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CO_2 and N_2 Adsorption on the Acid (HCl, HNO_3, H_2SO_4 and H_3PO_4) Treated Zeolites

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Abstract. CO_2 and N_2 adsorption on the acid treated natural and synthetic zeolites at 5°C and 25°C was studied. The system heterogeneity was higher for CO_2 than N_2 adsorption and decreased with acid treatment.

Keywords: adsorption, acid treatment, natural zeolites, heterogeneity

Introduction

Zeolites are porous crystalline aluminosilicates whose framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms to form an open crystal lattice containing pores of molecular dimensions into which molecules can penetrate. The negative charge created by the substitution of an AlO_4 tetrahedron for a SiO_4 tetrahedron is balanced by exchangeable cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}), which are located in the structural channels and cavities throughout the structure. These cations play a very important role in determining the adsorption and gas separation properties of zeolites. These properties depend heavily on the size, charge density, and distribution of cations in the porous structure (Zhao et al., 1998). There are more than 50 different available types of aluminosilicate zeolites with pore openings ranging from less than 0.5 nm to larger than 1 nm (Webster et al., 1999). Clinoptilolite is the most abundant of the natural zeolite mineral which have Si/Al ratio ranging between 3 and 5. Mineral compositions and purity vary widely among the many natural zeolite deposits found throughout the world (Ackley et al., 1991). Such deposits are commercially important because clinoptilolite rich tuffs are often rather pure and can be mined with simple techniques (Armbruster, 2001). Clinoptilolite containing tuffs represent major sources of microporous zeolites and are widely used as adsorbents for gas and liquid systems and its adsorption capacity being increased after chemical treatment (Tsitsishvili et al., 1992). Due to its superior structure properties, clinoptilolite has many industrial applications; gas, radioactive and wastewater cleaning, gas separation, and gas drying. For example natural zeolites, primarily chabazite and clinoptilolite have been used to purify natural gas contaminated with large amounts of CO_2, H_2S and H_2O (Armenta et al., 2001). Adsorption properties of natural zeolites can be tailored with different techniques. One of the techniques for altering these properties is the treatment of the natural zeolites with mineral acids. The acid treatment exchanges cations of the zeolite with H^+ and causes dealumination of the zeolite structure. Furthermore, dealumination can cause partial or total destruction of the zeolite framework. Acid treatment also leads to a modification in zeolite morphology, by destruction of channel-blocking impurities and the development of the secondary porosity (Hernandez et al., 1999). It's stated in literature that the treatment of zeolites with weak acids such as H_3PO_4, opens possibilities for the removal of impurities and for the improvement of the cationic composition of the sample with low dealumination and with a smaller decrease of crystallinity than with strong acids like HCl (Malharbe, 2001). In this study, the CO_2 and N_2 adsorption on acid treated natural zeolites and also synthetic zeolites at 5 and 25°C was investigated. Sips and Langmuir adsorption

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model equation parameters were analyzed in order to investigate the change in the energetic heterogeneity of the zeolites due to acid treatment and adsorption temperature.

Experimental

The adsorbents used in this study were natural zeolite from Gördes, Turkey and its acid treated forms as well as A and X type synthetic zeolites (Table 1). Natural zeolite was rich in clinoptilolite and its chemical composition (oxide wt.-%) was 14.1 Al_2O_3, 64.2 SiO_2, 1.8 MgO, 1.7 Na_2O, 5.3 K_2O, 1.0 CaO, 1.8 Fe_2O_3, and 10.3 H_2O. The cation variety of the natural zeolite (NCW) was decreased depending on the nature of the acid used and the conditions applied in acid treatment and so Si/Al ratio of the zeolites was increased. The characterization of these zeolites was given elsewhere (Becer, 2003). The acid treatment conditions and N_2 adsorption properties obtained by using Micromeritics ASAP 2010 device at 77 K are given in Table 1. As can be seen from the table accessible volume (V_{mic}) and surface area (A_L) were increased with acid treatment. By treating the zeolite with the weak acid H_3PO_4 the microporous structure was improved to high extend without decreasing the crystallinity. In the treatment of zeolite with strong acids; HCl and HNO_3 the crystalline structure was damaged. The gases used were highly pure (purity higher than 99%). CO_2 gas was further purified by using a three cartridge system filter to remove water, oxygen and hydrocarbons. The volumetric adsorption device Micromeritics (ASAP 2010) was used to perform CO_2 and N_2 adsorption experiments at 5 and 25°C. In order to be able to keep the adsorption temperature constant, circulating water bath was used and all the tubing was covered with the insulation material. Prior to adsorption experiments, the zeolites were outgased at 350°C for 24 hours under 10^{-5} mbar vacuum.

Results and Discussion

The CO_2 and N_2 adsorption isotherms are presented in Figs. 1 and 2 respectively. There is a sharp increase in the CO_2 amount adsorbed by the zeolites at low equilibrium pressure and the CO_2 adsorption isotherms are almost in rectangular shape. The zeolites which adsorb CO_2 the most are the synthetic zeolites namely 5A and 13X. The N_2 amount adsorbed by the zeolites changed almost linearly with equilibrium pressure for synthetic zeolites (Fig. 2). However, N_2 adsorption isotherms of natural zeolites are more favorable. Natural zeolites adsorb more N_2 than synthetic zeolites at low pressure. The CO_2 adsorption was not hindered by the zeolite structure as in the N_2 adsorption because CO_2 molecule is smaller than N_2 molecule (kinetic diameter: 0.330 and 0.364 nm for CO_2 and N_2 respectively). Consequently, the adsorbed amount of CO_2 is greater than that of N_2. Adsorption isotherms were somewhat affected by acid treatment; the slight decrease in CO_2 amount adsorbed at 91 kPa (q_{max}) was observed (Table 2). The cations in zeolite structure, whose amount are related to the Si/Al ratio, are the center of electrostatic interactions for the CO_2 molecules, these specific interactions are not expected for N_2 molecule. For that reason the effect of acid treatment was not clear in N_2 adsorption case, although it was determined that the accessible

Table 1. The adsorbents used in this study.

Zeolite code	Definition and treatment conditions	Si/Al	V^*_{mic}	A^*_{ext}	$A^{\#}_L$	r^+
NCW	Natural zeolite tuff washed with distilled water for 2 hours at 60°C	4.04	0.005	3.08	19	1.3
C3-3h	Treated with 3 M HCl Solution for 3 hours at 60°C	6.08	0.056	17.2	182	0.65
C5-6h	Treated with 5 M HCl Solution for 6 hours at 60°C	8.40	0.063	25.8	213	0.63
P1-6h	Treated with 1.1 M H_3PO_4 Solution 6 hours at 60°C	5.01	0.068	22.5	226	0.6
N2-6h	Treated with 2 M HNO_3 Solution for 6 hours at 60°C	6.18	0.04	6.5	118	0.6
S2-6h	Treated with 2 M H_2SO_4 Solution for 6 hours at 60°C	5.35	0.048	33.8	202	0.58
5A	Synthetic zeolite-Aldrich (Lot # 04224HA)	0.98	0.17	19.5	529	0.92
13X	Synthetic zeolite-Aldrich (Lot # 04603BR)	1.35	0.24	28.3	771	0.54

$^*V_{\text{mic}}$ Micropore volume (ml/g); A_{ext} external surface area, (m^2/g) from t-plot method.
$^{\#}A_L$ Langmuir surface area (m^2/g) from Langmuir method.
^+r Median Pore Diameter (nm) from Horvath Kawazoe method.

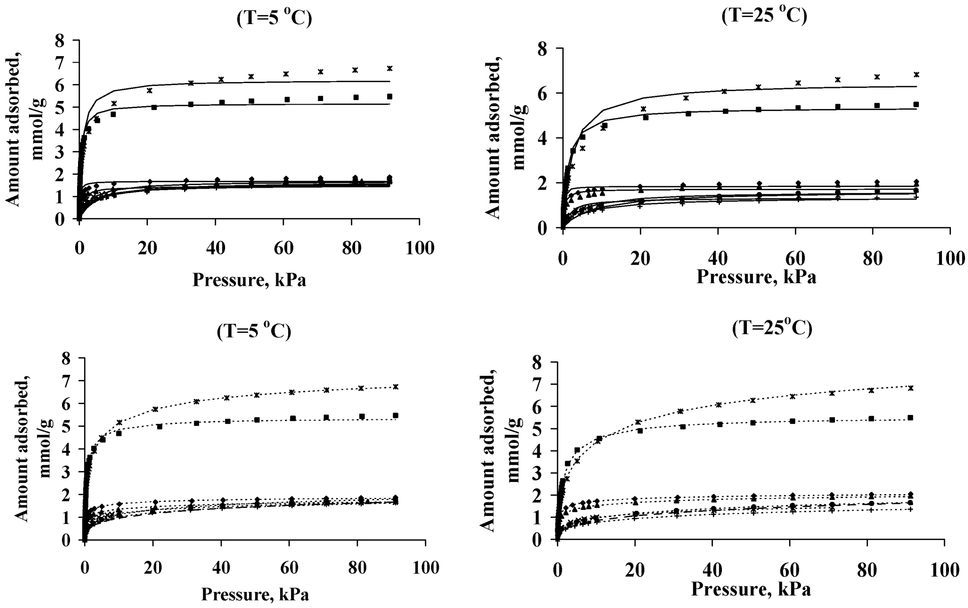

Figure 1. Experimental (symbols), Langmuir (line) and Sips model (dashed line) CO_2 adsorption isotherms of NCW (◇), C3-3h (●), C5-6h (×), P1-6h (▲), N2-6h (+), S2-6 h (- - -) , 5A (■), and 13X (*) zeolites at 5°C and 25°C.

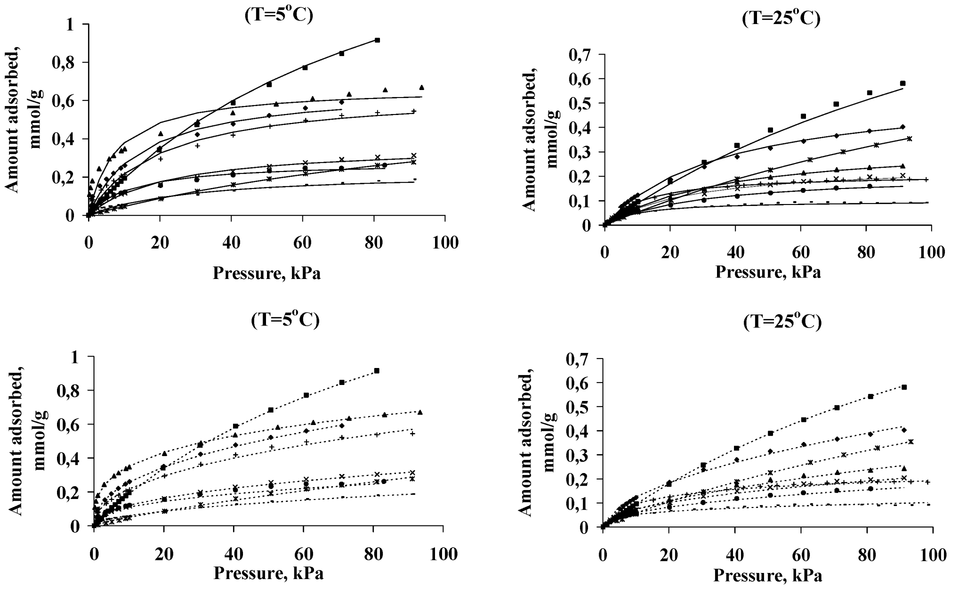

Figure 2. Experimental (symbols), Langmuir (line) and Sips model (dashed line) N_2 adsorption isotherms of NCW (♦), C3-3h (●), C5-6h (×), P1-6h (▲), N2-6h (+), S2-6h (- - -) , 5A (■), and 13X (∗) zeolites at 5°C and 25°C.

area (A_L) and volume (V_{mic}) were increased with acid treatment (Table 1).

As can be seen from Table 2, the $q_{\max}$ for N_2 molecule is influenced the most by the temperature increment while for the CO_2 adsorption temperature effect was not considerably high. This shows that the isosteric heat of CO_2 adsorption is independent of the temperature (Cao and Sircar, 2001).

Table 2. The amount adsorbed at 91 kPa and model parameters of the zeolites for CO_2 and N_2 Adsorption at 5°C.

				CO_2					N_2				
				Langmuir parameters		Sips parameters			Langmuir parameters		Sips parameters		
Zeolites	Si/Al	$q_{\max}$ for CO_2	$q_{\max}$ for N_2	b (kPa^{-1})	n_m (mmol/g)	b (kPa^{-1})	n_m mmol/g	t (−)	b (kPa^{-1})	n_m (mmol/g)	b (kPa^{-1})	n_m mmol/g	t (−)
NCW	4.04	1.87	0.59	5.09	1.68	2.25	2.03	2.41	0.067	0.67	4.9×10^{-5}	8.21	2.22
C3-3h	6.08	1.79	0.26	0.31	1.69	0.02	3.21	2.59	0.084	0.28	2×10^{-6}	7.94	2.54
C5-6h	8.4	1.66	0.31	1.15	1.46	0.05	2.64	3.07	0.045	0.37	7.9×10^{-6}	8.34	2.24
P1-6h	5.01	1.70	0.66	0.27	1.51	0.53	2.16	3.18	0.130	0.67	1.5×10^{-4}	3.56	2.94
N2-6h	6.18	1.63	0.54	0.26	1.57	0.026	2.76	2.49	0.050	0.65	3.6×10^{-5}	8.33	2.19
S2-6h	5.35	1.69	0.19	0.19	1.65	0.008	3.55	2.56	0.034	0.23	7.1×10^{-6}	8.44	1.94
5A	0.98	5.47	0.91	2.02	5.16	1.67	5.40	1.29	0.011	1.95	8.13×10^{-3}	2.26	1.05
13X	1.35	6.73	0.28	1.17	6.21	0.35	7.96	2.06	0.007	0.72	1.7×10^{-4}	8.33	1.25

Langmuir model equation: n (mmol/g) $= n_m$bP (kPa)/[1+bP (kPa)].
Sips equation: $n = n_m$ [bP (kPa)]$^{1/t}$/[1 + [bP (kPa)]$^{1/t}$].

Model Equations

Different model equations were applied to the data obtained from adsorption studies in order to get information regarding the heterogeneity of the adsorbent-adsorbate system and adsorbent affinity towards the adsorbate. The models applied to the data were Langmuir and Sips model equations (Figs. 1 and 2). For N_2 adsorption, correlation coefficients of Langmuir Model were higher than those for CO_2 adsorption at both temperatures (the correlation coefficients >98 and 95% for N_2 and CO_2 respectively). The consistency of the Sips Model with the experimental data was better than in Langmuir Model (the correlation coefficient >99%). The model parameters of the zeolites for adsorption at 5 and 25°C are given in Tables 2 and 3 respectively. Parameter b in Langmuir Model called the affinity constant is a measure of the strength of the interaction between adsorbate molecule and adsorbent surface.

The Langmuir b parameter calculated was considerably high for CO_2 adsorption indicating high affinity of the zeolites towards CO_2. This was due to its higher

Table 3. The amount adsorbed at 91 kPa and model parameters of the zeolites for CO_2 and N_2 Adsorption at 25°C.

				CO_2					N_2				
				Langmuir parameters		Sips parameters			Langmuir parameters		Sips parameters		
Zeolites	Si/Al	$q_{\max}$ for CO_2	$q_{\max}$ for N_2	b (kPa^{-1})	n_m (mmol/g)	b (kPa^{-1})	n_m mmol/g	t (−)	b (kPa^{-1})	n_m (mmol/g)	b (kPa^{-1})	n_m mmol/g	t (−)
NCW	4.04	2.05	0.40	6.64	1.84	1.77	2.30	2.58	0.027	0.56	5.7×10^{-5}	8.44	1.78
C3-3h	6.08	1.66	0.16	0.20	1.61	0.012	3.27	2.45	0.034	0.21	2.1×10^{-6}	8.33	2.19
C5-6h	8.4	1.44	0.20	0.56	1.32	0.042	2.38	2.63	0.038	0.25	3.5×10^{-6}	8.33	2.18
P1-6h	5.01	1.95	0.24	2.65	1.71	0.307	2.59	3.07	0.027	0.34	2.7×10^{-5}	8.33	1.74
N2-6h	6.18	1.36	0.19	0.17	1.35	0.009	2.78	2.44	0.082	0.21	4.6×10^{-2}	0.26	1.47
S2-6h	5.35	1.60	0.09	0.13	1.64	0.004	4.13	2.39	0.095	0.10	1.3×10^{-6}	1.58	3.34
5A	0.98	5.49	0.58	0.76	5.36	0.62	5.6	1.23	0.006	1.58	6.23×10^{-3}	1.62	1.00
13X	1.35	6.82	0.34	0.41	6.46	0.07	9.68	2.02	0.006	1.01	2.74×10^{-3}	1.58	1.10

Langmuir model equation: n (mmol/g) $= n_m$bP (kPa)/[1+bP (kPa)].
Sips equation: $n = n_m$ [bP (kPa)]$^{1/t}$/[1 + [bP (kPa)]$^{1/t}$].

Table 4. Change in the Henry's constant and selectivities towards CO_2.

		k_H (CO_2)		k_H (N_2)		S (CO_2/N_2)	
Zeolites	Si/Al	$T = 5°C$	$T = 25°C$	$T = 5°C$	$T = 25°C$	$T = 5°C$	$T = 25°C$
5A	0.98	10.39	4.09	0.021	0.0102	496	403
13X	1.35	7.29	2.62	0.005	0.006	1459	452
NCW	4.04	8.59	12.24	0.045	0.015	191	827
P1-6h	5.01	4.95	4.54	0.088	0.0093	56	488
S2-6h	5.35	0.31	0.21	0.008	0.010	38	21
C3-3h	6.08	0.52	0.33	0.024	0.007	22	45
N2-6h	6.18	0.41	0.23	0.033	0.017	13	14
C5-6h	8.40	1.68	0.73	0.017	0.0098	99	75

polarizabilitiy constant and larger quadruple moment than N_2 molecule (polarizability: 26.5×10^{-25} cc and 15.8×10^{-25} cc, quadruple moment: 4.30×10^{-26} esu-cm^2 and 1.52×10^{-26} esu cm^2 for CO_2 and N_2 respectively) that causes strong electrostatic interactions besides the dispersive forces. On the other hand in N_2 adsorption, dispersive forces are dominant and hence b parameter is low. The NCW (untreated zeolite), having the highest cation and aluminum content, had the highest b parameter for CO_2 adsorption. As temperature increases, the affinity of zeolites for N_2 decreased (lower b values) while temperature is not as effective as for CO_2 adsorption. Sips equation which can be reduced to Langmuir equation was applied to adsorption data and model equation parameters for the adsorption at 5 and 25°C are given in Tables 2 and 3 respectively. The difference between the Sips model equation and the Langmuir equation is the additional parameter "t" characterizing the system heterogeneity (Do, 1998). Comparison of the t values shows that CO_2-adsorbent system is more heterogeneous than N_2-adsorbent system and the heterogeneity decreased with increasing adsorption temperature. For N_2 adsorption this parameter was about unity for synthetic zeolites so their b values in Sips and Langmuir models were close to each other.

Pure component selectivity S(CO_2/N_2) was calculated by using the ratio of the Henry's constants obtained from the pure component adsorption data. The Langmuir equation was used to calculate Henry's constant, k_H (bn_m), which was related to the interaction parameter between the adsorbent surface and adsorbate molecules. Table 4 shows the change in the Henry's constants and the pure component selectivity towards CO_2. From the adsorption data much lower k_H values were obtained for N_2 than CO_2 adsorption. Therefore, the selectivities given in Table 4 were quite high. The highest selectivity was obtained for the zeolites; 13X at 5°C and for natural zeolite, NCW at 25°C. Although the lowest selectivity was obtained for the zeolite treated with HNO_3 it can still be used for the separation of CO_2 from N_2 since it's greater than 1.

Conclusions

Adsorption studies at low pressure showed that the adsorption temperature was not as much effective for CO_2 adsorption as for N_2 adsorption. Natural zeolite without having any acid treatment has superior capacity for CO_2 and its adsorption capacity decreased with acid treatment. The acid treatment applied in this study was very effective on CO_2 adsorption not on N_2 adsorption. This shows the presence of electrostatic interactions between CO_2 and cationic sites in zeolite even after acid treatment. Among the acid treated natural zeolites, the zeolite treated with 1.1 M H_3PO_4 has comparable amount of adsorption capacity with untreated zeolite. H_2SO_4 and HNO_3 treated zeolites have lower adsorption capacities. Synthetic zeolites 13X and 5A have the highest CO_2 and N_2 amount adsorbed at both temperatures respectively. The affinity of the zeolites towards gases decreased as adsorption temperature increased. Adsorbent-adsorbate heterogeneity was higher for CO_2 adsorption than N_2 adsorption and decreased with increasing temperature. The selectivity of the untreated natural zeolite towards CO_2 is higher than its acid treated forms. N_2 gas can be purified from CO_2 gas down to very low concentration by using either natural, acid treated or synthetic zeolites as shown in the study.

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