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Light gases saturation loading dependence on temperature in LTA 4A zeolite

Pasquale F. Zito [a, b], Alessio Caravella [b], Adele Brunetti [a], Enrico Drioli [a, b], Giuseppe Barbieri [a, *]

[a] National Research Council – Institute on Membrane Technology (ITM-CNR), Via Pietro BUCCI, Cubo 17C, 87036, Rende, CS, Italy
[b] The University of Calabria – Dept. of Environment and Chemical Engineering, Via Pietro BUCCI, Cubo 44A, 87036, Rende, CS, Italy

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ABSTRACT

The temperature dependence of saturation loading of H_2, CH_4, CO_2, CO and N_2 is evaluated for LTA 4A zeolite. For this purpose, the saturation loading is calculated at each temperature by applying a monovariate regression analysis to a number of experimental adsorption isotherms taken from previous publications in the literature within a wide range of conditions.

In performing this investigation, Langmuir and Sips adsorption parameters of H_2, CH_4, CO_2, CO and N_2 are also evaluated, obtaining a satisfactorily low degree of uncertainty. This type of data, characterizing the adsorption behaviour of the considered materials are of practical importance and can be directly used by material scientists and general end-users. The role of excess and absolute loading is also discussed, highlighting that an appreciable difference is found at a relative high pressure only.

1. Introduction

Adsorption is an important phenomenon based on which gas streams can be efficiently separated through a preferential affinity of some molecules with respect to others towards a solid surface. The extent of the gas-surface interactions depends on both the species properties, such as polarizability and dipole and quadrupole moments, as well as on the surface polarity [1]. The pure component adsorption properties can be adequately described by several models (see, among others, the book of Do for an exhaustive list [2]).

Among microporous materials, zeolites are interesting materials consisting of tetrahedral SiO_4 and AlO_4 units to form a structure of pores and channels. These materials can be used in several applications, such as adsorption, ion exchange, catalysis and gas and liquid separation. The Si/Al ratio can range from 1 to infinity, depending on the type of material [3]. The ability of material to exchange cations, such as Na^+ and K^+, depends on this Si/Al ratio and, in particular, increases with increasing Al-content. To this regard, frameworks with a higher Al-content are more polar and, thus, adsorb molecules more strongly [1].

The LTA zeolites (Linde Type A) consist of eight-membered ring structure with a cubic unit cell of 24.6 Å [4]. Their family includes 3A, 4A (or NaA) and 5A. The chemical formula for a single dehydrated NaA cell can be written as $Na_{12}Si_{12}\,Al_{12}O_{48}$ [5,6], with a Si/Al ratio of 1. Its pseudo-unit cell consists of eight large cavities (α-cage) of diameter 11.4 Å and eight small cavities (β-cage or sodalite) of 6.6 Å [7,8], with the large ones connected by windows with a diameter of 4.1 Å [9]. This material can be successfully used for H_2/nC_4H_{10} separation, achieving a selectivity higher than 100 at 298 K [10]. Furthermore, it should be promising also for light gases treatment involving carbon dioxide, since it shows a good adsorption affinity towards CO_2 [11].

Concerning the transport mechanism, the gas permeation through the zeolite micropores generally occurs by surface diffusion (especially at a low temperature) and, in a lesser extent, by Knudsen one. In addition, the strongly adsorbed species (e.g., CO_2) can affect the mass transport of the weakly-adsorbed species, whose transport is mainly driven by Knudsen diffusion (e.g., H_2) [12]. Therefore, adsorption can even control the diffusion of the weakly-adsorbed species and, thus, the estimation of the adsorption parameters (e.g., saturation loading) in micropores is an important step to characterize and describe the mass transport through LTA membranes.

In this work, the saturation loading temperature dependence of light gases in LTA 4A zeolite is investigated using, for the first time

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* Corresponding author.
E-mail address: g.barbieri@itm.cnr.it (G. Barbieri).

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to the best of our knowledge, a systematic monovariate regression analysis. Specifically, the saturation loading is evaluated at each temperature by a regression analysis using the Langmuir adsorption model applied to available experimental adsorption isotherms obtained by a number of worldwide different research groups. In this way, a point-by-point functionality of the saturation loading with temperature is achieved for the considered species (i.e., H_2, CH_4, CO_2, CO, N_2).

Moreover, a multivariate regression analysis is used to obtain the adsorption parameters, following the same approach reported in previous papers [13–15]. To perform this investigation, the Langmuir model is chosen because of its ideality, based on the homogeneous surface and absence of interaction among the adsorbed molecules, whereas the Sips one is chosen as a relatively simple non-ideal model including the surface heterogeneity by an empirical parameter (n, see Eq (C.3) in Appendix). For each species, the results of the two models are discussed and compared, to find out which one better fits the experimental data.

2. Experimental data available in the open literature

Table 1 summarizes the temperature and pressure ranges related to the experimental adsorption isotherms of H_2, CH_4, CO_2, CO and N_2 available in the open literature and used in this work [8,16–27] and the number of adsorption isotherms used for each species. As can be observed, the experimental data cover a wide temperature range and, thus, the number of isotherms taken from different authors is considered large enough for our investigation. It is useful to remind that some experimental data are not coherent with the majority ones because adsorption equilibrium is affected by several factors, e.g., the synthesis procedures and the Si/Al ratio. Concerning this issue, Cheung et al. [28] synthesized four samples of NaA with different crystallization temperature and time, obtaining quite different adsorption isotherms, in particular between the sample crystallized at 333 K and that at 303 K for 2 and 24 h, respectively. The same occurred to Palomino et al. [29], who observed different adsorption isotherms at 303 K in various LTA samples prepared with different Si/Al ratio ranging from 1 to ∞. Specifically, the maximum CO_2 adsorption capacity was achieved when Si/Al = 2, then a decrease with increasing Si/Al ratio occurred, since the interaction between CO_2 adsorbed and pore walls increases with increasing Al-content.

Based on these considerations, similarly to what done in previous works [13–15], the adsorption isotherms were preliminary screened to verify their consistency.

3. Results and discussion

The following sub-sections presents the obtained results in terms of calculated adsorption isotherms (Section 3.2) and of estimated Langmuir and Sips models parameters (Sections 3.3 and 3.4), comparing them to some literature values to verify the calculation consistency (Section 3.4). Finally, Section 3.5 is dedicated to monovariate regression analysis, allowing the temperature dependence of saturation loading to be obtained and discussed.

Prior to presenting results, a comparison between the properties estimated using absolute and excess of loading respectively is preliminarily carried out (section 3.1) in order to verify if the difference is relevant for the molecular loading calculation.

3.1. Absolute and excess of loading

As reported by Krishna et al. [30], the difference between absolute and excess of loading increases with increasing pore volume and pressure. Furthermore, this discrepancy becomes more relevant in case of weakly-adsorbing species, like hydrogen, at high pressure, whereas it is smaller for strongly adsorbed ones, like CO_2.

Fig. 1 compares the absolute and excess loadings for pure hydrogen (the weakest adsorbed species) at the lowest (40 K) and highest (298 K) temperatures among the available adsorption isotherms. Specifically, the grey and red lines indicate the trends of the absolute loading respectively evaluated with Eqs. (A.2) and (A.3) reported in Appendix A, whereas the black dashed-lines represent the excess of loading. As expected, it can be observed that all the curves are quite similar at low pressure, whereas they diverge only at high pressure. The negligible difference observed can be explained considering that pore volume of NaA (0.3 mL g^{-1} [23]) is quite small compared to those of the MOFs CuBTC, MIL-101 and Zn(bdc)dabco investigated by Krishna [30], which have pore volumes of 0.75, 1.38 and 0.67 mL g^{-1}, respectively. Both excess and absolute loadings were used for the evaluation of H_2 adsorption

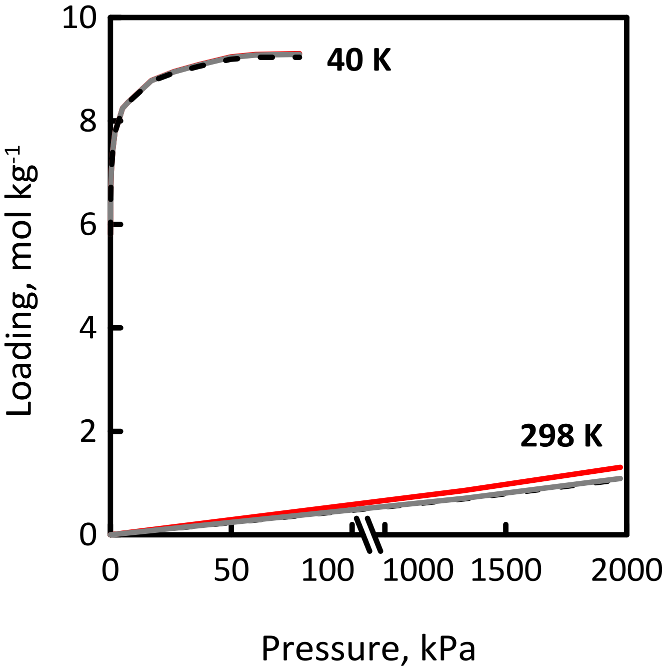

Fig. 1. Absolute and excess of loading for H_2 compared at 40 K and 298 K. Absolute loading evaluated with Eq (A.2) (grey lines), absolute loading evaluated with Eq (A.3) (red lines), excess of loading (black dashed lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
An overview of the operating conditions ranges concerning the published experimental adsorption isotherms used in the present work for LTA 4A zeolite.

Species	$T_{minimum}$/K	$T_{maximum}$/K	$P_{minimum}$/kPa	$P_{maximum}$/kPa	Si/Al	References	Number of isotherms
H_2	40	298	0.03	1970	N.A.	16, 23, 17	8
CH_4	195	308	5	830	1.1–1.6	24, 18, 19, 21, 22	10
CO_2	195	373	0.02	930	1.2–1.6	8, 24, 20, 22, 25, 26	13
CO	193	373	2.8	120	N.A.	24, 20, 27	8
N_2	195	283	3.9	550	N.A.	24, 19, 20, 21	10