

Adsorption Equilibrium and Diffusion of Methane and Carbon Dioxide on Binderless Beads of 13X Zeolite

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Introduction

To be used as adsorbents zeolite powder need to pelletized and this reduces it's working capacity in 20% or more which is the amount of inert clay binder generally used to give the necessary mechanical strength to the pellets in order be used in packed-columns and at the same time reduce pressure drop. Recently, a new technology was applied where the binder matter is converted to zeolite matter during the pelletization procedure [1]. The resulting binderless pellets can increase in this way the working capacities of existing zeolite adsorbent technologies.

The objectives of this work is to obtain data of equilibrium and kinetics of sorption of CO₂ and CH₄ on a new type of binderless on of 13X zeolite. The equilibrium data is measured in a breakthrough apparatus and the kinetic data by the ZLC technique.

Data obtained is compared to published one on binder pellets of the same type. Another goal is to determinate thermodynamic and kinetic parameters that are useful for the development of adsorption separation processes such as the ones calculated from modelling 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 diffusvity in porous adsorbents are revised by establishing a procedure to analyse conveniently such results introducing a simple criteria to evaluate which kind of systems can be measured macroscopically by ZLC.

Results and Discussion

We study the sorption and equilibrium of CO₂ and CH₄ on binderless beads of 13 X zeolite between 313 and 373 K an partial pressure up to 4 bar.

The sorption equilibrium isotherms of CO₂ show an amount adsorbed of CO₂ at 4 bar which is 20% higher than values reported in literature for 13X pellets with binder. The sorption equilibrium of CO₂ was modeled with the Fowler isotherm that accounts for lateral interactions between molecules adsorbed in adjacent sites. The CH₄ isotherms were fitted with the Langmuir model but are practically linear until 4 atm of pressure.

The crystal diffusivity of CO₂ on 13X was measured by ZLC. The diffusion coefficient of CO₂ in 13X at 373 K is around 5.4×10^{-15} m²/s which is comparable with a value reported in literature measured by a frequency response technique. Figure 1 shows the adsorption equilibrium isotherms of CO₂ and CH₄ and the effect of temperature on ZLC desorption curves for CO₂ measured through this work.

A simple equation to predict if a ZLC experiment can be performed in a macroscopic time is derived and applied for the present system proving that sorption of CO₂ in 13X zeolite can be measured macroscopically. The equation developed is also useful to check if diffusivity data calculated is consistent with a macroscopic experiment. The time of the experiments (that should be above a few seconds) is directly related with the following expression: $t_{0.1} \geq 7.02 \times 10^{-2} \frac{r_c^2}{D_c}$.

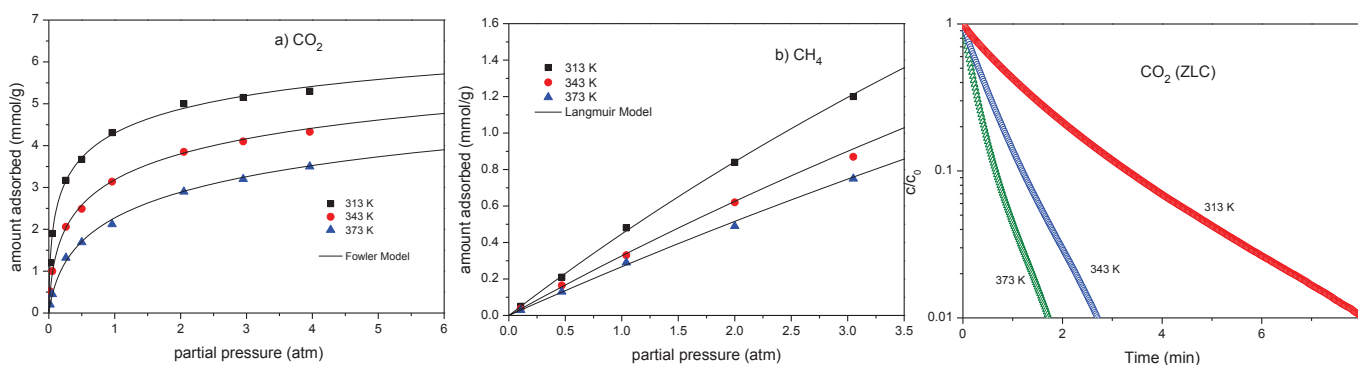


Figure 1. Adsorption equilibrium isotherms of CO₂ and CH₄ and ZLC desorption curves for CO₂ as a function of temperature on binderless beads of 13X zeolite.

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References

- [1] K. Schumann, B. Unger, A. Brandt, F. Scheffler, *Micropor. Mesopor. Mater.* (2011), doi:10.1016/j.micromeso.2011.07.015