added to 5.8 g DEDMP-OH 12.9% and stirred at room temperature for about 15 minutes. Then, 0.5 g of NH₄-Y (Zeolyst CBV712, Si/Al=6) as Aluminum source was added to the solution and stirred for another 30 minutes. The resulting solution was then transferred into 23 ml Teflon-lined autoclaves and heated at a temperature of 423 K under rotation for 7 days. The solid product was separated by vacuum filtration, washed with DI water, and dried at 353 K overnight. The as-made product was then calcined in air at 823 K for 8 hours.

To prepare a samples with very high Si/Al ratio, AEI (Si/Al=150), we followed a protocol similar to the one reported by Cao *et al.*[39]. 0.298 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ pre-dissolved in 3 grams of DI water was added to 26.2 g of an aqueous solution of DEDMP-OH 12.9 %wt, followed by 7.5 g of tetraethylorthosilicate (TEOS). The resulting mixture was continuously stirred for about 6 hours at room temperature until all TEOS was completely hydrolyzed. 0.04 g of seeds of AEI (Si/Al=11) was added to the synthesis gel, and then the mixture was heated to remove EtOH and H_2O to obtain a final gel composition of 1 SiO_2 : 0.0028 Al_2O_3 : 0.5 DEDMP: 0.6F: 3 H_2O .

The resulting mixture of solids was transferred to 23 ml Teflon-lined autoclaves and heated at a temperature of 423 K under rotation for 5 days. After cooling, the obtained solid was recovered by centrifuging, washed with distilled water, and dried at 353 K overnight.

Adsorbates: Carbon dioxide, methane, ethane, ethylene, propylene, and propane, all with purities of higher than 99% were obtained from Matheson.

2.2. Analytical Methods

Scanning Electron Microscopy (SEM) images of the calcined zeolites were obtained using a JEOL JSM7400F microscope, operating at an acceleration voltage of 3 keV, and a current of 10 μA . The X-Ray Powder Diffraction (XRD) patterns were collected at room temperature on a Philips X'Pert Panalytical diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The data were collected in a stepwise fashion with 2θ ranging from 5.0° to 50.0° with a step size of 0.02° and 2 s per step.

The liquid N_2 isotherms were measured using N_2 at 77 K with a Micromeritics 3Flex apparatus. Prior to the adsorption measurements, the calcined samples were outgassed at 623 K overnight under vacuum. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t-plot methods, respectively. ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker AVIII-500 solid-state NMR

spectrometer, operating at a Larmor frequency of 500.138 MHz for ^1H and 99.362 MHz for ^{29}Si . A 4 mm HX MAS probe was used for all measurements. All spectra were recorded at a MAS frequency of 10 kHz, controlled to with ± 2 Hz using a Bruker MAS controller. ^{29}Si single pulse and cross polarization (CP) measurements have been performed on each sample. For ^{29}Si single pulse MAS experiments, a 90° pulse with a width of 4.3 μs was used and the recycle delay was 30 s. For ^1H - ^{29}Si CP MAS experiments, ^1H 90° pulse duration was 2.5 μs , a linear amplitude ramp (80-100%) on ^1H was used with a contact time of 4.5 ms, and the recycle delay was 5 s. SPINAL64 ^1H decoupling with rf field strength of 100 kHz was applied during the acquisition period for both single pulse (SP) and CP MAS measurements.

2.3. Adsorption Isotherm Measurements

The gas adsorption isotherms at temperatures of 273 K, 303 K and 343 K, were measured up to the ambient pressure on a Micromeritics ASAP 2020 or on a 3Flex Micromeritics adsorption instruments. Before the adsorption measurements each sample was degased at a temperature of 623 K for 6 h under vacuum.

Langmuir (Eq.1) and Toth (Eq.2) models were used to fit the adsorption equilibrium isotherms:

$$q = q_m \frac{bP}{1+bP} \quad (\text{Eq.1})$$

$$q = q_m \frac{bP}{(1+(bP)^t)^{1/t}} \quad (\text{Eq.2})$$

where q is the amount adsorbed, q_m is the maximum adsorption capacity, P is the adsorption pressure, b and t are coefficients for Langmuir and Toth models.

The heats of adsorption (enthalpy of adsorption) at zero coverage were estimated using the *Clausius-Clapeyron* equation:

$$Q_{st}^o = -R \left[\frac{\partial \ln K_H}{\partial \left(\frac{1}{T} \right)} \right] \quad (\text{Eq.3})$$

where K_H is Henry's law constant, which is the intercept of the function $\ln(P/q)$ vs q from the virial equation

$$\ln \frac{P}{q} = -\ln K_H + A_1 q + A_2 q^2 + \dots \quad (\text{Eq.4})$$

The adsorption entropies were calculated as following [40]

$$\Delta S_{ads}^o = \frac{Q_{st}^o}{T} + R \ln K_{ads} \quad (\text{Eq.5})$$

where $K_{ads} = bP^o$, and $P^o=10^5$ Pa

3. Results and Discussion

3.1. Materials characterization

The crystallinity and particle morphology of the prepared AEI, CHA, RRO, and STT zeolites were determined by analysis of X-ray powder diffraction patterns and by SEM. The XRD patterns (Figure 2 and Figure S1) indicated that the samples are a single crystalline phase of the desired zeolite structure without any detectable impurities [37, 39, 41, 42]. In the case of the material with framework-type RRO, the diffraction peaks of the precursor layered silicate RUB-39 (intercalated with an organic dimethyldipropylammonium cation) shift to higher 2 theta degrees in the diffraction pattern of *calcined* RUB-41 due to a topotactic condensation of the RUB-39 silicate layers during the calcination process. SEM images (Figure 3) show that the morphology of the AEI sample is characterized by well-defined cuboid shape and a highly uniform particle size of 200 nm. RRO has a characteristic and uniform prismatic plate morphology of about 2 μm in length. CHA exhibit a pseudo-cubic and STT is formed of aggregates of plate-like crystals (Figure S2).

The associated Brunauer-Emmett-Teller (BET) surface area, microporous volume obtained by the t-plot method, and the theoretical pore opening of the four zeolites are reported in Table 1. The three-dimensional zeolites AEI, CHA, with cage-like structure, have narrower pore openings, but higher surface area and higher micropore volume compared to 2D zeolites RRO and STT, which have channel-like pore architecture.

The single-pulse ^{29}Si MAS NMR spectra of calcined high-silica AEI and RRO are showed in Figure 4. Only two peaks are observed for AEI, one very small peak at chemical shift δ of about -101 ppm is assigned to $\text{Si}(\text{OSi})_3\text{OH}$, a surface Q^3 -silicon group carrying one hydroxyl

functionality, and the other much larger peak at ~ -111.5 ppm is assigned to Q^4 ($Si(OSi)_4$) species. The observation of just one Q^4 peak could be the result a similar geometric environment of three T-atoms within the asymmetric unit of the siliceous AEI framework, which is similar to a ^{29}Si NMR study in high silica AEI ($Si/Al=8$) reported by M. Dusselier [43]. The cross-polarization 1H - ^{29}Si CP MAS NMR spectrum of this sample (not shown) shows one peak in the Q^3 region at the same positions that the small peak of the ^{29}Si MAS spectrum. The results of the ^{29}Si MAS NMR spectra reveal an absence of connectivity defects in RRO zeolite: there are no resonances at about 100 ppm indicative of Si-OH (Q^3) groups after calcination. We observe 4 peaks (110-116 ppm) belonging to Q^4 species in the spectrum of this zeolite (Figure 4), that is, one additional signal compared to the spectrum reported by Wang *et al* [37]. Since there are 5 T-atoms in the RRO asymmetric unit, the observation of four peaks confirms the high quality of the RRO sample synthesized here. The single pulse ^{29}Si MAS (Figure S3) and the 1H - ^{29}Si CP MAS NMR spectra of siliceous CHA and SSZ-23 (STT) are all similar to the above spectra showing very low concentration of defects sites in the samples synthesized in HF medium, as expected.

3.2. Adsorption isotherms

Adsorption isotherms of all adsorbates (see Table 2 [44] for properties) up to a total pressure of 101.3 kPa (Figure S5) reveal important differences between the properties of the adsorbates investigated. The adsorption isotherms for each adsorbate (Figure S5) show a gradual decrease in the adsorbed amount with increasing temperature, as expected of physical adsorption. The larger polarizability of CH_4 compared to N_2 leads to a stronger adsorption enthalpy despite the large quadrupole moment in N_2 . The higher adsorption heat of CH_4 was also observed in materials with the presence of strong electric fields [45, 46]. In siliceous zeolites, materials with low electric field gradients, our results (Figure 5) indicated that CH_4 is preferentially adsorbed compared to N_2 , reaching a capacity of 0.191 kg/mol compared to 0.127 kg/mol at 303 K and 101.325 kPa. The adsorption isotherms indicate that low-loading adsorption capacity correlates mostly with polarizability. Siliceous zeolites adsorb longer chain hydrocarbons preferably until

the maximum adsorption capacity is reached. For the materials investigated, the slope of the isotherm for C₂ hydrocarbons is higher than C₃ hydrocarbons at a pressure near 101 kPa (Figures 5 and S5) because zeolites were saturated by C₃ hydrocarbons but not by C₂ hydrocarbons at this point.

Our simulations [36] indicated that the electrostatic contribution to the heat of adsorption of CO₂ in the weak electric field hydrophobic zeolites is about 20-30% of the total adsorption heats due to the high quadrupole moment of CO₂. This leads to higher adsorption heats and adsorption capacities of CO₂ compared to CH₄ (Figure S5) even though these two molecules have the same polarizability. C₂ hydrocarbons are more polarizable than CO₂, thus they adsorbed on STT zeolite preferentially over CO₂ in the low-pressure regions. However, more CO₂ molecules can be packed in the pores at high pressure due to its lower molecular volume (Table 2).

Kim *et al.* [47] have used Grand Canonical Monte Carlo (GCMC) simulations to screen thousands of pure silica zeolites to identify optimum structures for the separation of ethane/ethylene mixtures. The authors found that most zeolite structures are not suitable for thermodynamic or kinetic separations of ethane/ethylene due to the geometric and physical similarities between the two gas molecules. However, the separation of C₂ from C₃ hydrocarbons is feasible based on the diffusion properties of these compounds in 8-ring zeolites as estimated by molecular dynamics simulations [48, 49]. We found that the adsorption isotherms of C₃ in AEI, CHA, and RRO zeolites need to be collected at higher temperatures than the adsorption isotherms of C₂ hydrocarbons (for example 273-343 K for C₂ and 368-408 K for C₃ in the case of CHA zeolite), indicating that C₂ has fast transport properties compared to C₃ and C₂/C₃ kinetic separation is experimentally feasible. The slow diffusions of C₃ hydrocarbons at low temperatures (<423 K) in small pore zeolites could explain for the decrease in the poisoning of C₃₊ hydrocarbon in Cu-exchanged zeolites for SCR catalysts studied by Lou *et al* [50]. The increase in the diffusion of C₂/C₃ out of the crystalline structures with temperature is consistent

with the MTO selectivity results reported by Barger [51] that the product shape selectivity of ethene/propene increases with temperature in the narrow-pore SAPO-34 (CHA-framework type).

In addition, the 8MR windows have a good fit to the molecular shape of propene allowing it to diffuse and adsorb much more rapidly than propane [6, 13, 35, 52]. The narrow 10MR material RRO has similar aperture dimensions compared to the 8MR of siliceous chabazite (Figure 1). We were unable to collect propane adsorption isotherms on siliceous AEI, CHA, and RRO at temperatures below 423 K due to the very slow diffusion of propane into these zeolite structures, thus revealing potential for propane/propene separations in these materials. Due to the small pore apertures of RRO zeolites, the material shows low adsorption capacity for CH₄, C₂H₄, and C₂H₆ (Figure 4) compared to other zeolites even though the adsorption heats calculated for hydrocarbons on RRO zeolite are quite similar to adsorption heats of other zeolites (Table 3).

Dueren *et al.* [53] have indicated that the important features of nanoporous materials controlling methane adsorption are primarily surface area, followed by free volume, framework density, and heat of adsorption. In agreement with their predictions, the materials with the highest surface area, AEI- and CHA- zeolites, showed the highest methane adsorption capacity (Figure 6). Pore size and shape also affect how adsorbate molecules bind in porous solids. Since AEI, CHA, and STT contain cavities of similar dimensions (Figure 1), the interactions of the zeolite walls with adsorbate molecules are similar among these zeolites at low pressure. This leads to similar adsorption capacity at low adsorbate loading (Figure 6). Since the free volumes of three-dimensional zeolites AEI and CHA are higher than that of the two-dimensional RRO and STT, they have more efficient molecular packing hydrocarbons in the larger cavities of AEI, CHA compared with two dimensional of RRO/STT. The adsorption capacity of AEI at high pressure is lower than that of CHA zeolite, especially in the case of the larger hydrocarbons. This could be due to the pear-shaped cavity of AEI that may not be efficient for hydrocarbon packing compared to the ellipsoidal cavity of CHA.

3.3. Enthalpy and entropy of adsorption of CO₂ and hydrocarbons in siliceous zeolites

Adsorption enthalpies at the limit of zero coverage were calculated based on equation 3 and 4 (Table 3). The heats of adsorption of light alkanes in siliceous chabazite are similar to results reported by Olson *et al.* [13] (Q_0^{st} for propene, ethane, and ethene are 33.5, 28.9, and 27.2 kJ/mol, respectively). RRO has the most confined pore system among the studied zeolites and it showed the highest adsorption heats of CO₂ and CH₄ (Table 3). This material also showed the highest pure-gas selectivity for CO₂/CH₄, indicating a potential for CO₂ separations from natural gas. With linear geometry, CO₂ fits well into any narrow pore channels and windows of RRO zeolite; however, spherical geometry CH₄ might only fits well in the intersections of RRO pore channels. This might lead to higher CO₂/CH₄ selectivity in RRO zeolite than the selectivity reported for hydrophobic materials such as DDR, MFI, BEA, MWW, LTA siliceous zeolites (3-8) [54-56], carbon-based adsorbents (2-12) [57, 58], and porous polymers (10-15) [59]. Similar methane enthalpy for adsorption has been observed in zeolites with similar pore structures (AEI, CHA and STT). Methane is a spherical molecule with no permanent electric moment, and as such, experience similar interactions in these materials with cages of similar size, but different shape. The presence of a small amount of Al in AEI samples may lead to slightly higher electric fields within the AEI cage, as compared to other zeolites. This leads to a higher quadrupole-electric field gradient interaction between CO₂ and the zeolite surface and this difference explains the larger zero coverage adsorption heat of CO₂ on AEI.

The isosteric heats of adsorption of small hydrocarbons at the limit of zero coverage increased as the polarizability of the adsorbates increases (Table 3), as was observed by Talu *et al.* [60]. Previous experimental [61-63] and computer simulation investigations [64-67] have shown that heats of adsorption in siliceous MFI increase approximately 10 kJ/mol with each carbon atom in the alkane chain. The data in Table 3 indicate that the incremental heat of adsorption per carbon atom is also about 10 kJ/mol for AEI, CHA, and STT adsorbents, but not in the case of RRO zeolite. This is probably related to the pore size and tortuosity on the

adsorption of hydrocarbons which has been studied by Lercher *et al* [68] in a number of zeolites frameworks such as TON, FER, and KFI.

Polarizability and permanent polar/quadrupole moments (Table 1) contribute to the energy of interaction between gases and zeolite adsorbents. Hydrophobic zeolites adsorb polar molecules to a lesser extent and preference for saturated hydrocarbons over unsaturated hydrocarbons is observed in Table 3 and Figure 5. On the other hand, hydrophilic zeolites have higher values of heats of adsorption at zero coverage of unsaturated hydrocarbon (ethylene) compared to saturated hydrocarbon (ethane). The large adsorption heats of unsaturated hydrocarbons arise from the electrostatic interaction of the π electrons of the double bond with the large electric field gradients, as has been observed in NaY [69] (23.6 and 36.5 kJ/mol for ethane and ethylene, respectively) and in our study in Na-chabazite (Si/Al=6 with 31.6 and 40.8 kJ/mol for ethane and ethylene, respectively). This phenomenon could be of practically importance for the removal of small amounts of olefin impurities from hydrocarbon streams in refineries.

Adsorption entropies were obtained using equation 5 (Table 4). A general trend was observed for higher adsorption enthalpy correlated with an entropic cost as it leads to a loss in degrees of freedom. The limiting heat of adsorption of alkanes on STT zeolite is plotted against the polarizability of the adsorbates and the adsorption entropies (Figure S4). The results indicated that the limiting heat of adsorption increases linearly with polarizability, the adsorption entropies, and carbon number in *n*-alkanes (compensation effect) [40, 60].

Isosteric heats of adsorption, Q_{st} , as a function of loading (Figure 7) were obtained from the isotherm data using the *Clausius–Clapeyron* equation (Eq. 3). Materials such as low silica zeolites have a heterogeneous adsorption landscape in which adsorbates will occupy the lower energy positions at low loading and higher energy positions at higher loading. This results in a decrease in the heat of adsorption with gas loading. Siliceous zeolites, in contrast, may be regarded as energetically homogeneous adsorbents because the absence of ions and silanol groups; potentially energetically preferred adsorption sites. Electrostatic energies are small in

comparison to van der Waals energy, therefore the major adsorption energy contribution is related to the dispersion and repulsion terms (that is, the polarizability). An increase in the heat of adsorption with gas loading (Figure 7) is characteristic of homogeneous adsorbents with constant gas-solid and increased adsorbate-adsorbate energies of interactions. The heat of adsorption of small gases such as CO₂, CH₄ increases only slightly over the whole range of coverage. However, as the size of the hydrocarbons increases, adsorbate-adsorbate interactions become more significant and the increase in the adsorption heat is larger. In the case of AEI samples, we observed a small decrease in adsorption heat of ethylene and ethane up to a coverage of 0.5-0.6 mmol/kg. The decrease in heat of adsorption with gas loading is characteristic of heterogeneous adsorbent with a wide distribution of gas-solid interaction energies caused either by the shape of AEI cavity or the presence of Al in this adsorbent.

4. Conclusions

Hydrophobic siliceous zeolites of framework types AEI, CHA, RRO, and STT were prepared with low silanol group concentration, and fully characterized by analytical methods. The adsorption of CO₂ and light hydrocarbons has been investigated using volumetric adsorption isotherms. The polarizability affects significantly the adsorption properties such as adsorption capacities, enthalpies and entropies of the hydrocarbons in the siliceous zeolites. For all the siliceous zeolites we have studied, the calculated heat of adsorption was found to increase linearly with alkane chain length, and alkanes adsorbed stronger than alkenes. Although the contribution of quadrupole-electric field gradient between CO₂ and siliceous zeolites to the total adsorption energy is low in comparison with low silica zeolites, we still observed a significant difference in the adsorption heats and adsorption capacity of CO₂ over CH₄ in these siliceous zeolites. With narrow pore openings, RRO seems to be a potential candidate for the separation of CO₂ from methane in natural gas mixture. At high adsorption pressure, lower liquid volume adsorbates pack more efficiently, thus occupied in the zeolite pores with higher concentration. The steric hindrance in AEI, CHA, and RRO zeolites allow only propylene to diffuse into the

materials pores, but exclude larger molecules. The feasibility of AEI, CHA, and RRO zeolites for propane-propylene separations based on both kinetic and adsorption equilibria needed to be further studied, particularly measuring the diffusion coefficients. Our experimental data is also useful for testing the validity of the assumptions and calculated adsorption isotherms using gas-solid molecular simulations.

AUTHOR INFORMATION

Corresponding Author: Raul F. Lobo

Contact information:

Email: lobo@udel.edu

Phone: 302-831-1261

Fax: 302-831-1048

Author Contributions

Trong D. Pham: Pure silica zeolites synthesis, Scanning Electron Microscope, X-Ray Diffraction, Adsorption isotherms and experimental data analysis.

Raul F. Lobo: Manuscript preparation and direction of research

ACKNOWLEDGMENT

This work was supported by the National Science Foundation through grant CBET-940768. Trong Pham acknowledges support from Vietnam Education Foundation (VEF). We thank SACHEM Inc for providing TMAdaOH, and DMDPA-OH chemicals, and Dr. Guangjin Hou at University of Delaware for the help with ^{29}Si MAS-NMR experiments.

REFERENCES

- [1] M. Kh. M, I. Ya. I, Catalytic Properties of Zeolites? A General Review, Molecular Sieves, AMERICAN CHEMICAL SOCIETY 1973, pp. 451-460.
- [2] A. Primo, H. Garcia, Zeolites as catalysts in oil refining, Chem Soc Rev, 43 (2014) 7548-7561.
- [3] O. Cheung, N. Hedin, Zeolites and related sorbents with narrow pores for CO₂ separation from flue gas, RSC Advances, 4 (2014) 14480-14494.
- [4] J. Li, H. Chang, L. Ma, J. Hao, R.T. Yang, Low-temperature selective catalytic reduction of NO_x with NH₃ over metal oxide and zeolite catalysts—A review, Catalysis Today, 175 (2011) 147-156.
- [5] S. Kesraoui-Ouki, C.R. Cheeseman, R. Perry, Natural zeolite utilisation in pollution control: A review of applications to metals' effluents, Journal of Chemical Technology & Biotechnology, 59 (1994) 121-126.
- [6] S.C. Reyes, D.H. Olson, H. Liu, K.G. Strohmaier, J.G. Santiesteban, Light hydrocarbon separation using 8-member ring zeolites, Google Patents 2008.
- [7] M.A. Saada, M. Soulard, B. Marler, H. Gies, J. Patarin, High-Pressure Water Intrusion Investigation of Pure Silica RUB-41 and S-SOD Zeolite Materials, J Phys Chem C, 115 (2011) 425-430.
- [8] M. Trzpit, S. Rigolet, J.L. Paillaud, C. Marichal, M. Soulard, J. Patarin, Pure silica chabazite molecular spring: A structural study on water intrusion-extrusion processes, J Phys Chem B, 112 (2008) 7257-7266.
- [9] E.M. Flanigen, J.M. Bennett, R.W. Grose, J.P. Cohen, R.L. Patton, R.M. Kirchner, J.V. Smith, Silicalite, a New Hydrophobic Crystalline Silica Molecular-Sieve, Nature, 271 (1978) 512-516.
- [10] G.X. Niu, Y. Huang, X.Y. Chen, J.M. He, Y. Liu, A. He, Thermal and hydrothermal stability of siliceous Y zeolite and its application to high-temperature catalytic combustion, Appl Catal B-Environ, 21 (1999) 63-70.
- [11] D.H. Olson, Light hydrocarbon separation using 8-member ring zeolites, The Trustees of the University of Pennsylvania, USA .2002, pp. 23 pp., Cont.-in-part of U.S. Ser. No. 768,943, abandoned.
- [12] R.B. Eldridge, Olefin Paraffin Separation Technology - a Review, Ind Eng Chem Res, 32 (1993) 2208-2212.
- [13] D.H. Olson, M.A. Camblor, L.A. Villaescusa, G.H. Kuehl, Light hydrocarbon sorption properties of pure silica Si-CHA and ITQ-3 and high silica ZSM-58, Micropor Mesopor Mat, 67 (2004) 27-33.
- [14] R.B. Eldridge, Olefin/paraffin separation technology: a review, Ind Eng Chem Res, 32 (1993) 2208-2212.
- [15] W. Zhu, F. Kapteijn, J. A. Moulijn, Shape selectivity in the adsorption of propane/propene on the all-silica DD3R, Chem Commun, (1999) 2453-2454.
- [16] M. Palomino, A. Corma, J.L. Jorda, F. Rey, S. Valencia, Zeolite Rho: a highly selective adsorbent for CO₂/CH₄ separation induced by a structural phase modification, Chem Commun, 48 (2012) 215-217.
- [17] M. Palomino, A. Corma, F. Rey, S. Valencia, New Insights on CO₂-Methane Separation Using LTA Zeolites with Different Si/Al Ratios and a First Comparison with MOFs, Langmuir, 26 (2009) 1910-1917.

- [18] A.M. Beale, F. Gao, I. Lezcano-Gonzalez, C.H.F. Peden, J. Szanyi, Recent advances in automotive catalysis for NO_x emission control by small-pore microporous materials, *Chem Soc Rev*, 44 (2015) 7371-7405.
- [19] F. Gao, J.H. Kwak, J. Szanyi, C.H.F. Peden, Current Understanding of Cu-Exchanged Chabazite Molecular Sieves for Use as Commercial Diesel Engine DeNO_x Catalysts, *Top Catal*, 56 (2013) 1441-1459.
- [20] U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity, *Angewandte Chemie International Edition*, 51 (2012) 5810-5831.
- [21] P. Tian, Y. Wei, M. Ye, Z. Liu, Methanol to Olefins (MTO): From Fundamentals to Commercialization, *ACS Catalysis*, 5 (2015) 1922-1938.
- [22] T. Pham, Experimental Investigations of the Structure-Property Relations of CO₂-Selective Zeolite Adsorbents, PhD thesis, (2015) 194-232.
- [23] S. Himeno, M. Takenaka, S. Shimura, Light gas adsorption of all-silica DDR- and MFI-type zeolite: computational and experimental investigation, *Molecular Simulation*, 34 (2008) 1329-1336.
- [24] W. Zhu, F. Kapteijn, J.A. Moulijn, Equilibrium adsorption of light alkanes in silicalite-1 by the inertial microbalance technique, *Adsorption-Journal of the International Adsorption Society*, 6 (2000) 159-167.
- [25] W. Zhu, F. Kapteijn, J.A. Moulijn, Adsorption of light alkanes on silicalite-1: Reconciliation of experimental data and molecular simulations, *Physical Chemistry Chemical Physics*, 2 (2000) 1989-1995.
- [26] M. Schenk, S.L. Vidal, T.J.H. Vlucht, B. Smit, R. Krishna, Separation of alkane isomers by exploiting entropy effects during adsorption on silicalite-1: A configurational-bias Monte Carlo simulation study, *Langmuir*, 17 (2001) 1558-1570.
- [27] R. Krishna, D. Paschek, Molecular simulations of adsorption and siting of light alkanes in silicalite-1, *Physical Chemistry Chemical Physics*, 3 (2001) 453-462.
- [28] A.J. O'Malley, C.R.A. Catlow, Molecular dynamics simulations of longer n-alkanes in silicalite: a comparison of framework and hydrocarbon models, *Physical Chemistry Chemical Physics*, 15 (2013) 19024-19030.
- [29] I. Hussain, J.O. Titiloye, Molecular dynamics simulations of the adsorption and diffusion behavior of pure and mixed alkanes in silicalite, *Micropor Mesopor Mat*, 85 (2005) 143-156.
- [30] A. Simmen, L.B. McCusker, C. Baerlocher, W.M. Meier, The structure determination and rietveld refinement of the aluminophosphate AIPO₄-18, *Zeolites*, 11 (1991) 654-661.
- [31] J.V. Smith, CRYSTAL STRUCTURES WITH A CHABAZITE FRAMEWORK .1. DEHYDRATED CA-CHABAZITE, *Acta Crystallographica*, 15 (1962) 835-&.
- [32] J.V. Smith, L.S.D. Glasser, F. Rinaldi, CRYSTAL STRUCTURES WITH A CHABAZITE FRAMEWORK .2. HYDRATED CA-CHABAZITE AT ROOM TEMPERATURE, *Acta Crystallographica*, 16 (1963) 45-&.
- [33] M.A. Camblor, M.J. Diaz-Cabanas, P.A. Cox, I.J. Shannon, P.A. Wright, R.E. Morris, A synthesis, MAS NMR, synchrotron X-ray powder diffraction, and computational study of zeolite SSZ-23, *Chemistry of Materials*, 11 (1999) 2878-2885.

- [34] M.A. Camblor, M.J. Diaz-Cabanas, J. Perez-Pariente, S.J. Teat, W. Clegg, I.J. Shannon, P. Lightfoot, P.A. Wright, R.E. Morris, SSZ-23: An odd zeolite with pore openings of seven and nine tetrahedral atoms, *Angewandte Chemie-International Edition*, 37 (1998) 2122-2126.
- [35] J.J. Gutiérrez-Sevillano, D. Dubbeldam, F. Rey, S. Valencia, M. Palomino, A. Martín-Calvo, S.a. Calero, Analysis of the ITQ-12 Zeolite Performance in Propane–Propylene Separations Using a Combination of Experiments and Molecular Simulations, *The Journal of Physical Chemistry C*, 114 (2010) 14907-14914.
- [36] T.D. Pham, R.C. Xiong, S.I. Sandler, R.F. Lobo, Experimental and computational studies on the adsorption of CO₂ and N₂ on pure silica zeolites, *Micropor Mesopor Mat*, 185 (2014) 157-166.
- [37] Y.X. Wang, H. Gies, B. Marler, U. Muller, Synthesis and crystal structure of zeolite RUB-41 obtained as calcination product of a layered precursor: a systematic approach to a new synthesis route, *Chem Mater*, 17 (2005) 43-49.
- [38] S.I. Zones, Y. Nakagawa, S.T. Evans, G.S. Lee, Synthesis, properties, and applications of small-pore zeolite SSZ-39 for use as petroleum refining catalysts, *Chevron U.S.A. Inc., USA* .1999, pp. 13 pp.
- [39] G. Cao, K.G. Strohmaier, H. Li, A.S. Guram, R.J. Saxton, M.T. Muraoka, J.C. Yoder, K. Yaccatu, Synthesis of AEI-type zeolites and their use in the conversion of oxygenates to olefins, *Exxonmobil Chemical Patents Inc., USA* .2005, pp. 33 pp.
- [40] B.A. De Moor, M.-F.o. Reyniers, O.C. Gobin, J.A. Lercher, G.B. Marin, Adsorption of C₂–C₈ n-Alkanes in Zeolites†, *The Journal of Physical Chemistry C*, 115 (2010) 1204-1219.
- [41] M.A. Camblor, M.-J. Díaz-Cabañas, J. Perez-Pariente, S.J. Teat, W. Clegg, I.J. Shannon, P. Lightfoot, P.A. Wright, R.E. Morris, SSZ-23: An Odd Zeolite with Pore Openings of Seven and Nine Tetrahedral Atoms, *Angewandte Chemie International Edition*, 37 (1998) 2122-2126.
- [42] M.-J. Diaz-Cabanas, P. A. Barrett, Synthesis and structure of pure SiO₂ chabazite: the SiO₂ polymorph with the lowest framework density, *Chem Commun*, (1998) 1881-1882.
- [43] M. Dusselier, M.A. Deimund, J.E. Schmidt, M.E. Davis, Methanol-to-Olefins Catalysis with Hydrothermally Treated Zeolite SSZ-39, *ACS Catalysis*, 5 (2015) 6078-6085.
- [44] J.R. Li, R.J. Kuppler, H.C. Zhou, Selective gas adsorption and separation in metal-organic frameworks, *Chem Soc Rev*, 38 (2009) 1477-1504.
- [45] J.A. Dunne, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, Calorimetric heats of adsorption and adsorption isotherms .2. O₂, N₂, Ar, CO₂, CH₄, C₂H₆, and SF₆ on NaX, H-ZSM-5, and Na-ZSM-5 zeolites, *Langmuir*, 12 (1996) 5896-5904.
- [46] B. Liu, B. Smit, Molecular Simulation Studies of Separation of CO₂/N₂, CO₂/CH₄, and CH₄/N₂ by ZIFs, *J Phys Chem C*, 114 (2010) 8515-8522.
- [47] J. Kim, L.-C. Lin, R.L. Martin, J.A. Swisher, M. Haranczyk, B. Smit, Large-Scale Computational Screening of Zeolites for Ethane/Ethene Separation, *Langmuir*, 28 (2012) 11914-11919.
- [48] A.F. Combariza, D.A. Gomez, G. Sastre, Simulating the properties of small pore silica zeolites using interatomic potentials, *Chem Soc Rev*, 42 (2013) 114-127.
- [49] A.F. Combariza, G. Sastre, A. Corma, Molecular Dynamics Simulations of the Diffusion of Small Chain Hydrocarbons in 8-Ring Zeolites, *The Journal of Physical Chemistry C*, 115 (2011) 875-884.
- [50] J.-Y. Luo, A. Yezerets, C. Aleksey, H. Hess, K. Kamasamudram, H.-Y. Chen, W. Epling, Hydrocarbon Poisoning of Cu-Zeolite SCR Catalysts, *SAE Technical Paper*, (2012) 1-11.

- [51] B. Paul, METHANOL TO OLEFINS (MTO) AND BEYOND, Zeolites for Cleaner Technologies, PUBLISHED BY IMPERIAL COLLEGE PRESS AND DISTRIBUTED BY WORLD SCIENTIFIC PUBLISHING CO.2002, pp. 239-260.
- [52] W. Zhu, F. Kapteijn, J.A. Moulijn, Shape selectivity in the adsorption of propane/propene on the all-silica DD3R, Chem Commun, (1999) 2453-2454.
- [53] T. Dueren, L. Sarkisov, O.M. Yaghi, R.Q. Snurr, Design of New Materials for Methane Storage, Langmuir, 20 (2004) 2683-2689.
- [54] J. Yang, J. Li, W. Wang, L. Li, J. Li, Adsorption of CO₂, CH₄, and N₂ on 8-, 10-, and 12-Membered Ring Hydrophobic Microporous High-Silica Zeolites: DDR, Silicalite-1, and Beta, Ind Eng Chem Res, 52 (2013) 17856-17864.
- [55] M. Palomino, A. Corma, F. Rey, S. Valencia, New Insights on CO₂-Methane Separation Using LTA Zeolites with Different Si/Al Ratios and a First Comparison with MOFs, Langmuir, 26 (2010) 1910-1917.
- [56] J.-M. Leyssale, G.K. Papadopoulos, D.N. Theodorou, Sorption Thermodynamics of CO₂, CH₄, and Their Mixtures in the ITQ-1 Zeolite as Revealed by Molecular Simulations, The Journal of Physical Chemistry B, 110 (2006) 22742-22753.
- [57] Y. Shen, J. Bai, A new kind CO₂/CH₄ separation material: open ended nitrogen doped carbon nanotubes formed by direct pyrolysis of metal organic frameworks, Chem Commun, 46 (2010) 1308-1310.
- [58] Q. Yang, C. Zhong, Molecular Simulation of Carbon Dioxide/Methane/Hydrogen Mixture Adsorption in Metal-Organic Frameworks, The Journal of Physical Chemistry B, 110 (2006) 17776-17783.
- [59] M. Saleh, H.M. Lee, K.C. Kemp, K.S. Kim, Highly Stable CO₂/N₂ and CO₂/CH₄ Selectivity in Hyper-Cross-Linked Heterocyclic Porous Polymers, ACS Applied Materials & Interfaces, 6 (2014) 7325-7333.
- [60] M.S. Sun, D.B. Shah, H.H. Xu, O. Talu, Adsorption Equilibria of C₁ to C₄ Alkanes, CO₂, and SF₆ on Silicalite, The Journal of Physical Chemistry B, 102 (1998) 1466-1473.
- [61] M.S. Sun, D.B. Shah, H.H. Xu, O. Talu, Adsorption Equilibria of C₁ to C₄ Alkanes, CO₂, and SF₆ on Silicalite, J. Phys. Chem. B, 102 (1998) 1466-1473.
- [62] H. Stach, K. Fiedler, J. Janchen, CORRELATION BETWEEN INITIAL HEATS OF ADSORPTION AND STRUCTURAL PARAMETERS OF MOLECULAR-SIEVES WITH DIFFERENT CHEMICAL-COMPOSITION - A CALORIMETRIC STUDY, Pure and Applied Chemistry, 65 (1993) 2193-2200.
- [63] Y.P. Ryazantsev, EQUILIBRIUM ADSORPTION OF C₅-C₈ ALKANES ON MGNAA ZEOLITE AT CRITICAL-TEMPERATURES, Zhurnal Fizicheskoi Khimii, 53 (1979) 504-506.
- [64] B. Smit, J.I. Siepmann, COMPUTER-SIMULATIONS OF THE ENERGETICS AND SITING OF N-ALKANES IN ZEOLITES, Journal of Physical Chemistry, 98 (1994) 8442-8452.
- [65] S.P. Bates, W.J.M. van Well, R.A. van Santen, B. Smit, Energetics of n-Alkanes in Zeolites: A Configurational-Bias Monte Carlo Investigation into Pore Size Dependence, J. Am. Chem. Soc., 118 (1996) 6753-6759.
- [66] S.P. Bates, W.J.M. vanWell, R.A. vanSanten, B. Smit, Location and conformation of N-alkanes in zeolites: An analysis of configurational-bias Monte Carlo calculations, Journal of Physical Chemistry, 100 (1996) 17573-17581.
- [67] B. Smit, SIMULATING THE ADSORPTION-ISOTHERMS OF METHANE, ETHANE, AND PROPANE IN THE ZEOLITE SILICALITE, Journal of Physical Chemistry, 99 (1995) 5597-5603.

[68] F. Eder, J.A. Lercher, On the Role of the Pore Size and Tortuosity for Sorption of Alkanes in Molecular Sieves, *The Journal of Physical Chemistry B*, 101 (1997) 1273-1278.
 [69] L. Rees, D. Shen, Chapter 13 Adsorption of gases in zeolite molecular sieves, *Introduction to Zeolite Science and Practice*, Elsevier 2001, pp. 579-631.

Tables

Table 1: Pore shape, dimension, surface area, and micropore volume of pure silica zeolites

Adsorbents	Pore dimension (window size)	Pore Shape	Surface area m ² /g	Micropore volume cm ³ /g
AEI	8x8x8	pear-shape	613	0.27
CHA	8x8x8	ellipsoidal	604	0.27
RRO	8x10	channels	452	0.19
STT	9x9	ellipsoidal	462	0.19

Table 2: Properties of adsorbate gases [44]

Gas	MW (g/mol)	Kinetics diameters (Å)	Liquid volume (cm ³ /mol)	Polarizability (x10 ⁻²⁵ cm ³)	Dipole (x10 ⁻¹⁸ esu.cm)	Quadrupole (x10 ⁻²⁶ esu.cm ²)
CH₄	16	3.8	37.8	26	0	0
C₂H₄	28	4.16	49.4	42.5	0	1.5
C₂H₆	30	4.44	55	44.3-44.7	0	0.65

C₃H₆	42	4.68	69.1	62.6	0.366	-
C₃H₈	44	4.3-5.17	75.7	62.9-63.7	0.084	-
CO₂	44	3.3	37.4	29.1	0	4.3
N₂	28	3.64	34.7	17.4	0	1.52

Table 3: Adsorption heats at zero coverage limit of gases and selectivity of CO₂/CH₄ over studied zeolites

Adsorbents	Q _o st (kJ/mol)						Selectivity CO ₂ /CH ₄
	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
AEI	26.2	16.6	23.4	26.7	-	-	4.7
CHA	23.1	16.8	25.5	26.4	33.8	-	5
STT	23.5	15.9	25.8	27.0	34.8	35.9	5.4
RRO	28.6	18.0	22.4	23.0	33.2	-	19.5

Table 4: Experimental adsorption entropies of adsorbates in siliceous zeolites

Adsorbents	ΔS (J.K ⁻¹ .mol ⁻¹)					
	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
AEI	91.5	68.5	72.3	74.2	-	-
CHA	83.5	70	77.8	74.4	81.4	-
STT	84.2	65.5	77	75.5	83	83.5
RRO	88.5	75.5	78.6	80.9	92.5	-

Figure captions

Figure 1. Structure of AEI, CHA, STT, and RRO framework-type zeolites

Note: Oxygen atoms were omitted for clarity. The distances reported in the pictures are Si-Si distances in each zeolite framework. The unrestrained distances for gas molecules to pass through are roughly obtained by subtracting the O atoms' diameters (~2.5 Å).

Figure 2. X-ray diffraction patterns of siliceous zeolites AEI and RRO-type materials. The second set of patterns displays the superposition of the as-made RUB-39 and the calcined RUB-41 zeolite

Figure 3. SEM images and XRD patterns of AEI (left) and RRO (right) siliceous zeolites

Figure 4. ²⁹Si MAS NMR spectra of AEI (left) and RRO (right) siliceous zeolites

Figure 5. Adsorption isotherms of CO₂, N₂, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ on STT siliceous zeolite at ambient temperature (303K) up to pressure 101.325 kPa

Figure 6. Adsorption isotherms of CO₂ (top-left), CH₄ (top-right), C₂H₄ (bottom-left), C₂H₆ (bottom-right), on AEI, CHA, STT, and RRO siliceous zeolites at ambient temperature (303K) up to pressure 101.325 kPa

Figure 7. Adsorption heats of CO₂ and small hydrocarbons adsorbed on AEI, CHA, STT, and RRO siliceous zeolites

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7: