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 CO₂ adsorption over ZSM-5 zeolite (Calleja et al. 1994, Calleja, Pau, and Calles 1998, Khelifa et al. 2004). It has been shown that CO₂ 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 CO₂ 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 CO₂ 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(NO₃)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 CO₂ on zeolites were performed with He/CO₂ 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/CO₂ gas mixture. The inlet CO₂ gas concentrations
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. Pretreatment 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.
Typical breakthrough curves for Ar and CO₂ concentration step changes are illustrated in Figure 2. The ordinate is the cumulative residence time distribution, $F(t)$, which is the concentration (mol%) of CO₂ in the gas phase at some time $t$, $y(t)$, divided by the feed gas concentration $y_0$, or
\[ F(t) = \frac{y(t)}{y_0} \] (1)

Assuming ideal gas behavior and that the adsorption of Ar on the zeolite is negligible compared to that of CO₂, the amount of CO₂ adsorbed per mass of zeolite or CO₂ loading, $q$, can be calculated using the differences in breakthrough curve between the Ar as tracer and CO₂ adsorbed as follows:
\[ q = \sum_{i=1}^{n_i} \frac{K_i P_{CO_2}}{1 + K_i P_{CO_2}} \] (3)

The adsorption equilibrium constant ($K$) can be expressed in terms of the enthalpy ($\Delta H$) and entropy ($\Delta S$) of adsorption as follows:
\[ K = e^{-\frac{\Delta H}{RT}} e^{\frac{\Delta S}{R}} \] (4)

Equation (4) can be reformulated in terms of the mean adsorption equilibrium constant ($K_m$) at the mean experimental temperature ($T_m$):
By nonlinear regression, Equations (3) and (5) were fitted to the adsorption data with the adjustable parameters $K_m$, $\Delta H$ and $q_{sat}$ for each adsorption site. The adsorption entropy, $\Delta S$, 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

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

(5)
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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
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.

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

### Table 1: The results of parameters fitted from Langmuir models

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>$q_{sat}$ (mmol/g)</th>
<th>$-\Delta H$ (kJ/mol)</th>
<th>$-\Delta S$ (J/(mol x K))</th>
<th>Langmuir model</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>2.150 ± 0.006</td>
<td>28.2 ± 0.1</td>
<td>81.8 ± 0.2</td>
<td>Single site</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.1 (Khelifa et al. 2004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.8 (Yamazaki et al., 1993)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>38.0 (Dunne et al. 1996)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaZSM-5</td>
<td>site 1: 1.522 ± 0.011</td>
<td>30.9 ± 0.3</td>
<td>85.2 ± 1.0</td>
<td>Dual site</td>
</tr>
<tr>
<td></td>
<td>site 2: 0.725 ± 0.021</td>
<td>59.9 ± 2.3</td>
<td>125.1 ± 2.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: The ‘t’ test method results for site 2 parameters in dual Langmuir model

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>‘t’ value for additional site 2 parameters</th>
<th>‘t’ test assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>0.3556, 0.8998, 0.8707</td>
<td>not significant *</td>
</tr>
<tr>
<td></td>
<td>$t_{95%} = 2.1009$, $t_{95%} = 2.1009$, $t_{95%} = 2.1009$</td>
<td></td>
</tr>
<tr>
<td>CaZSM-5</td>
<td>67.1837, 65.1973, 88.1254</td>
<td>significant *</td>
</tr>
<tr>
<td></td>
<td>$t_{95%} = 2.1788$, $t_{95%} = 2.1788$, $t_{95%} = 2.1788$</td>
<td></td>
</tr>
</tbody>
</table>

*Parameter significant if ‘t’ value > t distribution at 95% degree of confidence
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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