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Complex Sorption Kinetics of Carbon Dioxide in NaX-Zeolite Crystals*

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Abstract. Ad-/desorption-kinetic measurements were performed for carbon dioxide on a mono-disperse crystal sample of NaX-type zeolite (mean crystal diameter: $2R \cong (100 \pm 6)\ \mu\text{m}$) by a constant-volume–variable-pressure method in a "differential" concentration mode over ranges of temperature, (193–293) K, and pressure, (20–26,700) Pa. They revealed a complex sorption process in sorbate uptake and release during experiments of ad- and desorption, respectively, which is comprised of a slow, hitherto unknown rate mechanism superimposed on very fast intracrystalline diffusion of carbon dioxide. IR-spectroscopic data that evidence formation of chemisorption species in CO_2-NaX sorption systems may allow for a tentative interpretation of this finding. Circumstantial evidence for the correctness of this conclusion follows from sorption–kinetic experiments for carbon dioxide on BaKX-type zeolite crystals (mean crystal diameter: $2R \cong (120 \pm 6)\ \mu\text{m}$).

Keywords: NaX and BaKX zeolites, carbon dioxide, sorption kinetics, complex rate mechanism, IR spectroscopy, chemisorption

1. Introduction

Sorption processes for separation and purification of gases have found key-commercial applications in technological regimes of temperature and pressure-swing adsorption (TSA, PSA) with about 5,500 US patents granted during the last two decades (Sircar, 2001). In particular, inorganic and organic trace-impurity removal from air prior to cryogenic air-separation units became a major field of utilization of the sorption principle, and effective sorbent materials are sought for, continuously. For these purposes, zeolites offer many useful modifications, e.g., of the faujasite-type, FAU (Ojo et al., 1996; Bülow et al., 2000). Considering removal of carbon dioxide, CO_2, from air, the most important FAU modification is still NaX that has rendered possible strong improvement of related large-scale TSA purification processes. Their process-performance efficiency depends, inter alia, on fundamental sorption equilibrium and non-equilibrium properties. Sorption equilibria, in particular thermodynamics of various CO_2-NaX zeolite systems, are well known, cf., Habgood (1964), Barrer and Gibbons (1965), Barrer and Coughlan (1968), Avgul' et al. (1968), Dubinin (1972), Barrer (1978), Zhdanov et al. (1981), Vasiljeva et al. (1984), Khvoshchev and Zverev (1991), Dunne et al. (1996), Shen and Bülow (1998), Shen et al. (2000), and papers quoted therein. Contrarily, no CO_2-FAU molecular-mobility data at non-equilibrium condition is available from literature, and little is known at equilibrium, i.e., for CO_2-NaX self-diffusion (Kärger et al., 1993; Onyestyák et al., 1999; Malka-Edery et al., 2001). It is the goal of this report to contribute to an explanation of this surprising situation.

2. Experimental

Ad-/desorption-kinetic measurements for CO_2 were performed on single zeolite crystals of NaX and of BaKX by a constant-volume–variable-pressure method with computerized pressure vs. time-data acquisition. They were run in a concentration mode as close as possible to a "differential" one, over ranges of temperature,

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*This paper is dedicated to Professor Sergey P. Zhdanov, St. Petersburg, Russia, on the occasion of his 90th birthday on April 18, 2002.

(193–293) K, and equilibrium pressure, ca. (20–26,700) Pa. The technique and procedure are well known and were described frequently, e.g., by Bülow et al. (1983a, 1983b, 1984). “Differential” desorption-kinetic trials allowed for reaching a lower limit of equilibrium pressures, i.e., within a range, ca. (20–100) Pa, not achieved by adsorption experiments. A fast-response pressure sensor of *MKS Baratron*, type 615 (response time: 1 ms), was used. The time delay caused by the valve that connects the dosing volume and sorption vessel of the apparatus, is $t_0 \leq 0.1$ s. The valve is opened fully during that dead-time, t_0, after $t = 0$.

The NaX and BaKX-type crystals of homogeneous size and shape were provided by S.P. Zhdanov, St. Petersburg, and characterized in Bülow et al. (1983b, 1993), respectively. For NaX, the only difference between that and the actual sample refers to the mean radius, R, of spheroids circumscribing the crystals: it amounts to (50 ± 3) μm for the actual sample. For BaKX, $R \cong (60 \pm 3)$ μm, and the cation exchange potassium, K^+, vs. barium, Ba^{2+}, amounts to 70.0%. The atomic Si/Al ratio for NaX and BaKX equals to 1.18 and 1.58, respectively, as determined by ICP emission spectroscopy. Masses of 0.1583 g (NaX) and 0.1276 g (BaKX) of crystals activated in accordance with a procedure described in Bülow et al. (1983a) were spread over tufted glasswool filling the sorption vessel for the respective measurements. Therefore, intercrystalline mass and heat-transfer processes that affect generally sorption-kinetic behavior, should in neither case interfere significantly with monitoring intracrystalline transport processes.

3. Results and Discussion

Hitherto available information on molecular mobility in CO_2-NaX systems relates to conditions at or close to self-diffusion as provided by the techniques, ^{13}C PFG NMR (Kärger et al., 1993) and Frequency Response (Onyestyák et al., 1999; Malka-Edery et al., 2001), respectively. It is very scarce and comprises a few self-diffusivity values, only. Over a temperature interval, (170–330) K, their range is $(8 \times 10^{-11}$ to $3 \times 10^{-9})$ m^2/s with an activation energy, $E_a \cong 10$ kJ/mol, (NMR). They refer to a sorption-phase concentration, ca. (3–4) molecules per supercage of the FAU framework, which may amount to ca. (20 to 25)% of a saturation concentration assessed by information from literature (Shen and Bülow, 1998). This concentration is beyond that for the region of strong specific electrostatic interaction of the *Coulomb*-type between quadrupoles of CO_2 molecules and zeolitic cations. No molecular mobility data are known for CO_2-BaX systems.

In CO_2 sorption-kinetic experiments on NaX and BaKX zeolites, eight cycles of as many as 25 and 20 “differential” kinetic runs each, were executed for ad- and desorption, respectively, at temperatures, 193, 252, 273 and 293 K, and pressures between ca. 26,700 and 20 Pa as upper and lower equilibrium limits, respectively. This range corresponds roughly to ca. (5 to 0.5) and ca. (8 to 1) CO_2 molecules per supercage of NaX and BaKX, respectively, i.e., to phase-concentration intervals, the most part of which is covered by strong specific *Coulomb* interaction, cf., Shen and Bülow (1998).

Usually, to quantify sorption kinetics on microporous sorbents, normalized uptake curves, $\gamma_v(t)$ and $\gamma_d(t)$, in terms of pressure in the dosing volume and sorption vessel, respectively, as defined by

$$\gamma_i(t) = \frac{p(t)_i - p(0)_i}{p_\infty - p(0)_i} \quad i = d, v, \quad t \geq 0, \qquad (1)$$

are considered, cf., Bülow and Micke (1990, 1994, 1995). Herein, primary curves, pressure, (p/Pa), vs. square root of time, sqr t (t/s), are used to characterize ad-/desorption kinetics. The reason for this becomes obvious when considering results of the sorption-kinetic measurements. Typical and relevant results for the kinetic trials on the CO_2-NaX system (dotted curves) are exemplified in Figs. 1–3 (adsorption at 252, 273 and 293 K) and Fig. 4 (desorption at 293 K). In Figs. 1–4, sorption kinetic curves for the CO_2-BaKX system are also included. Therein, pressure is plotted in arbitrary units to allow for a comparison between CO_2 uptake by the two zeolites, for which sorption equilibria differ significantly. Plots are shown for comparable sorption-phase concentrations identified in the captions. Dependences p vs. sqr t simulated for the dosing volume and sorption vessel of the experimental arrangement are shown as well (solid curves); they differ from each other in the region of very small time, and they coincide when sorption time increases. These dependences visualize intracrystalline diffusion presupposed as the only rate process to occur with diffusivities that accord to above-mentioned literature data on CO_2 self-diffusion, cf., caption to figures. The software ZEUS (Bülow and Micke, 1990) was used for those simulations.

The main conclusions be drawn from Figs. 1–4 are as follows: (i) Sorption kinetics of the system

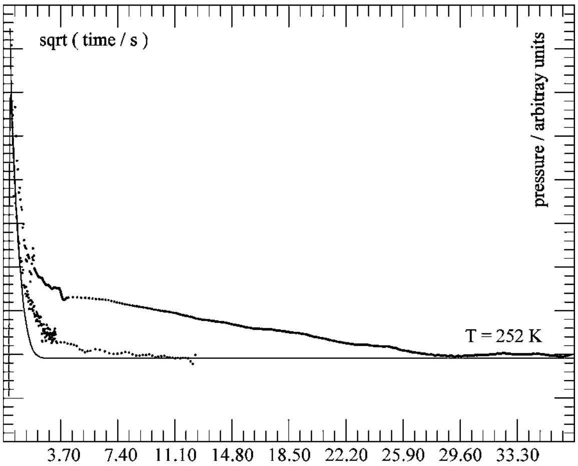

Figure 1. Adsorption kinetic runs for CO_2 on NaX and BaKX crystals, at 252 K. Dotted curves: experimental data for NaX (upper) and BaKX (lower). Solid curve: simulated uptake curve for *Fickian* diffusion with $D = 1.0 \times 10^{-10}$ m^2/s. Sorption-phase concentration ranges covered: $\Delta n^{(i)} \cong (0.368–0.402) n^{(i)}{}_{sat}$ (superscript "i" and subscript "sat" denote the zeolite modification and micropore saturation, respectively).

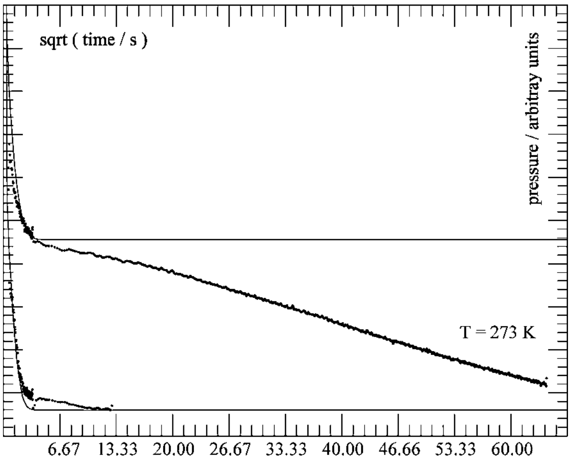

Figure 2. Adsorption kinetic runs for CO_2 on NaX and BaKX crystals, at 273 K. Dotted curves: experimental data for NaX (upper) and BaKX (lower). Solid curves: simulated uptake curves for *Fickian* diffusion with $D = 3.0 \times 10^{-11}$ m^2/s for the real experimental equilibrium loading (lower curve) and a loading of ca. 40% of the latter (upper curve). Sorption-phase concentration ranges covered: $\Delta n^{(i)} \cong (0.129–0.142) n^{(i)}{}_{sat}$ (superscript "i" and subscript "sat" denote the zeolite modification and micropore saturation, respectively).

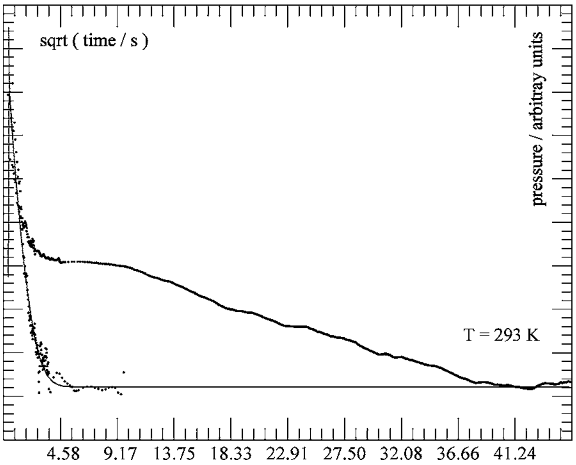

Figure 3. Adsorption kinetic runs for CO_2 on NaX and BaKX crystals, at 293 K. Dotted curves: experimental data for NaX (upper) and BaKX (lower). Solid curve: simulated uptake curve for *Fickian* diffusion with $D = 1.0 \times 10^{-10}$ m^2/s. Sorption-phase concentration ranges covered: $\Delta n^{(i)} \cong (0.217–0.243) n^{(i)}{}_{sat}$ (superscript "i" and subscript "sat" denote the zeolite modification and micropore saturation, respectively).

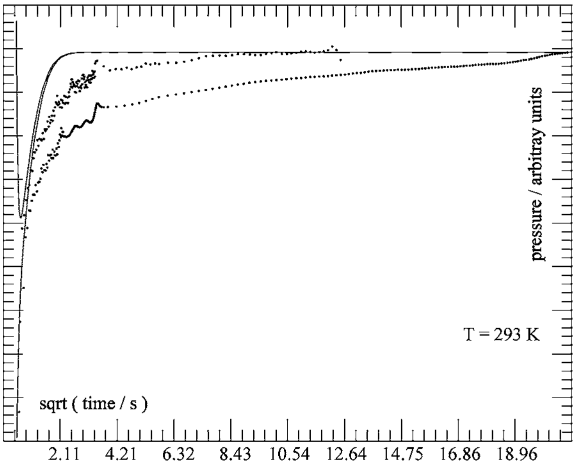

Figure 4. Desorption kinetic runs for CO_2 on NaX and BaKX crystals, at 293 K. Dotted curves: experimental data for NaX (lower) and BaKX (upper). Solid curve: simulated desorption curve for *Fickian* diffusion of CO_2 in BaKX with $D = 3.0 \times 10^{-10}$ m^2/s. Sorption-phase concentration ranges covered: $\Delta n^{(i)} \cong (0.173–0.194) n^{(i)}{}_{sat}$ (superscript "i" and subscript "sat" denote the zeolite modification and micropore saturation, respectively.)

CO_2-NaX differs spectacularly from that for the CO_2-BaKX system; (ii) for CO_2-BaKX, it may reflect intracrystalline diffusion that proceeds almost entirely outside the time "window" of the apparatus with an estimated lower limit of intracrystalline diffusivity, $D \geq 1 \times 10^{-10}$ m^2/s, for regions of temperature and sorption-phase concentration considered; (iii) for CO_2-NaX, experimental sorption-kinetic curves in conjunction with those simulated for intracrystalline diffusion evidence clearly that a complex of at least two mechanisms govern uptake and release of CO_2 by NaX crystals, in the concentration range covered; (iv) the first mechanism is extremely fast with a half-time as long as a few seconds at ambient temperature, despite the large crystal size (this mechanism may represent intracrystalline (*Fickian*) diffusion, cf., upper curve in Fig. 2); (v) superimposed is another, very slow process as compared to the presupposed diffusional one, which makes its pronounced mark on overall–rate curves, governing them strongly; (vi) the half-time of the second process ranges from minutes to hours (at low temperature); (vii) from the macroscopic experiments executed in "differential" steps, it also follows that the mass fraction ad-/desorbed, which is controlled by the latter process, may amount to about 50% (or even more) of the overall one, depending on pressure, i.e., sorption-phase concentration, and temperature (cf., Figs. 2 and 3); (viii) the specific sorption-kinetic features are symmetric with regard to ad- and desorption, as it follows from Fig. 4 (the discrepancy between the experimental and simulated curves for BaKX will be discussed elsewhere).

Attempts to model experimental kinetic curves within the given concentration range on the basis of *Fickian* diffusion fail because of the complex overall-rate behavior. Moreover, neither of the usually considered rate-influencing processes that might be superimposed on intracrystalline diffusion, such as physical sorption-heat release, surface-barrier penetration, or framework structure-related immobilization of sorbing species (Micke and Bülow, 1993; Micke et al., 1994), nor external mass and heat exchange, could be identified reliably as the specific rate-limiting mechanism. Despite a certain similarity between curves, (p/Pa), vs. square root of time, sqr t (t/s), shown in this paper and those modeled for intracrystalline diffusion superimposed by a first-order reaction–rate mechanism, cf., Micke and Bülow (1993), the actual system seems to be even more complex.

Rather than those phenomena, it might be assumed tentatively that formation of CO_2-chemisorption complexes could influence remarkably on molecular mobility as observed at non-equilibrium. Such complexes may exist due to a pronounced specific interaction between quadrupoles of CO_2 molecules and strong intracrystalline electric-field gradients created by Na^+ cations, in conjunction with negative charges on FAU framework-oxygen atoms in their neighborhood, $Na^+ \cdots O^{\delta-}$. Proof of evidence for their existence has been provided by IR-spectroscopic investigation of related CO_2-NaX systems (Bertsch and Habgood, 1963; Habgood, 1964; Angell, 1966; Ward and Habgood, 1966; Kiselev and Lygin, 1972; Jacobs et al., 1973; Förster and Schuldt, 1974; Nabijev et al., 1976; Garrone et al., 1998).

Their main results are summarized as follows. Sorption of CO_2 by NaX crystals proceeds in two forms, beside that of non-specific volume filling at high sorption-phase concentration. One form represents a relatively weak specific interaction with cations that exhibits both an asymmetric and a symmetric stretching frequency at 2355 and 1380 cm^{-1}, respectively, which become IR-active upon sorption. Such CO_2 molecules can be removed from intracrystalline sites by extended evacuation at ambient temperature or above 100°C. The other form comprises CO_2 molecules that undergo strong chemisorption interaction that creates carboxylates and/or carbonates within zeolite cavities. This results into two pairs of bands, viz., those at 1485 and 1425 cm^{-1} for a stronger chemisorption form removable by evacuation above 300°C, only; and a weaker chemisorption form related to bands at 1580 and 1365 cm^{-1}. The amount of such chemisorbed CO_2 species corresponds to a few percent of the specifically sorbed CO_2 molecules. Most probably, the sites responsible for such chemisorption, comprise Na^+ cations in conjunction with high negative charges on the surrounding framework-oxygen atoms, $Na^+ \cdots O^{\delta-}$. The existence of at least two types of specific sorption sites for CO_2 molecules in NaX crystals ($\mathrm{Si/Al} \cong 1.0$) was confirmed recently by broad-range DRIFT-spectroscopic measurements (Kazansky et al., 1999).

Chemisorption in CO_2-NaX systems was found to be an activated process since the intensity of corresponding bands increases with time, while that of physically sorbed species decreases. Sorption of CO_2 by FAU with cations of alkaline, Li^+, Na^+, K^+, Rb^+, and alkaline-earth types, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, at CO_2 concentrations up to five molecules per supercage gave information on related centers. The asymmetric vibration-band *maxima* in the region, (2300–2400) cm^{-1}, that refers to CO_2 molecules sorbed specifically on cations, was revealed to depend on the nature of cations. Alkaline-earth FAU modifications do not undergo carbonate formation (Angell, 1966; Ward and Habgood, 1966). Therefore, it becomes clear why sorption kinetics in the CO_2-BaKX system seems to be governed almost completely by intracrystalline diffusion, in contrast to that of the CO_2-NaX system, as shown in Figs. 1–3.

Since bivalent cations do not occupy SIII sites in FAU, strong CO_2 chemisorption in NaX should take place on Na^+ in SIII sites in conjunction with framework-oxygen atoms, $Na^+{}_{SIII} \cdots O^{\delta-}$. In NaX, carbonates appear already at ambient temperature, to an extent of up to three CO_2 molecules chemisorbed per unit cell (Jacobs et al., 1973; Förster and Schuldt, 1974). Conclusions on the occurrence of two species, i.e., carboxylic and carbonate, on $Na^+{}_{SIII} \cdots O^{\delta-}$ centers within NaX and their mutual transformation were confirmed by Nabijev et al. (1976), by comparing CO_2 sorption on Li^+, Na^+ and K^+-exchanged FAU, with reference to Angell (1966) and Kiselev and Lygin (1972), who, in addition, addressed the role of water as a possible catalyst for the chemisorption reactions, cf., also Beljakova et al. (1970). This accords with sorption heats of CO_2 as dependence on sorption-phase concentration (Vasiljeva et al., 1984). Calorimetry for CO_2 on FAU forms has identified very high (chemi-)sorption heats on NaX at low sorption-phase concentration, amounting to values, >70 kJ/mol, as well as a temperature-dependent transition of CO_2 between sorption states, which confirms the IR-spectroscopic findings (Amari et al., 1992).

Considering the complex sorption behavior of CO_2 molecules in NaX crystals, it is logical to assume tentatively that CO_2 chemisorption-complex formation, i.e., that of carboxylates and carbonates, and their mutual transformation, could influence on molecular mobility in this system. Interaction between CO_2 quadrupole moments and strong intracrystalline electric-field gradients created by Na^+ cations in conjunction with framework oxygen, $Na^+{}_{SIII} \cdots O^{\delta-}$, may depress the genuine physical ad-/desorption rates of CO_2. One could speculate on a few causes for the sorption-rate mechanism for CO_2, such as on formation of chemisorption complexes propagating as a moving front of transport obstacles ('shell'-like within single crystals, or as to a 'shrinking-core' model), migration of CO_2 molecules coupled with that of cations, and/or a rate process that takes places cooperatively with mutual transformation between those chemisorption species. As to the inherent complexity, for (hydrated) NaX crystals, the Na^+-cation mobility—presupposedly involved with that mechanism to some extent—revealed to be complex *per se*, due to heterogeneous Na^+-cation siting in the FAU framework. It is comprised of processes of activated diffusion and first-order quasi-chemical reaction superimposed upon each other, with activation energies that amount to 40.6 and 19.9 kJ/g-ion, respectively (Brown et al., 1971; Brown and Sherry, 1971). Since the quasi-chemical reaction rate is independent of crystal size, the size-variation approach to overall kinetics may help to find pieces of the answer sought. Variation of occupancy of SIII sites by Na^+ cations (from as many as possible to zero) by a Si/Al-ratio variation of the Na-FAU framework may allow to assess the relevance of both carbonate formation and the carboxylate $\Leftrightarrow$ carbonate transfer-rate process, for the CO_2-NaX sorption kinetics.

As to self-diffusion methods referred to above, they may not be able to reveal time-retarded non-equilibrium processes such as the discussed ones, because they monitor equilibrium mobility in "windows" of observation time at different *loci* of its scale. They rather respond to a mobile phase of sorbing CO_2 species, a conclusion supported by their relatively low activation energy of self-diffusion at a comparatively high sorption-phase concentration. Such a phase seems to exist simultaneously with the slow one, the former having been evidenced, although with difficulty, by the macroscopic sorption-kinetic method at the lower end of the sorption-time scale.

4. Conclusions

The rather unusual sorption kinetics of CO_2 on NaX-zeolite crystals deserves further investigation from the viewpoints of fundamental phenomena involved and their significance for a practical utilization of NaX-based sorbents in processes for carbon-dioxide removal from air, which deals with trace concentrations as high as several hundred ppm. An in-depth experimental study is needed to elucidate and to describe comprehensively sorption kinetics of CO_2 on NaX crystals as dependence on their crystal size and Si/Al ratio, which should be combined with time-dependent IR spectroscopy. This effort could lead to a continuation of theoretical work on simulation of sorption-reaction rate mechanisms in zeolitic micropores, which, besides, are of general interest.

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