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# Sorption and kinetics of $CO_2$ and $CH_4$ in binderless beads of 13X zeolite

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ABSTRACT

The sorption equilibrium of $CO_2$ and $CH_4$ in binderless beads of 13X zeolite has been investigated between 313 and 373 K and pressure up to 4 atm. The amount adsorbed of $CO_2$ and $CH_4$ is around 5.2 mmol/$g_{ads}$ and 1.2 mmol/$g_{ads}$, respectively, at 313 K and 4 atm. Comparing these values with the ones in literature the value of $CO_2$ is 20% higher than in CECA 13X binder pellets. It is also found that isotherms are pronounced Type I for $CO_2$ and almost linear for $CH_4$. The $CO_2$ isotherms were modeled using a simple deviation from Langmuir isotherm that takes into account interaction between adsorbed molecules at adjacent sites (Fowler model) suggesting a moderate repulsion. Henry's constants range from 143 to 11.1 mmol/$g_{ads}$.atm for $CO_2$ and 0.45 to 0.27 mmol/$g_{ads}$.atm for $CH_4$ between 313 and 373 K, respectively. The heats of sorption at zero coverage are 43.1 kJ/mol for $CO_2$ and 9.2 kJ/mol for $CH_4$.

The sorption kinetics has been investigated by the Zero-Length Column technique (ZLC). Recipes to analyze ZLC desorption curves in pellets of adsorbents are reviewed and it is derived a criteria which indicates that for the sorption rate be measured macroscopically the time of the experiment (that should be above a few seconds) is directly calculated with the following expression: $t_{0.1} \geq 7.02 \times 10^{-2} \frac{r_c^2}{D_c}$. Based on such criteria it is shown that crystal diffusivity of $CO_2$ in 13X can be measured macroscopically by ZLC, being the same measurement for $CH_4$ practically impossible. The crystal diffusivity of $CO_2$ measured experimentally is $5.8 \times 10^{-15}$ m$^2$/s and $1.3 \times 10^{-15}$ m$^2$/s at 373 and 313 K, respectively. These values are comparable to the ones measured by a frequency response and pulse chromatography techniques reported in literature. The ZLC desorption curves for $CH_4$ were measured under an equilibrium regime.

## 1. Introduction

The reduction of carbon dioxide and methane emissions to atmosphere is a matter of great concern nowadays since both gases can contribute significantly to the so-called greenhouse effect that describes the trapping of heat near earth's surface by gases in the atmosphere. Indeed, carbon dioxide is necessary because there are calculations showing that if it were not present in the atmosphere earth will be 30 °C cooler. The presence of $CO_2$ in the atmosphere is ruled by the carbon cycle but today that balance has probably been upset. At the same time $CO_2/CH_4$ separations are of great economical and technological importance in treating gas streams like landfill gas, biogas and coal-bed methane. Accordingly, there is a need to investigate on this topic and that can be done with improved efficient technologies to separate or remove $CO_2$ and $CH_4$ from exhaust gases.

Two recent reviews discuss this matter with great detail concerning the use of adsorbent based techniques to handle $CO_2$ capture and $CO_2/CH_4$ separations [1,2]. A new class of adsorbents named Metal–Organic Frameworks (MOFs) are focused being clear that in future they can be an excellent alternative to zeolite adsorbents generally used nowadays. However, MOFs need to be further refined regarding its production in large scale, chemical and thermal stability, which are properties already well-established in zeolites.

There are today adsorption processes based in zeolites like Pressure Swing Adsorption – PSA to store and separate compounds such as $CO_2$ and $CH_4$. To be used as adsorbents zeolite powder needs to transformed into molecular sieves and this reduces its working capacity in 20% or more which is the amount of adsorptive inert clay binder generally used to give the necessary mechanical strength to the pellets or beads in order to be used in packed-columns and at the same time reduce pressure drop. To increase the working capacity the binder can also be converted to zeolite matter leading to the so-called binderless pellets or beads [3,4] but this technology has not received great attention from companies that produce molecular sieves. Recently, this technology has been recovered and applied for the synthesis of binderless beads of 13X zeolite where the non-zeolitic components (temporary binder) is converted to zeolite during a hydrothermal conversion after the manufacturing procedure [5]. The resulting binderless beads can

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**Nomenclature**

| | |
|---|---|
| $b$ | isotherm equilibrium constant, Pa$^{-1}$ |
| $c$ | outlet concentration of the ZLC, mol/m$^3$ |
| $c_0$ | saturation concentration of the ZLC, mol/m$^3$ |
| $D_c$ | crystal diffusivity, m$^2$/s |
| $D_p$ | macropore diffusivity, m$^2$/s |
| $D_m$ | molecular diffusivity, m$^2$/s |
| $D_K$ | Knudsen diffusivity, m$^2$/s |
| $F$ | purge flowrate n ZLC, m$^3$/s |
| $H$ | Henry's law, mol/g.Pa |
| $K$ | adsorption equilibrium constant (Henry's law constant), dimensionless |
| $L$ | ZLC model parameter, dimensionless |
| $p$ | pressure, Pa$^{-1}$ |
| $q$ | amount adsorbed, mol/kg |
| $q_m$ | amount adsorbed at the saturation of the adsorbent, mol/kg |
| $r_c$ | crystal radius, m |
| $R_p$ | pellet radius, m |
| $w$ | is the extra energy (Fowler isotherm), J/mol |
| $R$ | ideal gas constant, J/mol.K |
| $t$ | time, s |
| $T$ | temperature, K |
| $V_s$ | volume of adsorbent, m$^3$ |
| $R_p$ | pellet radius, m |

*Greek symbols*

| | |
|---|---|
| $\rho_p$ | pellet density, kg/m$^3$ |
| $\varepsilon_p$ | pellets porosity. Dimensionless |
| $\Gamma_p$ | tortuosity, dimensionless |
| $\beta_1$ | roots of transcendental Eq. (4), dimensionless |
| $\theta$ | coverage equal to $q/q_m$; the same as degree of filling of sites, dimensionless |

increase in this way the working capacities of existing zeolite adsorbent technologies.

In literature we can find several data and modeling regarding the sorption of $CO_2$ and $CH_4$ in zeolites [6–10] and MOFs [11–17]. Among the zeolites one of the most interesting is zeolite 13X due to its large cages that can accommodate a large amount of mass and at the same time the presence of cations that produce electric field that interacts with strong quadropole moment molecules such as $CO_2$. This gives rise to an increased selectivity between $CH_4$ (apolar) and $CO_2$ that has been exploited in cyclic processes [18–21].

For the modeling of adsorption processes it is of fundamental importance to analyze conveniently thermodynamic data. The books of Barrer [22], Ruthven [23], Guiochon et al. [24] and Do [25] highlight in great detail the basics to analyze such data. For Type I isotherms which are the most frequent in zeolites, localized adsorption models such as: Langmuir, dual-site-Langmuir, Fowler, Nitta, etc. are used extensively due to their simplicity and at the same time being thermodynamic consistent giving insight into sorption events in a comprehensive way.

The measurement of sorption kinetic is also fundamental for modeling adsorption cyclic processes since the transport of mass into and out of the adsorbent can affect significantly the performance of industrial processes. For the measurement of sorption kinetics there are several techniques, one is microscopic (PFG, NMR) and the other is macroscopic (uptake rate, chromatographic) [26–28]. Since its introduction by Eic and Ruthven [29] for the measurement of intracrystalline diffusivities in strongly adsorbed species the Zero-Length Column (ZLC) technique has been used extensively for the measurement of sorption rates in porous media due to its apparent simplicity [30–33]. However, special attention in the use of model parameters from which kinetic data are obtained is required since there are models with the same mathematical form in completely different regimes that when used without previous calculations can produce erroneous results [34]. Extensions for using the technique for liquid systems [35,36], pellets of adsorbents [37], analyses of influence of heat effects [38,39], effect of non-linear equilibrium [40], effect of surface barriers [41,42] and also for the measuring of adsorption equilibria have been developed [43], being now possible to use the technique in a broad range of systems sorbate-sorbent.

The goal of this work is to access data of equilibrium and kinetics of sorption of $CO_2$ and $CH_4$ on a new type of binderless beads of 13X zeolite. The equilibrium data are measured in a breakthrough apparatus and the kinetic data by the ZLC technique.

Attention is made regarding the comparison of these results with published data on pellets of the same zeolite type with binder. At the same time thermodynamic and kinetic parameters are obtained that are useful for the development of adsorption separation processes such as the ones calculated from modeling of equilibrium and kinetic of sorption: heats of sorption, Henry's constants, equilibrium constants, working capacities, inter and intracrystalline diffusivities. Through this work some ideas about the use ZLC technique for the measurement the diffusivity in porous adsorbents are revised by establishing a procedure to analyse properly such results introducing a simple criteria to evaluate which kind of systems can be measured macroscopically by ZLC.

## 2. Experimental section

### 2.1. Binderless 13X zeolite

The powder of 13X from which the binderless beads were formed is from Chemiewerk Bas Kostritz GmbH (Germany) with a Si/Al ratio of 1.18. Metakaolin is used to manufacture the beads. The synthesis and characterization procedure is described in detail elsewhere [5]. Briefly, the beads formed consist in spherical particles with a diameter ranging from 1.2 to 2.0 mm. The size of the zeolite crystals are around 2 μm. Table 1 summarizes the characteristics of the beads.

### 2.2. Adsorption equilibrium and ZLC apparatus

The equilibrium and kinetics studies were performed in the apparatus illustrated in Fig. 1. Briefly, it consists in two sections: i) a gas preparation system; and ii) a Gas Chromatograph with a

**Table 1**
Physical properties of zeolite 13X beads and adsorption column characteristics.

| | |
|---|---|
| *Physical properties of binderless 13X beads*[a] | |
| $SiO_2/Al_2O_3$ ratio | 2.35 |
| Crystal dimensions (μm) | ≈2 |
| Beads dimension (spherical) (mm) | 1.2–2.0 |
| Average pore diameter (μm) | 0.6 |
| *Adsorption column characteristics* | |
| Length (cm) | 8 |
| Internal diameter (mm) | 4.6 |

[a] From Ref. [5].