



Thermodynamic Study of Light Organic Molecules Adsorption onto ZK-4 Zeolite

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ABSTRACT

In this work, we were interested to the interactions of various light gases (critical temperature not exceeding 31 °C) with the zeolite ZK-4 and its varieties exchanged at temperatures close to ambient. The interest first practice since these gases are frequently encountered in industry, and most separations, that concern them by pressure swing adsorption (PSA) are carried at room temperature. By working in these conditions, we will be in the scope of application of Henry's law, which will allow us to better characterize the adsorption of the first molecules (gas-solid interaction). The thermodynamic study should enable us to identify the type of adsorption (localized, non-localized) by applying a theoretical model explaining the experimental results. The choice of the adsorbate was guided by the behavior of the introduced molecules toward the compensating cations present in the zeolite framework. These probe molecules having a specific interaction with zeolitic cations: N₂, CO₂ (highly quadrupolar), C₂H₄ (double bond) or C₃H₈ which do not exhibit neither. Final results show that adsorption of nitrogen on ZK-4 sodic form is made in a located way on five sites following Langmuir model and none of CO₂ and C₂H₄ chemisorptions was revealed. Besides, the gaseous molecules interactions in presence of divalent cations replacing sodium in ZK-4 are much less higher than in the case of zeolite 4A, and are characteristic of physisorption on relatively heterogeneous sites.

Keywords: ZK-4 zeolite; Adsorption isotherm; Langmuir model; Calorimetry.

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INTRODUCTION

Zeolite ZK-4 belongs to the LTA type in the IUPAC system (Meier and Olson, 1987) and it is isomorphic to zeolite Na-A or 4A, which it differs only by a Si/Al greater than one (1.1 to 1.9) instead of 1 for zeolite 4A. It was synthesized for the first time by Kerr (Kerr, 1966), which established the stoichiometric domain in which it crystallizes, and then by a small number of authors (Melchior et al., 1982; Ikeda et al., 2003; Kerr, 1966; Leigenger et al., 2008; Eddy et al., 1986) who have studied the structural properties of the cubic lattice. It has been shown that the adsorption of organic molecules such as n-hexane and n-octane (Kerr, 1966) on Na-ZK-4 (Si/Al=1.7) depend directly on cations Na^+ position even more when they are replaced by K^+ cations (Ikeda et al., 2008; Oh et al., 2002). Furthermore, other works (Sadlo et al., 2009) show only silver dimers are stabilized, whereas in Linde 4A silver hexamers were trapped in the sodalite cage. In this work, a certain ZK4 samples have been synthesized, cationic exchange with Ni^{2+} , Co^{2+} and Ca^{2+} have been performed and finally the ratio Si/Al for each cationic variety was determined. Adsorbed quantities of nitrogen, carbon dioxide and ethylene have been measured at temperatures above Kelvin temperature and the experimental results applied to the theoretical Langmuir model using manometric adsorption technique and calorimetry. The discovery of a new catalytic material, ruthenium nanoparticles stabilized by ZK-4 zeolite framework, for this important reaction has been reported by Zahmakiran (Zahmakiran, 2012). This new catalyst system was prepared by borohydride reduction of ruthenium (III)-exchanged ZK-4 zeolite in water at room temperature. The characterization of the resulting material by advanced analytical tools shows the formation of ZK-4 zeolite dispersed ruthenium nanoparticles.

EXPERIMENTAL

Chemicals

The ZK4 zeolite synthesis requires highly reactive products; For this, we used sodium aluminate (Carlo Erba weight composition: $\text{Al}_2\text{O}_3 = 56\%$, $\text{Na}_2\text{O} = 37\%$) as a source of aluminum and Césacol (colloidal solution 40%, purchased from Rhone-Poulenc Specialty Chemicals) as the silicon source. The organic ion is tetramethylammonium hydroxide as TMAOH.5H₂O from Fluka. Other reagents used are the sodium hydroxide pellets from Prolabo, and deionized water.

Synthesis

We used the method described by Kerr (Kerr, 1961 and 1966) slightly modified with a fixed molar composition from: 8TMA₂O, 1.46 Na₂O, 1 Al₂O₃, 5.33SiO₂, 320 H₂O. An example of synthesis consists in dissolving 3g of SiO₂ in 64 mL of TMAOH 2.5M (representing 14.38g of pure TMAOH). This operation is carried with constant stirring for 3 days in a Teflon flask. Aluminate solution was prepared from aluminum hydroxide (1.46g) dissolved in the sodium hydroxide solution (1.09g NaOH) by heating and to which were added 45.5 cm³ of is distilled water. Aluminate gel so obtained is poured into the silicate solution with vigorous stirring for 150 min; the mixture was aged at 30 °C for 48 to 72 hours and then heated in an oven for 24 h at 100 °C. The final product was washed, filtered and dried.

Exchanged forms divalent cations such Ca^{2+} , Ni^{2+} et Co^{2+} were obtained, in aqueous media, from a ZK4 sample totally recationated to sodium by NaOH treatment. Thus, 2 to 3g of zeolite Na-ZK4 previously calcined at 500 °C were put together with 50 mL of distilled water in a beaker and mixed to 100 mL of 0.1M of cation exchanger solution. After an amply contact time between the two phases under agitation at ambient temperature, the solution was filtered then dehydrated under vacuum at 400 °C.

Characterization

X-rays diffraction analysis is composed of a generator of X-rays (Philips brand PW 1710) and of a vertical goniometer equipped with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). Indexation of the diffraction peaks in the cubic system Pm3m allows calculation of the lattice parameter of the zeolite ZK-4 by the relation $a = (h^2 + k^2 + l^2)^{1/2}$.

The gas adsorption measurements were carried out on a Micromeritics 2100 E entirely automated, which includes an introduction part with two pressure sensors connected to vacuum and gas inlets. The adsorption part comprises a cell containing the sample in a thermostatic chamber and a device for nitrogen by pressurizing pumping is connected to a temperatures regulator to achieve the desired temperature quickly. The micropores volume accessible V_m to the adsorbate for an activated zeolite is calculated by (Gurvitsch, 1915):

$$V_m = \frac{n_s}{\rho_T} M$$

With n_s : mole of adsorbate per unit mass of adsorbent; ρ_T : density of the liquid adsorbate at the temperature T and M : molecular weight of the adsorbate. In this study, we report our results in n_a number of molecules per cavity α (abbreviated: *molec. cav*⁻¹) and therefore the correspondence between *cm*³STP.g⁻¹ and *molec. cav*⁻¹ was deduced from the chemical formula of the zeolite ZK -4 (Si/Al =1.78) and amounted to:

$$1 \text{ molec. cav}^{-1} = 13.68 \text{ cm}^3 \text{ STP. g}^{-1}$$

Morphological study by scanning electron microscopy SEM was performed on a JSM 6400 instrument from JEOL.

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of calcined samples; the H^+ cation was introduced to insure the crystal electro neutrality. Sodium zeolite has a Si / Al ratio of 1.78 and is slightly different in its varieties exchanged with cobalt and nickel while in the calcium zeolite, it drops to 1.29.

Table 1: Chemical formulae and Si/Al ratio values of ZK-4 zeolite samples and their exchanged forms

Designation	Chemical formula	Si/Al ratio	Lattice parameter a_0/A^0
ZK4-1	$Na_{8.33}H_{0.31}Al_{8.64}Si_{15.36}O_{48}, 22.18 H_2O$	1.78	12.158
Ca-81	$Na_{1.60}Ca_{4.26}H_{0.37}Al_{10.49}Si_{13.51}O_{48}, 24.82 H_2O$	1.29	12.238

Deduced by XRD analysis, the lattice parameter is practically identical to the samples, indicating that no alteration has affected the zeolite structure. This is confirmed by microscopy SEM showing cubic crystallites with homogeneous dimensions ($\sim 3\mu m$) for the samples prepared; Tangles of these cubic forms and the observed overgrowths appear to be due to a secondary nucleation on the crystallites walls rather than a coalescence of two particles during their growth (figure 1).

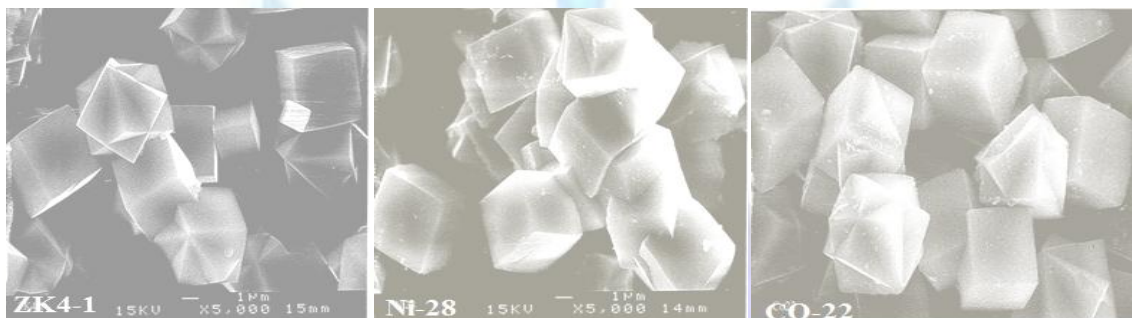


Figure 1: SEM pictures of zeolite crystals Na-ZK-4 and its varieties exchanged with nickel (Ni-28) and cobalt (Co-22).

Adsorption of O_2 (Fig. 2-a) and adsorption of N_2 (Fig. 2-b) at 77K is represented by isotherms for the variety samples of ZK-4, which are of type I according to IUPAC classification characteristic of microporous solids with a broad horizontal plateau over the whole domain of relative pressures.

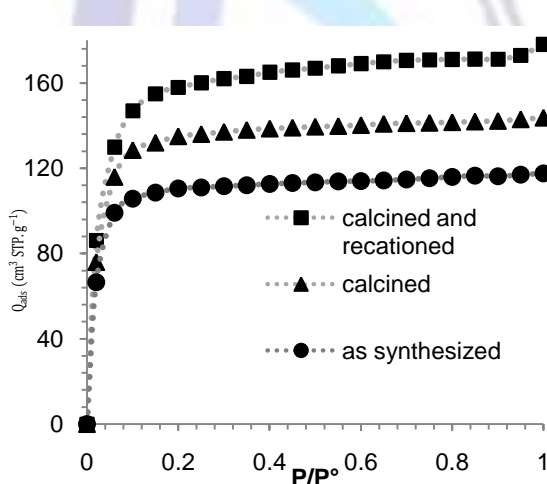


Figure 2-a: Oxygen adsorption isotherms at 77 K of zeolite ZK-4-1 (Si/Al=1.78) degassed under vacuum at 400 °C: (■) Na-ZK-4 calcined and reationised; (▲) Na-ZK-4 calcined; (●) Na-ZK-4 as-synthesized.

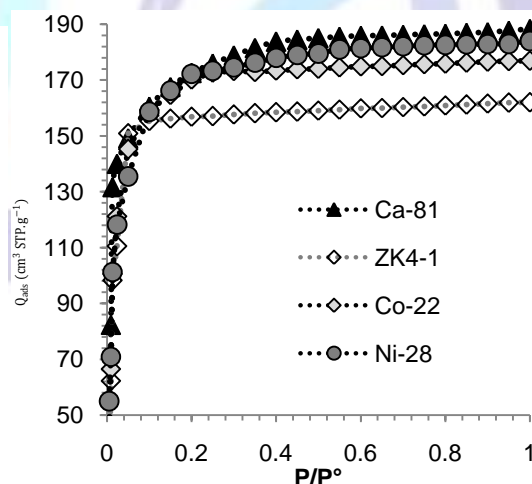


Figure 2-b: Nitrogen adsorption isotherms at 77 K on zeolite ZK-4 (◇ ZK-4-1) and its varieties exchanged at: calcium (▲) Ca-81, cobalt (●) Ni-28 and nickel (◇) Ni-28.

Based on the interception ratio (IR) which is a good indication of micropores presence if $1 < IR < 2.2$ (Kerr, 1961), the accessible microporous volumes to nitrogen and oxygen can be evaluated as shown in table 2; Thus, nitrogen penetrates into the sodium zeolite ZK-4, in contrast to zeolite 4A, suggesting that the cavity α becomes accessible to the N_2 molecule, with the reduced number of Na^+ cations (≥ 9) in the structure, instead of 12 Na^+ in 4A zeolite.

Table 2: Values of accessible volume and RI criteria of N₂ and O₂ at 77 K

Samples	ZK-4-1	Ca-81	Ni-28	Co-22
RI Criteria /N ₂	1.029	1.057	1.048	1.041
RI Criteria /O ₂	1.009	1.008	1.014	1.002
V_m (nm ³ cav ⁻¹) accessible to N ₂	0.604	0.679	0.688	0.570
V_m (nm ³ cav ⁻¹) accessible to O ₂	0.524	0.572	0.573	0.519
V_m (N ₂) / V_m (O ₂)	1.153	1.187	1.201	1.098

To verify the localized character of adsorption in zeolite, we study the adsorption of nitrogen in the range – 80 °C to 0 °C where adsorption takes place in the large cavity α . The upper limit of 0 °C is justified by the low adsorbed quantities. n_a/P vs. n_a plots show that isotherms are fairly close to straight lines (figure 3), taking into account experimental errors in the domain $n_a < 3$ which indicates that the Langmuir equation is applicable in this domain. The gradual exchange of Na⁺ by divalent cations leads to concave curves, interpreted as a growing heterogeneity of adsorption sites; these straight lines intersect the x-axis to $n_a = 5 \text{ molec. cav}^{-1}$ which implies the existence of five identical adsorption sites without interaction by cavity.

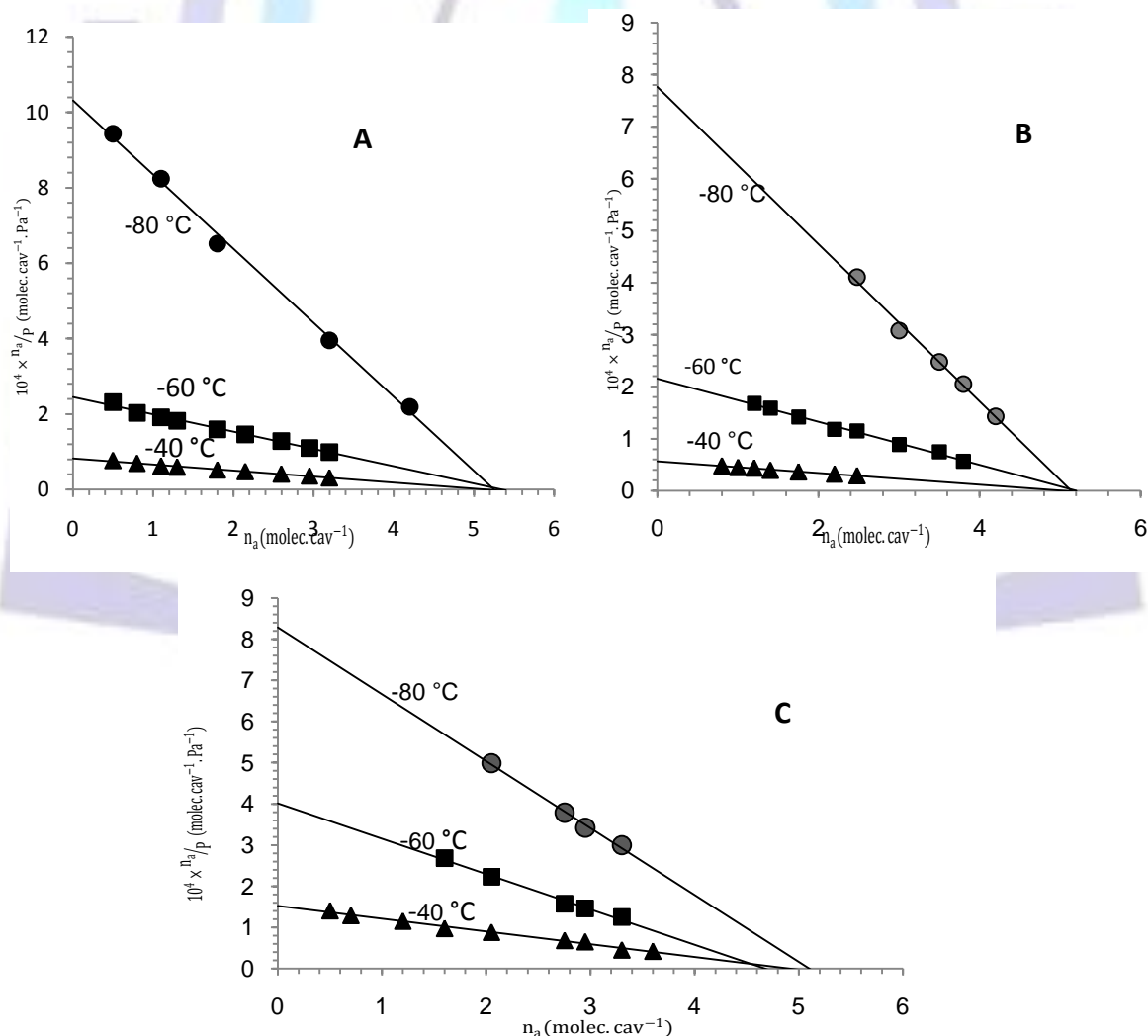


Figure 3: Nitrogen adsorption isotherms on A: zéolite ZK-4-1 (Si/Al=1.78); B: Co-22 and C: Ni-28 at: (●) –80 °C ; (■) –60 °C ; (▲) –40 °C and (—) Langmuir model to 5 sites.

From there, table 3 shows the results after adjustment of the Langmuir equation parameters by fixing n_a^m to five sites per cavity; it is observed that nitrogen adsorption onto ZK-4-1 is done on five equivalent sites, among of the eight sites I of the crystal unit cell. As for cationic varieties, the sites I of Co-22 sample contain respectively 6.6 Na^+ and 0.97 Co^{2+} or 6.3 Na^+ and 1.25 Ni^{2+} for Ni-28 sample suggesting that Na^+ constitute privileged adsorption sites compared to the divalent cations which are more inserted in the 6 oxygen-ring. However, it is more reasonable to think that the adsorption sites have a complex energy distribution.

Table 3: Langmuir equation parameters adjustments for each adsorbent-adsorbat couple (sites number fixed at 5)

Designation	k_0/Pa^{-1}	$U_0/\text{kJ.mol}^{-1}$	$-\ln k (0^\circ\text{C})$
ZK4-1	$5.22 \cdot 10^{-11}$	24.48	8.006
Co-22	$1.15 \cdot 10^{-9}$	18.05	7.738
Ni-28	$1.87 \cdot 10^{-8}$	14.36	6.575

Propane molecule with critical diameter 4.89 Å does not adsorb onto zeolite Na-A to ambient, whereas in Ca-A, the adsorption capacity is 0.130 grams adsorbate per gram of zeolite¹². Propane adsorption isotherms are of type I for ZK-4-1 and Ca-81 samples and much more propane is adsorbed in the zeolite exchanged with calcium than the sodic zeolite for both temperatures (figure 4). In n_a/P vs. n_a plot, the Langmuir model describe the propane adsorption onto Ca-81 sample for a number of sites touched by adsorption that not exceed 2 ($n_a < 1.5 \text{ molec.cav}^{-1}$), much fewer than those engaged in nitrogen adsorption as shown in figure 5.

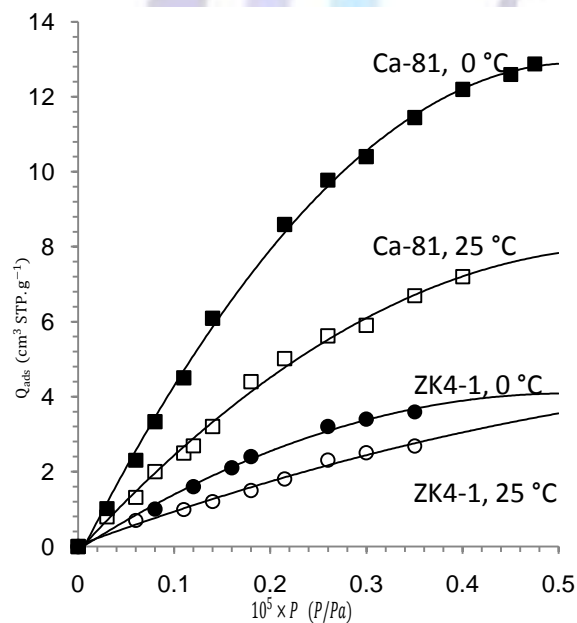


Figure 4: C_3H_8 adsorption isotherms on zeolite ZK-4 and Ca-81 at 0°C (● ZK-4-1; ■ Ca-81) and 25°C (○ ZK-4-1; □ Ca-81).

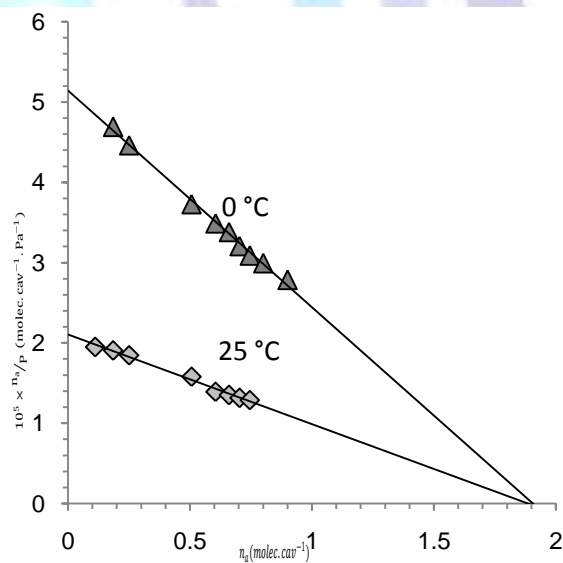


Figure 5: Adsorption isotherms of $\text{C}_3\text{H}_8/\text{Ca-81}$ couple in coordinates: $n_a/P = f(n_a)$ at 0°C (●) and 25°C (■); (—) theoretical curve of Langmuir.

We can explain, in the case of the sodium form, by the fact that, the propane molecule exhibiting neither double bond nor quadrupole or dipole moment, does not have a required orientation relative to the surface. It is therefore less sensitive to the nature of the cation and two neighboring molecules may have with respect to each other in the most energetically favorable way, which explains the large lateral interaction. For the calcium form, it thus seems that the accessible Ca^{2+} cation to propane molecule is a significant factor in favour of a localised adsorption by being more polarizing than Na^+ and could be explained by an adsorption of one C_3H_8 molecule on 2 Ca^{2+} together.

Calorimetric method has been used for CO_2 and C_2H_4 uptakes at 25°C to characterize the sites most accessible to adsorption. Figure 6 represents adsorption isotherms of CO_2 in ZK-4-1 in coordinates $n_a = f(P)$. wherein n_a is equal to $13.68 \text{ cm}^3 \text{ STP.g}^{-1}$ calculated for this type of zeolite. All isotherms are type I and corresponding to Langmuir equation, noting however that the adsorption rate is very low for the first experimental points. Calculation indicates 123 mg of CO_2 adsorbed per gram of zeolite ZK-4-1 at room temperature, which makes it as very good CO_2 adsorbent. Figure 7 shows

that CO₂ adsorption at close to room temperature (0 - 25 °C), affects a number of nearby five sites by lattice, so characteristic of the localized adsorption without lateral interactions while the slight concavity upwards is due to certain energy heterogeneity.

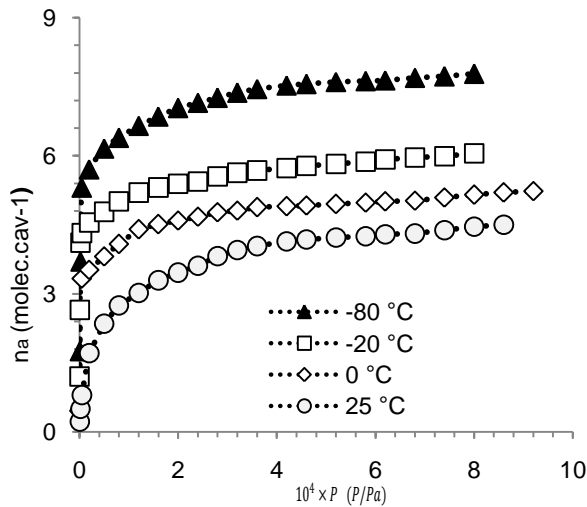


Figure 6: CO₂ sorption isotherms on zeolite ZK-4-1: (▲) -80 °C; (□) -20 °C; (◇) 0 °C; (○) 25 °C

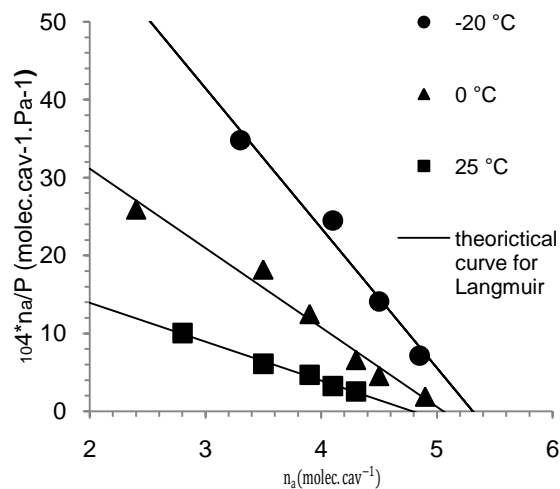


Figure 7: Langmuir model applied to the CO₂ sorption in ZK-4-1 in coordinates: $\frac{n_a}{P} = f(n_a)$: (●) -20 °C; (▲) 0 °C; (■) 25 °C; (—) theoretical curve of Langmuir

Heats of adsorption of CO₂ measured in ZK-4-1 sample and exchanged forms (Fig. 8) show a value up to 80 kJ.Mol⁻¹ for the first gas introduction (< 0.029 molec. cav⁻¹) in all samples; However, they do not enable to say if a CO₂ chemisorption occurs for low adsorbed amounts. Similarly, after cation exchange, the fact that only the first introduction of CO₂ result in a relatively high heat of adsorption (80-90 kJ. Mol⁻¹) does not assume that there is another type of site where takes place chemisorptions. This is not comparable with those obtained for the 4A zeolite which is about 120 kJ.mol⁻¹, and which calorimetry and IR spectroscopy studies indicate the chemisorptions onto zeolite 4A (Ginoux and Bonnetain, 1991; Amari et al., 1994; Delaval et al.,1986; Takaishi et al., 1975) leading to two possible forms: carboxylate or carbonate; it explains the high heats observed for n_a less than 0.3molec.cav⁻¹. The principal CO₂ adsorption sites in the ZK-4 zeolite are of type Na (I), responsible of a strong heat of physical adsorption and absence of the CO₂ chemisorptions in ZK-4 could be explained starting from the assumption that CO₂ is chemically absorbed on a cationic pair, in fact the missing Na (II) -Na (III) pair in ZK-4 (Ginoux, 1983). Thus, these results may indicate the existence of energetically equivalents adsorption sites, characteristic of physisorption in a very wide range of adsorbed amounts.

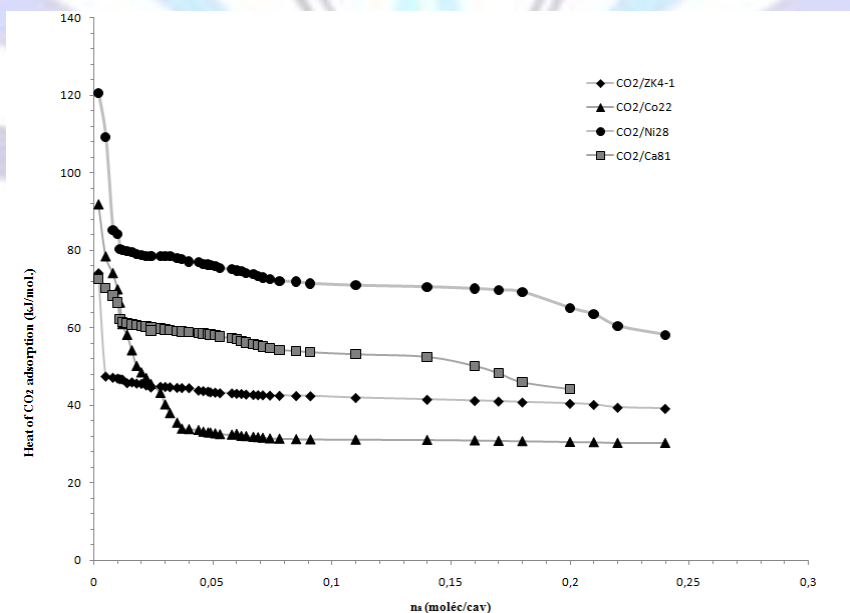


Figure 8: Enthalpies of CO₂ adsorption onto zeolite ZK-4 and its varieties exchanged with divalent cations: (◆) ZK4-1; (▲) Co-22; (●) Ni-28; (■) Ca-81

The heat of adsorption of ethylene measured at room temperature, are significantly lower ($\sim 40 \text{ kJ.mol}^{-1}$) for the first introductions and stabilize at 30 kJ.mol^{-1} over the domain $n_a < 2 \text{ molec.cav}^{-1}$ with significant difference between samples (Fig. 9). It appears for ZK-4-1 sample that all sites are energetically equivalents (4 or more) per cavity α , attributable to the cations Na^+ in site I. When divalent cations replace the sodium, the behavior of the zeolite with respect to ethylene changes compared with it was with the sodium form of the zeolite. There is increasing initial energy of interaction with the nature of the cation. Presumably polarizing power of the exchanged cations in the structure is not completely converted into energy of interaction cation-adsorbate, probably due by a displacement of sites I towards the β cavity. Ultimately, the mixed influence of the introduction of divalent shows that the adsorption of C_2H_4 may well be by the interaction of π –electrons with all cation-6-oxygen rings and not only with the assumed cation invariably exposed to the adsorbate.

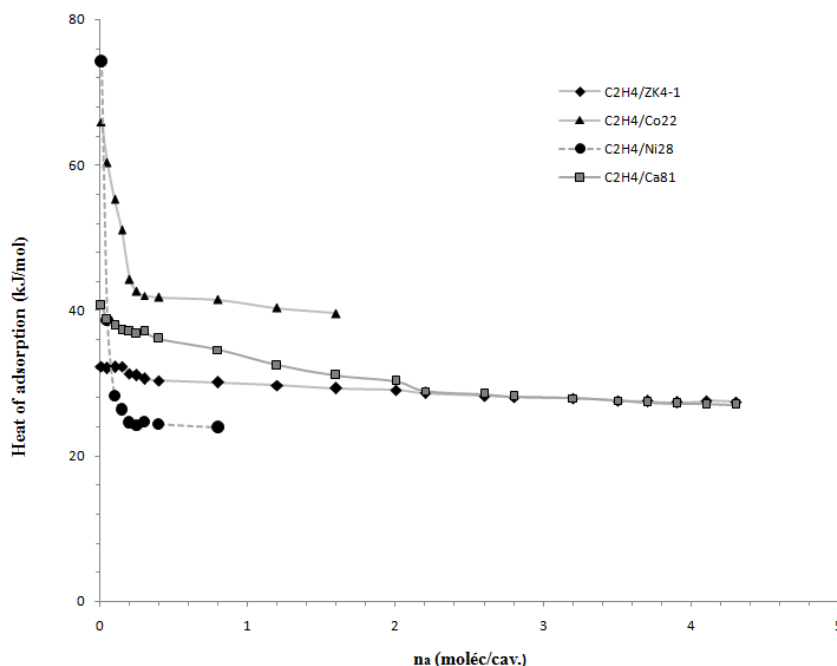


Figure 9: Enthalpies of C_2H_4 adsorption on zeolite ZK-4 and its varieties exchanged with divalent cations: (♦) ZK4-1; (▲) CO-22; (●) Ni-28; (■) Ca-81

CONCLUSION

N_2 adsorption onto ZK-4 zeolite in sodic form and exchanged with nickel and cobalt (< 30%) at temperatures close to ambient allowed the identification of five sites of adsorption, probably the cationic sites Na I. The adsorption of C_3H_8 is done in a localised way on the variety of ZK-4 exchanged with calcium whereas the sodium form lets think that Na^+ ions less polarizing than Ca^{2+} one are responsible for very energetic interactions adsorbate -adsorbent that cannot be described by Langmuir model. Even it does not generate chemisorptions, a relatively high enthalpy of adsorption has been observed in the range of small quantities of CO_2 adsorbed. The absence of this one is attributed to the cations absence in site II and III. Heats of about 30 kJ Mol^{-1} are noted in the case of C_2H_4 adsorption onto Na-ZK-4 for the entire range till 5 molecules/ cavity which is the ethylene adsorption limit. For the studied n_a range, the heat of adsorption become important with weak adsorbed quantities, in the case of cationic forms of nickel and cobalt to stabilize then at 28 kJ.Mol^{-1} . This phenomenon is due to the strong interaction which is created between the divalent cations and the ethylene molecule mitigated by a more or less large sinking of the cation in the 6-oxygen ring.

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