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Effect of Ion Exchanged to the CO_2 Adsorption on MFI Zeolites

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The adsorption of CO_2 on MFI (HZSM-5) and ion exchanged MFI (CaZSM-5) zeolites were studied by a temperature programmed desorption (TPD). The adsorption measurements were conducted at temperatures from 323 to 473 K at atmospheric pressure. The results showed that CO_2 was adsorbed on HZSM-5 by one type of adsorption, and on CaZSM-5 zeolites by at least two types of adsorption over the temperature range studied. One was a weak adsorption probably due to interaction with the framework of ZSM-5, and the other was a stronger adsorption caused by interactions with the Ca cations of ZSM-5. The adsorption behavior for HZSM-5 was described by a single site Langmuir adsorption model but for CaZSM-5 a dual site Langmuir model was used. The TPD results indicated that the quantity of irreversibly adsorbed CO_2 on HZSM-5 was undetectable.

Keywords: CO_2 adsorption; ZSM-5; Step change response; Langmuir adsorption model; FTIR spectra

INTRODUCTION

Attention has been given to CO_2 adsorption for separation purposes. CO_2 sequestration based on pressure swing adsorption separation has been studied widely for biogas and natural gas purification with the gas system of CO_2/CH_4, CO_2/N_2 and other CO_2 gas mixtures (Harlick and Tezel 2004, Katoh *et al.* 2000, Siporin *et al.* 2003). Effective CO_2 adsorbents are required for the processes discussed. Thus, the choice of adsorbent becomes the most crucial design consideration for separation methods based on adsorption processes. One of the most widely used adsorbents for CO_2 separation are zeolites especially the MFI type, especially ZSM-5. Highly crystalline zeolites with a high surface area and a three-dimensional pore structure are expected to be a high-performance adsorbent for CO_2 removal. The framework charge of ZSM-5 was balanced by positive charged cations. These cations are exchangeable and influence the adsorption capacity and transport properties of the zeolite. There are many publications concerning CO_2 adsorption over ZSM-5 zeolite (Calleja *et al.* 1994, Calleja, Pau, and Calles 1998, Khelifa *et al.* 2004). It has been shown that CO_2 is more strongly adsorbed on MZSM-5 (M = Na, Li, K) than on HZSM-5 or Silicalite-1 (Choudhary and Mayadevi 1996, Dunne *et al.* 1996, Golden and Sircar 1994, Otto *et al.* 1991, Sun *et al.* 1998, Yamazaki *et al.* 1993). However, the temperature and pressure ranges studied in the literature have been lower than our proposed studied. Higher pressure and temperature observations are needed for the industrial scale application especially for CO_2 removal from water gas shift reaction, natural gas, and hydrogen production for fuel cells. The present work also combines experiments and modeling to fit adsorption isotherms that quantify the types of adsorbed species which has not been dealt with in the cited literature.

In this study transient step change response experiments are carried out to determine the effect of Ca-ion exchange on CO_2 adsorption behavior on HZSM-5 zeolites. This method offers the possibility for determining both the single and multi-component gas adsorption behaviors and studying mass transport and diffusion of components in zeolite particles with a relatively short observation time. In-situ temperature-programmed desorption (TPD) measurements was performed to estimate the adsorption sites and quantities of adsorbed species at different temperatures and gas compositions. Multi-site Langmuir adsorption models could describe how the exchanged cations affect the adsorption strength of different species.

EXPERIMENTAL METHODS

Material Preparation

Ca-ion-exchanged ZSM-5 zeolites. The CaZSM-5 adsorbents were prepared by a conventional triple ion exchange method (Ohman *et al.* 2002) from a commercial HZSM-5 sample (Eka Chemicals, Sweden). This material was ion-exchanged in 0.5 mM solutions of Ca $(NO_3)_2$ at 333K for 3 hours for each ion-exchange stage. The zeolite samples were dried overnight at 383 K and calcined at 773 K for 6 h. A 10 K/min temperature ramp was used to reach the calcination temperature. The composition of the samples was then analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results from the elemental analysis revealed that HZSM-5 samples had Si/Al molar ratios of 27 and CaZSM-5 sample had Ca/Al molar ratio of 0.35.

Gas mixtures. Transient step change adsorption studies of CO_2 on zeolites were performed with He/CO_2 gas mixtures (He as an inert gas). The total gas flow rate was 100 mL/min (ambient). Commercially available carbon dioxide, argon and helium gases with purities greater than 99.999% (AGA, Sweden) were used.

Adsorption and TPD measurements

The adsorptions were performed in a flow reactor with the possibility to switch the feed between pure He to a He/CO_2 gas mixture. The inlet CO_2 gas concentrations

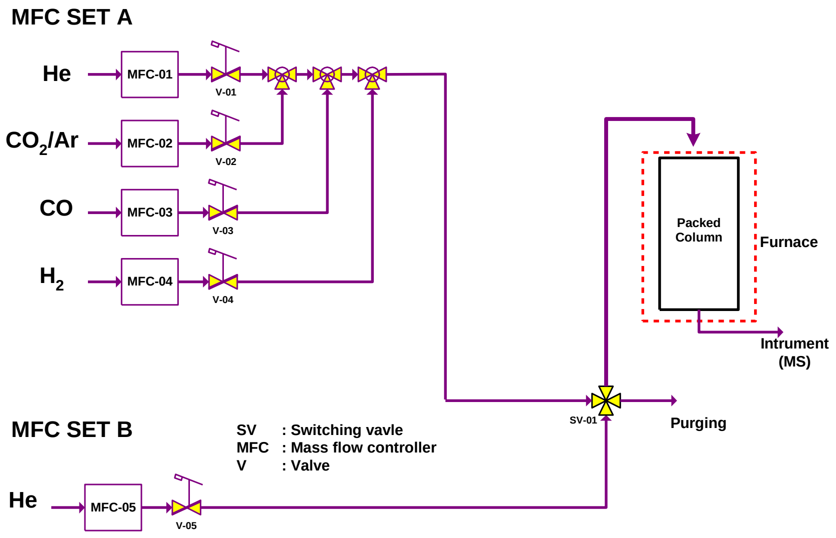

Fig.1: Scheme of adsorption equipment setup

ranged from 10 to 80%. Experiments were conducted with adsorption temperatures of 323, 373 and 473 K and a total pressure of 1 atm. Temperature-programmed desorption (TPD) was conducted to determine the strength of adsorption of species and also to quantify strongly adsorbed species. The temperature ramp used was 15 K/min. Outlet gas concentrations from the reactor were detected by a mass spectrometer (MS). The Mass spectrometer was a triple filter quadrupole gas analyzer, equipped with a dual filament ionizer assembly (Thoriated Iridium), and dual detectors for a fast response (< 100 ms). Tracer experiments using He/Ar gas mixtures were conducted with the adsorbent samples to measure dispersion and time lag effects in the adsorbent bed and reactor system. Pre-treatment of samples involved heating them in a flow of He at 723 K for 4 hours. After the sample was cooled to the desired adsorption temperature, the gas feed was switched to the appropriate adsorption mixture.

Powdered samples of 1.5 to 1.75 g were placed in a quartz glass tube reactor with an inside diameter of 25 mm, length of 70 mm and supported by a quartz glass frit. The feed gas flowed down through the adsorbent bed. Inside the quartz tube and directly downstream the adsorbent bed a thermocouple was placed. The thermocouple measured both the actual adsorbent bed temperature and it regulated the operation of the furnace. The quartz reactor was placed inside a cylindrical shaped furnace. Feed gases were supplied to the reactor system from gas cylinders and their flowrates were regulated by individual mass-flow controllers (MFC). The MFCs were arranged into two sets. Each set of MFCs produced a different mixture of feed gas that could be fed to the reactor. A 4-way valve was used to control which of the feed gas mixtures was fed to the reactor. The gas mixture not fed to the reactor was vented. The scheme of the adsorption setup is presented in Figure 1.

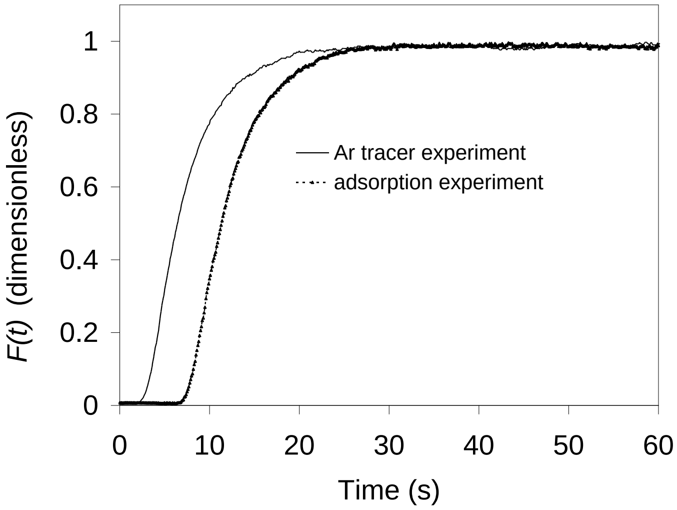

Fig.2: Typical Breakthrough Curve (F(t) vs. time) for tracer and adsorption experiments

Typical breakthrough curves for Ar and CO_2 concentration step changes are illustrated in Figure 2. The ordinate is the cumulative residence time distribution, *F(t)*, which is the concentration (mol%) of CO_2 in the gas phase at some time *t*, *y (t)*, divided by the feed gas concentration y_0, or

$$F(t) = \frac{y(t)}{y_0} \tag{1}$$

Assuming ideal gas behavior and that the adsorption of Ar on the zeolite is negligible compared to that of CO_2, the amount of CO_2 adsorbed per mass of zeolite or CO_2 loading, *q*, can be calculated using the differences in breakthrough curve between the Ar as tracer and CO_2 adsorbed as follows:

$$q = \frac{N_{tot} . y_0 \left[\int_{t=0}^{t=t_e} F(t)_{Ar} dt - \int_{t=0}^{t=t_e} F(t)_{CO_2} dt \right]}{w} \tag{2}$$

where N_{tot} is the total feed flowrate in mmol/s, t_e is the equilibrium time (s) and *w* is the weight of the zeolite sample in gram.

The adsorption data was further analyzed by fitting it to multi-site Langmuir adsorption models (Krishna and Baur 2003). For *i* adsorption sites, the quantity of CO_2 adsorbed is:

$$q = \sum_{i=1}^{ns} q_{sat,i} \frac{K_i P_{CO_2}}{1 + K_i P_{CO_2}} \tag{3}$$

The adsorption equilibrium constant (*K*) can be expressed in terms of the enthalpy (Δ*H*) and entropy (Δ*S*) of adsorption as follows:

$$K = e^{\left(\frac{-\Delta H}{RT} \right)} e^{\left(\frac{\Delta S}{R} \right)} \tag{4}$$

Equation (4) can be reformulated in terms of the mean adsorption equilibrium constant (K_m) at the mean experimental temperature (T_m):

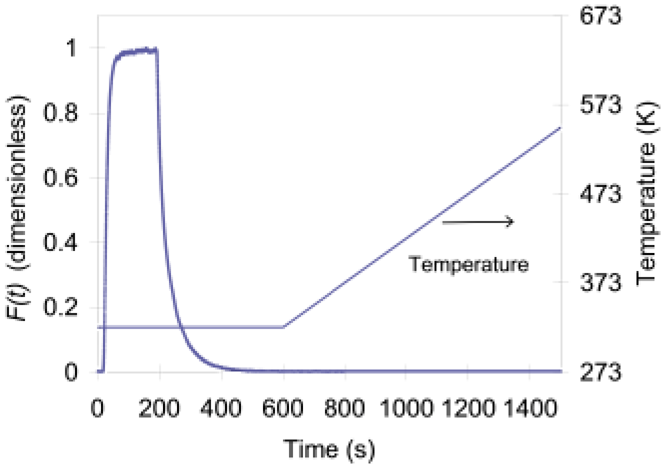

Fig.3: F(t) vs t for CO_2 adsorption, He flushing and TPD on H-ZSM-5 sample (adsorption temperature = 323 K and inlet gas concentration = 80%)

$$K = K_m e^{\left(\frac{-\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right)} \tag{5}$$

By nonlinear regression, Equations (3) and (5) were fitted to the adsorption data with the adjustable parameters K_m, ΔH and q_{sat} for each adsorption site. The adsorption entropy, ΔS, was later calculated from the fitted parameters via Equation (4). Equation (5) and the mean adsorption equilibrium constant (K_m) were used in the regression instead of Equation (4) because of the strong correlation in the enthalpy and entropy of adsorption that would result from the direct use of Equation (4). Statistical analysis was performed including the calculation of individual confidence intervals for each parameter, a correlation analysis, and also parameter significance was examined using the *'t' test* method (Draper and Smith 1998).

RESULTS AND DISCUSSION

Adsorption and TPD

The transient adsorption response (breakthrough curve) of CO_2 adsorption on HZSM-5 is depicted in Figure 3 which contains not only the adsorption results but also the results of He flushing and TPD. The corresponding result for CaZSM-5 can be seen in Figure 4. The amount of zeolites used for HZSM-5 samples was 1.5 g and for CaZSM-5 samples was 1.75 g. Figure 3 and 4 provide only an example of the results from the inlet gas concentrations and temperature variation used. The breakthrough curves show that the gas-phase concentration of CO_2 for HZSM-5 samples (1.5 g) rises faster to achieve equilibrium, than for CaZSM-5 samples (1.75 g). The equilibrium time is the time required for the gas phase concentration of CO_2 to equal the feed concentration (*F(t)* = 1) and the temperature to re-stabilize at the

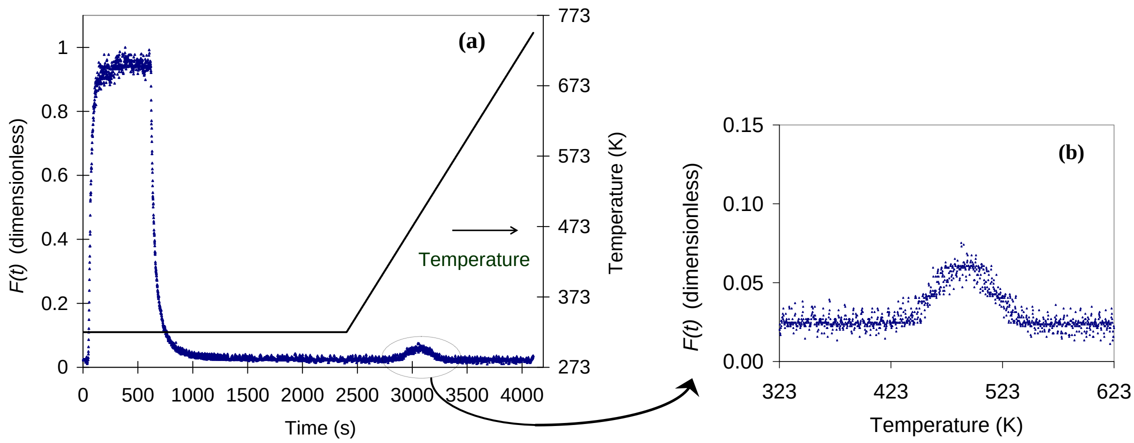

Fig.4: (a) F(t) vs t for CO_2 adsorption, He flushing and TPD on CaZSM-5 sample (b) *F(t)* vs desorption temperature during TPD (adsorption temperature = 323 K and inlet gas concentration = 80%)

adsorption temperature. The equilibrium times for HZSM-5 was about 60-150 s, but for CaZSM-5 it was about 200-500 s. These differences are not only due to the different sample masses but also due to the different adsorption capacities of the samples and residence time distributions of CO_2 in the reactor. During the adsorption period, the bed temperature temporarily increased by about 3-5 K depending on the zeolite sample used and the adsorption conditions. This phenomenon was expected since adsorption is an exothermic process.

Temperature programmed desorption (TPD) experiments were conducted to find out whether adsorbed CO_2 is distributed between physisorbed CO_2 and irreversibly adsorbed species depending on the Si/Al molar ratio and the exchangeable cation. TPD was conducted following saturation with adsorbed CO_2 at 323 K and flushing with He.

The *F(t)* curves during adsorption, flushing and TPD are depicted in Figure 3 and 4. It can be seen that most of the adsorbed CO_2 is released when the samples are flushed with He at 323 K. The release is mainly from physisorbed species. It took a longer period of time to flush the CO_2 from the Ca exchanged samples indicating that there may be a slow release of more strongly adsorbed species from these samples during flushing. After the CO_2 concentration was nearly undetectable, TPD was started by increasing the temperature up to 773 K with a 15 K/min ramp. Additional CO_2 was desorbed during TPD (see Figure 4 (b). The rate of desorption of CO_2 during the TPD started to increase at about 430 K with a maximum at about 495 K and finally became almost undetectable at about 600 K. This observation indicates that chemisorbed (or irreversibly adsorbed) CO_2 was formed during the adsorption on the Ca exchanged samples. However, for the HZSM-5 samples no desorption of CO_2 was detected during TPD.

Data from the step change response experiments have been used to determine the amount of CO_2 adsorbed on the

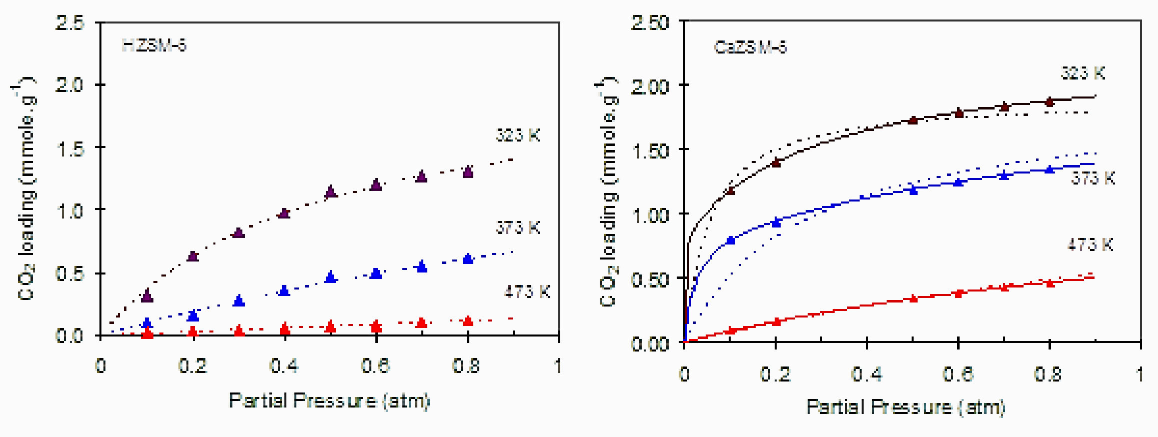

Fig. 5: CO_2 isotherm adsorption curves and Langmuir model fitting (dashed line : single Langmuir model, solid line: dual site Langmuir model; symbols : experimental values)

zeolite samples vs temperature using Equation (2). These results are given in Figure 5 for the temperature range from 323 to 473 K. The isotherm adsorption curves and Langmuir model fitting results for the different samples and temperatures are also presented in Figure 5. It can be seen that the CO_2 loading q increased with the CO_2 partial pressure and decreased with the adsorption temperatures, as was expected. The results revealed that by exchanging the proton for Ca cations, the adsorption is much higher, especially at low partial pressures of CO_2. This suggests that there is a strong interaction between CO_2 and the Ca cations. It is expected that the exchanged cations should neutralize the acidity and develop the basicity of the zeolite framework for adsorbing acidic CO_2 (Barthomeuf, Coudurier, and Vedrine 1988). Thus CaZSM-5 is considered to provide CO_2 molecules with two kinds of adsorption sites; strong adsorption on the cation site and a weaker adsorption on the pore wall itself. The isotherms measured in this study are also consistent with results in the literature for various other cation-exchanged ZSM-5 zeolites (Harlick and Tezel 2004, Choudhary and Mayadevi 1996, Dunne *et al.* 1996, Golden and Sircar 1994, Yamazaki *et al.* 1993). However, the adsorption temperatures studied in the literature were mostly lower than those used in this study.

Langmuir isotherm model

The adsorption isotherms depicted in Figure 5 enabled an estimate of the adsorption capacity (q_{sat}) based on extrapolation of Langmuir type adsorption models to the high pressure region of the adsorption isotherm. The adsorption isotherms were further utilized to evaluate the heat and entropy of adsorption by applying Equations (3), (4), and (5). Single and dual site Langmuir adsorption models were used.

$$q = q_{sat,1}\frac{K_1 P_{CO_2}}{1+K_1 P_{CO_2}} + q_{sat,2}\frac{K_2 P_{CO_2}}{1+K_2 P_{CO_2}} \qquad (6)$$

Table 1: The results of parameters fitted from Langmuir models

Zeolites	q_{sat} (mmol/g)	-Δ*H* (kJ/mol)	-Δ*S* (J/(mol × K))	Langmuir model
H-ZSM-5	2.150 ± 0.006	28.2 ± 0.1 26.1 [a] (Khelifa *et al.* 2004) 28.8 [a] (Yamazaki et al., 1993) 38.0 [a] (Dunne *et al.* 1996)	81.8 ± 0.2	Single site
CaZSM-5	*site 1* 1.522 ± 0.011 *site 2* 0.725 ± 0.021	*site 1* 30.9 ± 0.3 *site 2* 59.9 ± 2.3	*site 1* 85.2 ± 1.0 *site 2* 125.1 ± 2.2	Dual site

[a])results from literature

Table 2: The *'t' test* method results for *site 2* parameters in dual Langmuir model

Zeolites	't' value for additional *site 2* parameters			*'t' test* assignment
	q_{sat}	Δ*H*	Δ*S*	
H-ZSM-5	0.3556 $t_{95\%}$ = 2.1009	0.8998 $t_{95\%}$ = 2.1009	0.8707 $t_{95\%}$ = 2.1009	not significant [a]
CaZSM-5	67.1837 $t_{95\%}$ = 2.1788	65.1973 $t_{95\%}$ = 2.1788	88.1254 $t_{95\%}$ = 2.1788	significant [a]

[a])parameter significant if 't' value > t distribution at 95% degree of confidence

The results of the model fitting are shown in Figure 5. Listed in Table 1 are the parameter values along with their 95% confidence intervals.

The high quality of the fit of the single site model for HZSM-5 and the dual site model for CaZSM-5 suggest that the assumption that the heat of adsorption is constant, is valid at least for the range of conditions used. The evaluated heats of adsorption for HZSM-5 compare well with values reported in the literature (Choudhary and Mayadevi 1996, Dunne *et al.* 1996, Golden and Sircar 1994, Yamazaki *et al.* 1993). The *'t' test* method was applied to examine whether the additional parameters for the 2nd site in the dual site model are significant. The dual site model was fitted to the results for HZSM-5 and CaZSM-5 samples however it was only for the CaZSM-5 sample that the additional parameters for the 2nd site were significant (see Table 2). These modeling results further confirm that the Ca-cation exchanged samples have a second adsorption site with about double the heat of adsorption.

CONCLUSIONS

The CO_2 adsorption behavior of HZSM-5 and CaZSM-5 zeolites could be studied by a step change adsorption method.The TPD results indicated that CO_2 was adsorbed on CaZSM-5 zeolites by at least two types of adsorption over the temperatures range studied. There is a weak adsorption due to interaction with ZSM-5 framework, and a strong adsorption caused by interactions with the Ca-Ion of CaZSM-5. The adsorption behavior can be modeled by using a single site Langmuir isotherm for the HZSM-5 and a dual site isotherm for CaZSM-5.

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