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Adsorption of CO, CO_2 and H_2 in Silicalite-1: measurements and simulations

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Single component and mixture adsorption of CO_2, CO and H_2 in Silicalite-1 was studied with the step response experiments and through molecular simulations. Experiments were performed at 323.15, 373.15 and 473.15 K, and in the pressure range 10.13 to 81.06 kPa. CO_2 adsorption was favored over CO during all studied conditions. The adsorption enthalpies were -24.3 and -13.5 kJ/mol for CO_2 and CO respectively. Adsorption simulations were performed using the Grand Canonical Monte Carlo method. A new zeolite framework potential was derived, and was shown to give good agreement with the experimental results. The major reason for the higher saturation loading of CO_2 compared to CO is however the stronger sorbate-zeolite attraction for CO_2. The affinity for CO_2 also causes a decrease in the adsorbed molar fraction of CO due to the competition with CO_2.

***Keywords**:* Silicalite, Adsorption, Experiments, Monte Carlo Simulations, CO_2, CO, H_2

INTRODUCTION

Understanding of gas adsorption in zeolites is of considerable interest due to the wide application of zeolites in industrial separation and purification processes (Sircar and Myers 2003). Zeolite adsorbents are used in the separation of landfill gas into CO_2 and methane. For the industrial separation of CO_2 from steam-methane reformer gas (mixture of H_2, CO_2, CO, methane, water and trace N_2), zeolite adsorbents are however considered unsuitable due to the slow desorption rate at the typical operating temperature (294 to 311 K) (Sircar and Myers 2003). At higher temperatures, desorption limitations will decrease, and the choice of adsorbent can therefore be made based on the high adsorbent capacity of zeolites. MFI type zeolites have been investigated for CO_2 separation from for example nitrogen, methane, ethane and propane (Calleja et al. 1998, Harlick et al. 2002, 2003, 2004, Katoh et al. 2000). The high selectivity for CO_2 adsorption compared to many other gases in MFI zeolites have been further supported by membrane separation experiments, where CO_2 adsorption at low temperature blocks the pore system of Silicalite-1 for H_2 permeation, yielding a higher flux of CO_2 than H_2, despite the higher diffusivity of H_2 (Bakker et al. 1996).

Experimental determination of single component adsorption isotherms is straight forward, requiring only that the increase in sample weight or the decrease in gas pressure upon adsorption is measured. Single component adsorption isotherms for CO_2 in Silicalite-1 are reported in references (Choudhary et al. 1996, Dunne et al. 1996, Golden and Sircar 1994, Otto et al. 1991, Rees et al. 1991, Sun et al. 1998, Yamazaki et al. 1993). Adsorption of CO and H_2 are reported by Golden and Sircar 1994 and Otto et al. 1991. To determine multi-component adsorption isotherms, more sophisticated experiments are required compared to the single component case, since the multi-component gas mixture needs to be analyzed. The number of multi-component adsorption studies is therefore low. No studies have been found reporting the adsorption of binary or tertiary mixtures of CO_2, CO and H_2 in Silicalite-1. To overcome the shortage of multi-component adsorption experiments, correlations like the ideal adsorbed solution theory (IAST) is often used to estimate the multi-component composition from single component experiments.

An alternative method to predict the multi-component mixture composition is to use molecular simulation techniques, such as Grand-Canonical Monte Carlo (GCMC) simulations. The advantage of using this type of simulations compared to correlations, like IAST, is that molecular simulations also yield detailed atomistic information about the system. Whereas GCMC simulation studies of single component adsorption of gases are becoming common, the number of multi-component GCMC simulations are still rather limited (Fuchs and Cheetham 2001). Single component adsorption of CO_2 has been studied in Silicalite-1 (Hirotani et al. 1997. For H_2, single component adsorption simulations have been reported for NaA (Darkrim et al. 2000) and NaLSX (Weinberger et al. 2005). Simulations of multi-component adsorption have been performed for CO_2 and N_2 over Silicalite-1, ITQ-3 and ITQ-7 (Goj et al. 2002) and for CO_2, N_2 and H_2 over NaA (Akten et al. 2003).

In the current study, experimental single and multi-component adsorption of CO_2, CO and H_2 in Silicalite-1 is presented. The adsorption of CO_2 is shown to be favored under all studied conditions. The experimental results are compared to GCMC simulations using two framework potentials taken from literature (Hirotani et al. 1997, Watanabe et al. 1995). Some deviations between experiments and simulations were found for both the potentials. The new framework potential was therefore derived by adjusting the Watanabe-Austin framework potential (Watanabe et al. 1995) to reproduce single component adsorption results from the current study and from the literature. This adjustment resulted in a slight improvement of the ability of the simulations to predict the experimental results.

EXPERIMENTAL DETAILS

Sample Preparation

The Silicalite-1 sample was prepared by crystallization from a precursor sol prepared by hydrolyzing TEOS with a dilute TPA solution at room temperature on a shaker for 24 hours. The molar composition of the solution was 9 TPAOH : 25 SiO_2 : 480 water : 100 ethanol. The silicate solution was then heat-treated for 72 h at 373 K under reflux and without stirring. The crystals were purified by repeated centrifugation and dispersion. The samples were finally calcined at 823 K for 6 hours (Li et al. 2000, Ohrman et al. 2004). The resulting material had a BET surface of 433 m^2/g. Based on the preparation method, the Silicalite-1 framework was free of aluminum.

Adsorption Experiments

Transient step change adsorption studies of CO, CO_2, CO/CO_2, H_2/CO_2 and $H_2/CO/CO_2$ were performed on the prepared Silicalite-1 powder. The adsorption experiments were performed in a vertically mounted quartz glass tube reactor (diameter 25 mm), with a downward gas flow to avoid particle fluidization. The total gas flow was 100 mL/min (ambient conditions), corresponding to a space velocity of 2400 /h. The powdered sample (1.5 g, 2.5 cm^3) was supported on a quartz frit to distribute the gas evenly over the reactor cross-section. The reactor was heated in a cylindrical oven and the temperature was controlled by a thermocouple mounted directly downstream from the sample bed.

Separate mass flow controllers (Bronskhorst Hi-Tec) were used to mix the reactor feed stream from H_2, CO, CO_2 and He (AGA gas, Sweden, purities greater than 99.999 %). He was used as the sweep gas in all experiments. The mass flow controllers were arranged in two sets, connected through a 4-way valve (Valco Instruments model VICI 90 A) to the reactor, to enable switches of the reactor feed between sweep gas (He) and the He/sorbate gas mixture. Outlet gas concentrations from the reactor were detected by a quadrupole mass spectrometer (Fison Gaslab 300).

Prior to each adsorption experiment, the sample was degassed at 723 K for 4 hours in He. The sample was cooled to the desired adsorption temperature in He. All experiments were carried out at a total pressure of 101.325 kPa and at temperatures between 323 and 473 K. For single component adsorption, sorbate (CO or CO_2) partial pressure ranged from 10.13 kPa to 80.06 kPa. For mixture experiments, the sorbate (H_2, CO and CO_2) partial pressure of each component was varied between 10.13 kPa and 60.80 kPa. The sweep gas pressure was used to balance the total pressure, and was at least 20.27 kPa in all experiments.

The dispersion and time lag of the reactor system was determined from tracer experiments with 40.53 (323 K) or 60.80 (373 and 473 K) kPa H_2 over the sample. H_2 was used as the tracer gas, since it has been reported to have a negligible uptake compared to CO and CO_2 (Golden and Sircar 1994) The uptake of each component was calculated by integrating the difference between the normalized time response curves of the tracer experiment and the sorbent experiment as detailed in Wirawan and Creaser (2006).

SIMULATION DETAILS

Molecular Simulation

Molecular simulations were used to calculate single and multi-component adsorption isotherms of CO_2, CO and H_2 in Silicalite-1. The gas phase composition was selected to enable comparison with experimental data. The total system energy was calculated as the sum of the interaction energies between the zeolite framework and the sorbates, and between the sorbates. Both of these interaction energies were expressed as sums over pairwise additive potentials (u_{ij}) dependent on the atomic distance (r_{ij}).

$$u_{ij} = \varepsilon_{ij}\left[\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - 2\frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right] + \frac{q_i q_j}{r_{ij}} \qquad (1)$$

The first part of the pairwise potential is the Lennard-Jones interaction and the second part is Coulomb interaction. The Lennard-Jones parameters (ε_{ij} and σ_{ij}) and partial charges (q_i) attributed to the atoms are given in Table 1. Three zeolite framework potentials denoted FF A, FF B and FF C. The first two of these (FF A and FF B) were taken from Hirotani et al. (1997) and Watanabe et al. (1995). When simulation results from these potentials were compared with single component adsorption experiments some deviations were found, as shown in Figures 2 and 3. The third framework potential (FF C) was therefore derived as an attempt to improve the prediction of single component adsorption by adjusting some framework parameters. FF C is based on FF A (Watanabe et al. 1995), but the Lennard-Jones well depth and partial charge of zeolite oxygen was adjusted to replicate adsorption results for CO, CO_2 and H_2 from Golden and Sircar (1994) and the single component adsorption isotherms from the current study.

Simulation Method

The adsorption isotherms for single components and mixtures of CO, CO_2 and H_2 were simulated with the sorption toolbox in the Accelrys Cerius^2 4.2.1 software package. For the long-range electrostatic interactions, the Ewald summation method was applied, and for the short-range interactions, the minimum-image convention with a cut-off distance of 12 Å, was used. The sorption toolbox uses a Metropolis Monte Carlo algorithm in the Grand Canonical ensemble. All simulations were performed over at least 5 million Monte Carlo steps, where the first 3 million steps were used for equilibration before the averaging was initiated. The convergence of the simulation was checked by plotting the total energy of the system.

RESULT AND DISCUSSION

Adsorption Measurements

The single component adsorption isotherms, determined using the transient step response method experiments, are presented in Figure 1. Figure 1 also compares the results from the present study with previous reports (Dunne et al. 1996, Golden and Sircar 1994, Yamazaki et al. 1993). The CO_2 results show good agreement when the difference in temperature is taken into account. For CO adsorption, the only relevant literature reference (Golden and Sircar 1994) showed approximately 20 % lower CO uptake compared to the current study.

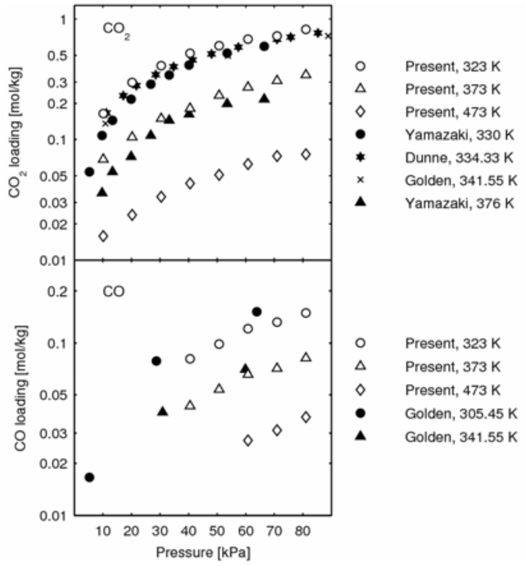

Figure 1. Single Component Adsorption Isotherms for CO_2 (upper) and CO (lower)

Apart from the direct comparison of the absolute uptake results, the temperature dependence of the results is compared with literature data (Choudhary et al. 1996, Dunne et al. 1996, Golden and Sircar 1994, Savitz et al. 2000, Llewelly et al. 1993, Yamazaki et al. 1993) in Table 2. The enthalpy of adsorption was determined by fitting single site Langmuir models as described in Wirawan and Creaser (2006). The fitted adsorption enthalpies for both CO_2 and CO are within the range of previously reported values. Literature results for CO adsorption enthalpy range between 10 and 17 kJ/mol, indicating large discrepancies between different studies. The reason for the large range of experimental values can possibly be explained by different Si/Al ratios for the different samples, since Llewellyn and Maurin (2005) have reported that the adsorption enthalpy for CO in HZSM-5 vary from approximately 16 kJ/mol for Si/Al = 20 to approximately 11 kJ/mol for Si/Al = 1000. Golden and Sircar (1994) have reported a Si/Al = 167, while our sample has no detectable levels of aluminum.

Single Component Adsorption

Experimental single component adsorption isotherms for CO_2, CO and H_2

are compared with simulated isotherms in Figure 2 and 3. Three different framework potentials (FF A, FF B and FF C, see Table 1) were used in the simulations. The fitted framework parameters for the FF C potential (Lennard-Jones well depth and partial charge of zeolite oxygen) are within the range of the parameters given for FF A (Watanabe et al. 1995) and FF B (Hirotani et al. 1997)(compare Table 1). From Figure 2 and 3, it can be concluded that all three potentials yields good, but not excellent predictions of the experimental results. All three framework potentials overestimate the experimental H_2 adsorption at low pressure in Figure 2. The reason for the deviation is thus expected to be due to the H_2 sorbate potential. The development of a new H_2 sorbent potential is however outside the scope of the current study.

There is also a systematic underestimation of the CO results in Figure 3 for all three framework potentials, while no such deviation could be detected for the CO results in Figure 2. The simulations are thus in better agreement with the lower CO uptake reported by Golden and Sircar (1994). This should however not be considered as further support for the experimental data by Golden and Sircar, since the used CO potential was selected based on its ability to give reasonable results for this dataset. Finally, all three potentials tend to overestimate the CO_2 uptake at 305 K and high pressure (1698 kPa). Finally, all three potentials tend to overestimate the CO_2 uptake at 305 K and high pressure (1698 kPa).

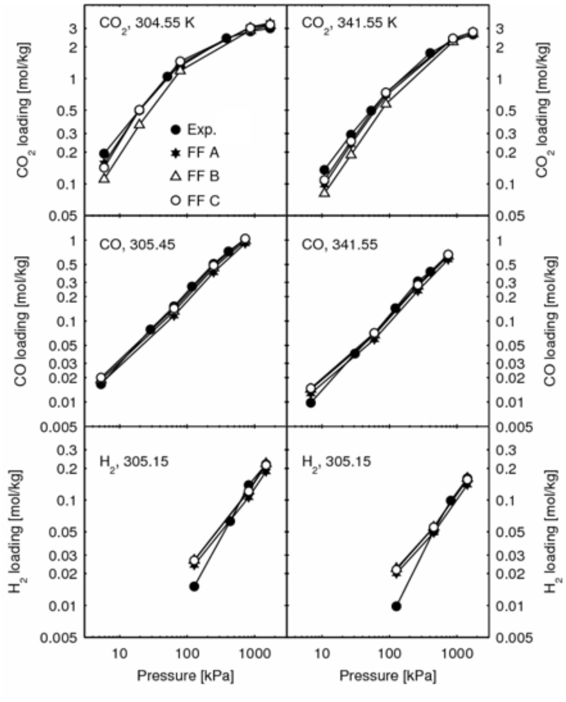

Figure 2. Single Component Adsorption Isotherms for CO_2 (Upper), CO (Middle) And H_2 (Lower) at Approximately 305 K (Left) and Approximately 342 K (Right).

Focusing on the differences between the simulation results with different framework potentials, simulations with FF B have a tendency to underestimate the CO_2 uptake at low temperatures. This is especially pronounced for the 305 K results in Figure 2 and for the 323 K results in Figure 3. Simulations with FF A and FF C gives better predictions of the experimental CO_2 results. The major deviation from the experimental results is an overestimation of CO_2 adsorption at sorbent pressures above 50 kPa at 323 K in Figure 3. The problem with framework potential FF A is that it has the largest deviations compared to the experimental CO results in Figure 3.

Table 1. Interaction Parameters Used for Molecular Simulations

		Lennard-Jones parameters		Partial charge	Reference
		ε/kB [K]	σ [Å]	[e]	
CO_2	C	28.13	3.094	+0.6512	Harris and Yung (1995)
	O	80.52	3.4044	-0.3256	
CO	C	13.19	4.299	-0.75	Straub and Karplus (1991)
	O	80.06	3.5021	-0.85	
	center of mass	0	0	1.6	
H_2	H	12.51	2.9072	0	Cracknell (2001)
Zeolite potential FF A	Si	18.63	0.76	+2	Watanabe et al. (1995)
	O	101.7	3.04	-1	
Zeolite potential FF B	Si	18.63	0.76	+0.8	Hirotani et al. (1997)
	O	128.4	3.04	-0.4	
Zeolite potential FF C	Si	18.63	0.76	+1.368	Current work
	O	124.8	3.04	-0.684	

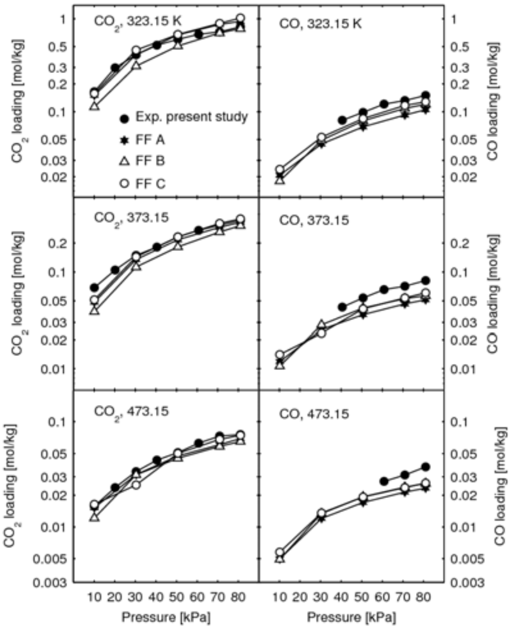

Figure 3. Single Component Adsorption Isotherms For CO_2 (left) and CO (right) at 323.15 K (upper), 373.15 K (middle) and 473.15 K (bottom).

Based on the comparisons above, framework potential FF C is equal good, or better, at predicting the experimental results when compared to FF A or FF B. This conclusion is further supported by the residual sum of squares from the potential fitting. For FF C it is 55 % lower than for FF A and 32 % lower than for FF B. FF C is thus well suited to study the separation of mixtures of the studied sorbates, even though the selectivity for CO_2 over CO is expected to be slightly over estimated.

Multi-Component Adsorption

In Figure 4, multi-component adsorption measurements are compared with single component experiments and with single and multi-component simulations using the FF C framework potential. During all of these experiments and simulations, the temperature was 323.15 K and the total pressure of the sorbates was 81.06 kPa. The results from binary adsorption of CO_2 and H_2 are shown in Figures 4 A and B. The CO_2 uptake is unaffected of the H_2 concentration, even when the H_2 to CO_2 ratio is 3:1. The simulations also show that the H_2 uptake is suppressed by a factor of two or more by the CO_2 adsorption. The interaction between H_2 and the zeolite framework is thus so weak that H_2 can not compete with CO_2 for the adsorption sites.

In contrast to the CO_2/H_2 mixture, the CO_2/CO mixture experiment results (Figures 4 C and D) show a small decrease of the adsorption of CO_2 compared to the single component adsorption experiments, as well as a suppression of the CO adsorption. The same trends are found when the mixture simulations are compared to the single component simulations. Even though the simulations tend to underestimate CO adsorption, the relative suppression of adsorption for the mixture compared to the single component isotherms is well predicted for all CO_2 points and for CO at low CO_2 partial pressures. At high CO_2 partial pressures the simulations overestimates the decrease in CO adsorption, as seen from the increasing relative difference between simulated and measured CO loading. This is attributed to the overestimation of the single component CO_2 loading at 323 K for pressures above 50 kPa, shown in Figure 3. From the binary CO_2/CO experiments and simulations, it is thus clear that the interaction energy for CO is high enough to compete with CO_2 for the adsorption sites. When 20.27 kPa H_2 is added to the mixture (Figures 4 E and F), the results are not significantly altered compared to the pure CO_2/CO case. Again, it is thus concluded that H_2 has too weak interactions with the framework to compete with the other components for the adsorption sites.

Table 2. Single Site Langmuir Model Parameters For CO_2 And CO Fitted To Experimental Single Component Adsorption Isotherms In Current Work, Compared With Literature.

Sorbate	q_{sat} [mmol/g]	-ΔH [kJ/mol]	-ΔS [J/(mol*K)]	Reference
CO_2	1.85 ± 0.15	24.3 ± 0.8	75.5 ± 1.8	Current work
		24.1		Golden and Sircar (1994)
		23.4		Yamazaki et al. (1993)
		27.2		Dunne et al. (1996)
		21.7		Choudhary et al. (1996)
		24.6		Rees et al. (1991)
CO	0.82 ± 0.04	13.5 ± 0.9	53.6 ± 2.1	Current work
		16.7		Golden and Sircar (1994)
		17		Savitz et al. (2000)
		10		Llewelly et al. (1993)

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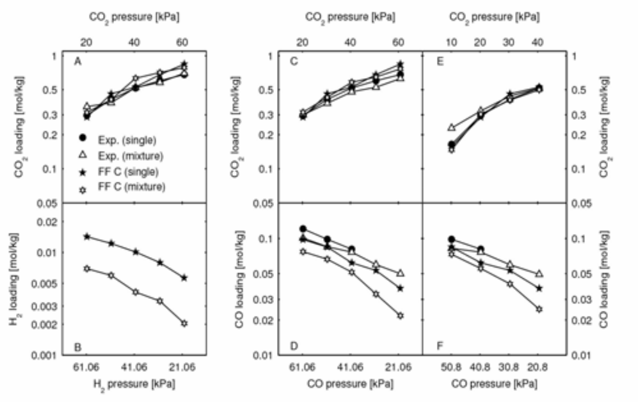

Figure 4. Mixture Adsorption Isotherms for CO_2/H_2 (A, B), CO_2/CO (C, D) And $CO_2/CO/H_2$ (E, F) at 323.15 K Compared with Single Component Adsorption Results at The Same Pressure.

CONCLUSIONS

Experimental single component adsorption experiments, using the step response method, show good agreement with previous studies for CO_2. The enthalpy of adsorption determined from the experiments in the current study was 24.3 and 13.5 kJ/mol for CO_2 and CO respectively. This is within the range of previously reported values.Three framework potentials are used to predict experimental single component isotherms for CO_2, CO and H_2. All three potentials show good, but not excellent predictions of the experimental data. The framework potential FF C was concluded to have the best overall performance in predicting the experimental results.

Binary and tertiary mixture adsorption simulations were performed and compared with the corresponding experiments. H_2 was found to have too weak zeolite interactions to significantly affect the uptake of the other components. Competition for the adsorption sites between CO_2 and H_2 left the CO_2 results unchanged while the H_2 concentration was suppressed with a factor of more than two even at 3:1 H_2 to CO_2 ratio. The CO – zeolite interactions were however strong enough to cause a decrease in the CO_2 uptake. The even stronger interaction with the framework for CO_2 did however significantly suppress the uptake of CO due to the competition between CO_2 and CO.

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