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Thermodynamic adsorptive properties of exchanged chabazite-like aluminophosphate SAPO-34

Salima Bellatreche [a], [b], [*], Mohammed Abdelkrim Hasnaoui [a], Rachid Ghezini [a], Abdelkader Bengueddach [a]

[a] *Laboratory of Chemistry of Materials LCM, University of Oran, 1 Ahmed Ben Bella, BP 1524 Oran El M'Naouer, Algeria*
[b] *Department of Pharmacy, Faculty of Medicine, University of Oran, 1 Ahmed Ben Bella, BP 1510 Oran El M'Naouer, Oran, Algeria*

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ABSTRACT

The carbon dioxide adsorption behavior of synthesized chabazite-like M-SAPO-34 and modified with alkali metals (M = Li, Na, K, Cs), processed using volumetric method at different temperatures, was explored. The study allowed to see that the adsorption capacity increases according to the sequence: $Na^+ > Li^+ > K^+ > Cs^+$, and all adsorption isothermal are type I according to Brunauer classification. Thermodynamic studies have been treated by the determination of the adsorption affinity, entropy and isosteric heat of these systems CO_2-M-SAPO-34 with temperature variation between 273 and 298 K. The adsorption affinity shows the same trend for all the M-SAPO-34 at low coverage at 273 K. However, at high coverage, the isosteric heats of exchanged (H, Na, Li)-SAPO-34 present a homogeneous profile indicating dominance of adsorbate-adsorbate interaction. The differentials entropies were found to increase slightly with the coverage. Furthermore, the entropy of K-SAPO-34 at 273, exhibits values less than other exchanged M-SAPO-34. This Confirms pore blockage effect in the case of K-SAPO-34 and leads to reduction of free volume, while the Li-SAPO-34 shows the highest values of entropies with large free volume due to small size of Li^+ cation.

1. Introduction

Since their discovery in 1980 by Union Carbide, the family of aluminophosphates attends a great progression [1]. In order to develop catalytic properties and acidity, this involves insertion of silicon into the framework of zeolite like [2,3]. SAPO-34 finds an effective role in the conversion reaction of methanol to olefin (MTO) [4,5]. SAPO-34 offers the advantage of a great catalyst with small pores and moderate acidity, very good thermal stability, selectivity with an interesting surface.

Furthermore, in the last decade, the field of adsorbents have made rapid progress where molecular sieves such as, X, Y, A, ZSM-zeolites, natural zeolite, etc. have been widely studied [6–10], and even mesoporous silica's material as well as MOF, give similar interest [11–14].

Chabazite reveals interesting adsorption capacity and afford an efficiency in ion exchange [15], as natural chabazite is a promising way in the elimination of heavy metals and radio active in waste [16–19] and gas separation possibilities, while membranes SAPO-34 showed a high selectivity for separation of CO_2/CH_4 [20,21].

Today the problem of global warming preoccupies the attention of researchers throughout the world for this reason air pollution by the greenhouse gases are widely studied, among the solution proposed is capture of carbon dioxide by the adsorption process. The zeolites exchanged with the alkaline cations are promising materials for removal of CO_2, Jun Zhang et al. [22] studied synthetic exchanged zeolite chabazite with alkali and alkaline earth metal in capture of carbon dioxide at different temperatures below 120 °C using volumetric apparatus, dual-site Langmuir model was used to study the isotherm measurements, isosteric heat of adsorption was determined and the results were compared with commercial NaX-zeolite, NaCHA and CaCHA. Nanoporous silicoaluminophosphate SAPO-34 was also used as adsorbent by Ana G. Arévalo-Hidalgo et al. for separation of CO_2 from light gas mixtures [23].

The cation sites affect phenomena of adsorption. Cation sites in Chabazite cages for SAPO-34 have been previously studied [24]. There are four main sites (Fig. 1): Site I is situated at the center of the hexagonal prism, Site II is situated at the center of the six-ring

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[*] Corresponding author. Laboratory of Chemistry of Materials LCM, University of Oran, 1 Ahmed Ben Bella, BP 1524 Oran El M'Naouer, Algeria.
E-mail address: bel.sas@yahoo.com (S. Bellatreche).

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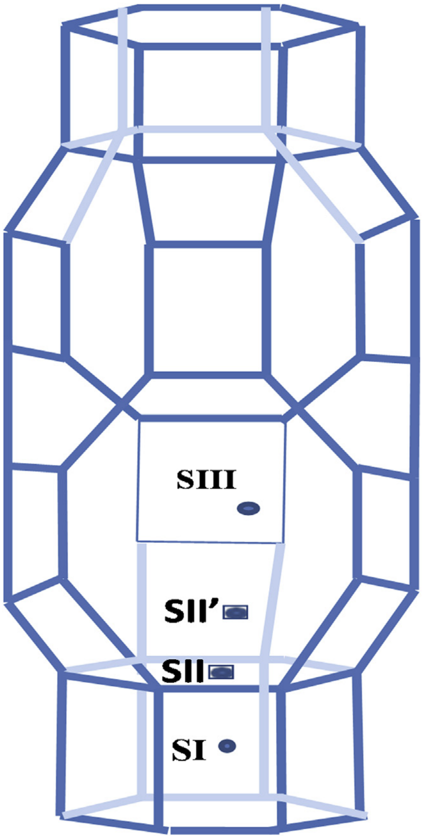

Fig. 1. Structure of the SAPO-34 with main sites.

window of D6R, Site II$^{'}$ takes position in the cavity and Site III situated near the center of the eight-ring window.

The localization of cations depends on the nature of exchanged cations. Indeed, it was reported that the size cation potassium causes a blockage of the pore in the structure, which leads to a decrease of adsorption capacity. The potassium position in aluminosilicate chabazite has been well studied by Calligaris et al. [25].

In this work, we report the adsorption measurements processed using volumetric method on synthesized and modified SAPO-34 by alkali metals at different temperatures. Different adsorption models were used to explore the adsorption phenomenon of M-SAPO-34/CO_2 systems. A thermodynamic study of the adsorption affinity, entropy and isosteric heat, as well as parameters, the strength of interaction between CO_2 molecule and zeolite framework, cation size and charge have an effect on the adsorption capacity of CO_2.

2. Experimental

2.1. Synthesis

The synthesis of SAPO-34 by the hydrothermal method described according to Prakash et al. [26]. With initial molar composition: 1Al_2O_3:**1**P_2O_5:**2.09**Morpholine:**1.08**SiO_2:**66**H_2O. The preparation of the gel by dissolving the aluminum isopropoxide in water, after the addition of phosphoric acid, morpholine and fumed silica, the mixture was stirred; the gel was transferred into the autoclave, at a temperature of 200° C. After 24 h the product was recover to filter, wash and dry at 90° C all night. The product was calcined at 550° C. for 6 h. (See Table 1)

Table 1
Characteristic of reagents used in the synthesis of SAPO-34.

Chemical name	Source	Mass purity	Purification
Aluminum isopropoxide	Prolab	89%	distillation
phosphoric acid	MERCK	85%	–
morpholine	Aldrich	99%	–
fumed silica	Aerosil200, Degussa	99%	–

2.2. Ion exchange

Commercial products used to prepare the exchanged forms, are sodium chloride NaCl (Prolabo), potassium chloride KCl (Merck), lithium chloride LiCl (Prolabo) and cesium chloride CsCl (Prolabo). The ion exchange procedure was carried out, by mixing, under stirring, 1 g of calcined SAPO-34 with 100 ml of the corresponding salt solution at 25 °C, on polypropylene bottles.

2.3. Adsorption apparatus for adsorption isotherm

The experimental apparatus used for the adsorption of carbon dioxide on each ion-exchanged zeolite sample (M-SAPO-34) were measured using a Micromeritics ASAP 2020 volumetric instrument. Prior to the measurements, each sample was heated at 473 K for 6 h under vacuum conditions at pressure 4.10^{-3} mmHg. The sample was then maintained at 269 K, 273, 288 K and 298 K, respectively, during adsorption measurements using a constant temperature water bath equipped with ethanol coolant. Adsorption isotherms were obtained for each material at pressures up to 760 mmHg.

2.4. Characterization

The samples were characterized by X-ray powder diffraction recorded on a 2002 Seifert powder diffractometer. The scanning rate was 2°/min and Cu-Kα radiation was used. The chemical composition of the sample was determined with a Philips Magix-PW2540Vrc X-ray fluorescence (XRF) spectrometer. The scanning electron microscopy images have been obtained on Philips XL 30 microscope.

3. Results and discussion

Analysis of the ion exchange effluent shows an agreement with the chemical analysis of solid in the case of exchanged sodium cation, according to Table 2, the number of unit cell varied from 26.08 to 27.24 10^{19} per unit mass.

The XRD patterns of the SAPO-34 and exchanged materials are given in Fig. 2.

This figure clearly present characteristic peaks of SAPO-34 at $2\Theta = 9.42$, 12.77 and 15.92° which corresponds to the reflections (101), (110) and (021) respectively. Indicating the formation of well crystallized SAPO-34 [27] and attesting that the structure of SAPO-34 exchanged forms are obtained without structure modification.

The crystal morphology of synthesized and exchanged SAPO-34

Table 2
The molar compositions of the different sample.

Sample	Molar composition	Number of unit cells per gram x 10^{-19}
H-SAPO-34	$Al_{17.88}\ O_{72}\ Si_{7.51}\ P_{13.77}\ H_{4.11}$	26.88
Na-SAPO-34	$Al_{16.94}\ O_{72}\ Si_{6.94}\ P_{12.87}\ Na_{1.5246}\ H_{2.55}$	26.46
Li-SAPO-34	$Al_{16.82}\ O_{72}\ Si_{6.81}\ P_{12.75}\ Na_{0.34}\ H_{2.55}\ Li_{1.18}$	27.24
K-SAPO-34	$Al_{13.98}\ O_{72}\ Si_{8.88}\ P_{13.1}\ Na_{0.2}\ H_{0.08}\ K_{0.6}$	27.21
Cs-SAPO-34	$Al_{17.31}\ O_{72}\ Si_{6.4047}\ P_{12.81}\ Na_{0.81}\ H_3\ Cs_{0.69}$	26.08

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