TOPOCAL REVIEW

Advances in principal factors influencing carbon dioxide adsorption on zeolites

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Abstract

We report the advances in the principal structural and experimental factors that might influence the carbon dioxide (CO₂) adsorption on natural and synthetic zeolites. The CO₂ adsorption is principally governed by the inclusion of exchangeable cations (counterions) within the cavities of zeolites, which induce basicity and an electric field, two key parameters for CO₂ adsorption. More specifically, these two parameters vary with diverse factors including the nature, distribution and number of exchangeable cations. The structure of framework also determines CO₂ adsorption on zeolites by influencing the basicity and electric field in their cavities. In fact, the basicity and electric field usually vary inversely with the Si/Al ratio. Furthermore, the CO₂ adsorption might be limited by the size of pores within zeolites and by the carbonates formation during the CO₂ chemisorption. The polarity of molecules adsorbed on zeolites represents a very important factor that influences their interaction with the electric field. The adsorbates that have the most great quadrupole moment such as the CO₂, might interact strongly with the electric field of zeolites and this favors their adsorption. The pressure, temperature and presence of water seem to be the most important experimental conditions that influence the adsorption of CO₂. The CO₂ adsorption increases with the gas phase pressure and decreases with the rise of temperature. The presence of water significantly decreases adsorption capacity of cationic zeolites by decreasing strength and heterogeneity of the electric field and by favoring the formation of bicarbonates. The optimization of the zeolites structural characteristics and the experimental conditions might enhance substantially their CO₂ adsorption capacity and thereby might give rise to the excellent adsorbents that may be used to capturing the industrial emissions of CO₂.

Keywords: zeolites, chemisorption, physical adsorption, carbon dioxide, surface structure

(Some figures in this article are in colour only in the electronic version.)
1. Introduction

The increased use of fossil fuels during the past 200 years contributes to the steady rise of CO$_2$ level in the atmosphere, a major green house gas that contributes significantly to global warming [1, 2]. Several technologies to separate and capture the industrial emissions of CO$_2$ have been developed. Among them, certain technologies are based on the CO$_2$ adsorption/desorption by using natural and synthetic zeolites [3, 4]. The zeolites are a subclass of tectosilicates that possess a framework formed by a three-dimensional assemblage of tetrahedra [SiO$_4$] and [(AlO$_4$)$_3$]-. This assemblage gives rise to diverse framework structures including those shown in figure 1. The packing of zeolite structure allows the formation of regular cavities joint by the channels, where the molecules with an appropriate size such as the gas as CO$_2$, water and the metallic exchangeable cations (Li$^+$, Na$^+$, K$^+$, Ca$^{2+}$, Ba$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Mg$^{2+}$, etc) can penetrate and compensate for the negative charges created by the substitution of AlO$_4$ tetrahedron by SiO$_4$ tetrahedron (figure 2) [6, 7]. The CO$_2$ usually undergoes a physical adsorption (physisorption) and chemical adsorption (chemisorption) at the surface of zeolites. The zeolites are recognized to be the potent CO$_2$ adsorbents that are able to adsorb and desorb CO$_2$. The most of known zeolites have a capacity of CO$_2$ adsorption at high pressures and low temperatures which varies from 0.15 to 5.5 mmol of CO$_2$ (g of zeolite)$^{-1}$ at 273–373 K (tables 1–3) [9–20]. The degree of irreversible adsorption of CO$_2$ on zeolites M-ZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) which has been evaluated under a pressure inferior to 6.7 × 10$^{-2}$ MPa, was less than 10% of the total adsorption [21]. The adsorption capacity of zeolites depends on several factors including the size, polarizing power, distribution and the number of cations in their porous structure, Si/Al ratio, size, the form of their pores, the polarity and size of adsorbed molecules, the presence of water and other gas and presence of carbonates at their surface. Experimental conditions such as pressure and temperature are also among the factors influencing the adsorption capacity of zeolites.

In this study, we report an advanced analysis of the most important factors influencing CO$_2$ adsorption on natural and synthetic zeolites. The objective of this study is to enhance the understanding of the mechanism for CO$_2$ adsorption on zeolites and provide data that could be used to evaluate the potential of their industrial application.

2. Theory

2.1. Influence of the structural characteristics of zeolites on the CO$_2$ adsorption

2.1.1 Influence of the basicity. The basic properties of zeolites brought by cations allow a strong capitation of acidic molecules by enhancing the electron density of the framework oxygen [22, 23]. The basic strength of these sites increases with the electropositivity of exchangeable cations [24]. More specifically, certain works have indicated that the basic strength of cationic zeolites containing the cations of Group 1A increases as following: Li$^+$ < Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$ [25, 26]. Study of CO$_2$ adsorption on three zeolites, including natural hershelite-sodium chabazite (sodium aluminosilicate), clinoptilolate (sodium aluminosilicate) and clinoptilolite (potassium calcium sodium aluminosilicate), have also revealed that the capacities and rate of CO$_2$ adsorption of natural hershelite-sodium chabazite

![Figure 1. Scheme showing the portions of the framework structures of (a) zeolite A, (b) faujasite (type X, Y) and (c) zeolite ZSM-5 (reprinted from [5] with permission from Trans Tech Publications).](image1.png)

![Figure 2. Schematic diagram of zeolite 4A showing the sodium cations within cavities. The atoms of silicon, aluminum, oxygen and sodium in zeolite 4A are indicated in yellow, purple, red and green, respectively (reprinted with permission from [8] © 2004 American Chemical Society).](image2.png)
alkaline earth oxides, are considered to be more strongly basic sites of basic metal oxides such as rare earth oxides and the capacity of CO$_2$ adsorption on zeolites NaX and NaY caused a rise of the basicity and of occluded CsO.

| Zeolite | Si/Al | Temperature (K) | Pressure (kPa) | Adsorption capacity (mmol g$^{-1}$) | Reference |
|--------|-------|----------------|---------------|-----------------------------------|-----------|
| H-ZSM-5 | 15 | 281 | 81.63 | 2.148 | [10] |
| 15 | 293 | 91.02 | 2.114 | | |
| 15 | 309 | 88.75 | 1.869 | | |
| 30 | 281 | 84.58 | 1.902 | | |
| 30 | 293 | 94.94 | 1.832 | | |
| 30 | 309 | 92.33 | 1.602 | | |
| 60 | 281 | 52.54 | 1.375 | | |
| 60 | 293 | 81.44 | 1.377 | | |
| 60 | 309 | 84.67 | 1.279 | | |
| 280 | 313.15 | 101.3 | 1.24 | | [11] |

and clinoptilolite (sodium aluminosilicate) are greater than clinoptilolite (potassium calcium aluminosilicate) [27]. This difference of adsorption has been attributed to the higher basicity of the surface of natural harsheleite-sodium chabazite and clinoptilolite (sodium aluminosilicate) as compared to that of clinoptilolite (potassium calcium sodium aluminosilicate), resulting from a greater amount of sodium ions on the natural harsheleite-sodium chabazite and clinoptilolite (sodium aluminosilicate). Moreover, it has also been reported that the basicity of oxygen atoms of framework zeolites NaX and NaY is strongly decreased by the substitution of Na$^+$ cations by the Ba$^{2+}$ cations [22]. This phenomenon might be caused by a decrease of partial negative charge of oxygen atoms adjacent to Ba$^{2+}$ cations. In this matter, an analysis of the CO$_2$ adsorption on zeolites KX, BaX and LaX has effectively indicated that the zeolite KX was the most basic among these three zeolites [28]. In contrast, a study of CO$_2$ adsorption on the clinoptilolite has indicated that the substitution of Na$^+$ and K$^+$ by Ca$^{2+}$ caused a rise of the basicity of the framework oxygen acting as basic center [7]. The basic strength and the capacity of CO$_2$ adsorption of zeolites might also be increased significantly by occlusion of alkali metal oxides. The basic sites of basic metal oxides such as rare earth oxides and alkaline earth oxides, are considered to be more strongly basic than those of ion-exchanged zeolites [26]. In this matter, it has been observed that the occlusion of oxides of cesium (CsO$_2$) in the zeolites NaX and NaY caused a rise of the basicity and capacity of CO$_2$ adsorption on these zeolites, and the increase of the capacity of CO$_2$ adsorption was proportional to amount of occluded CsO$_2$ [29].

### 2.1.2 Influence of the polarizing power, distribution, size and number of exchangeable cations

The adsorption of gas by the zeolites is also determined by the polarizing power of the exchangeable cations and their distribution, size and number that influence the local electric field and the polarization of adsorbed molecules on the zeolites [12]. In general, the polarizing power of the cations is inversely proportional to its ionic radius [30]. For instance, the diameters of cations from Group 1A vary as following: Cs$^+$ (3.3 Å) > Rb$^+$ (2.9 Å) > K$^+$ (2.7 Å) > Na$^+$ (1.9 Å) > Li$^+$ (1.4 Å) and their polarity: Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ > Cs$^+$ [31, 32]. Hence, the zeolites such as ZSM-5 and M-ZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) which have small cations might penetrate more easily within channels, are able to interact more strongly with the CO$_2$ [19, 33]. This is in agreement with the results from a study performed by Yamazaki et al. [21]. They showed that energy of the interaction between the CO$_2$ and the cations sites of zeolites M-ZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) decreases with the increase of the size of these cations sites. In parallel, the distribution of exchangeable cations in the different sites of the zeolites structure causes the heterogeneous character of the CO$_2$ adsorption [17]. For example, it has been established for faujasite-type zeolites that molecules of CO$_2$ might be adsorbed only in the supercage, and more specifically in sites localized within sodalite cage and/or in the hexagonal prism [22, 34, 35]. The position of extraframework cations

| Zeolite type | Temperature (K) | Pressure (kPa) | Adsorption capacity (mmol g$^{-1}$) | Reference |
|-------------|----------------|---------------|-----------------------------------|-----------|
| 13X and NaX | 298.15 | 2068 | 5.2 | [13] |
| 293 | 0.55 | 1.07 | | |
| 273.15 | 102 | 4 | | |
| 293.15 | 102 | 3.4 | | |
| 313.15 | 102 | 2.75 | | |
| 333.15 | 102 | 2.3 | | |
| 353.15 | 102 | 2.0 | | |
| 303 | 2000 | 5.5 | | |
| 313 | 2000 | 5.0 | | |
| 323 | 2000 | 4.8 | | |
| 304.55 | 28.5 | 5.416 | | |
| 305.95 | 68.73 | 4.618 | | |
| 303 | 46.93 | 5.04 | | |
| 303 | 1320 | 3.068 | | |
| 303 | 1000 | 3.551 | | |
| 373 | 120 | 2.121 | | |
| 373 | 1000 | 3.168 | | |
| 373 | 120 | 0.239 | | |
| 573 | 1000 | 1.039 | | |
| Na-ZSM-5 | 297.25 | 71.52 | 1.908 | | |
| 303 | 200 | 1.209 | | |
| 333 | 200 | 1.438 | | |
| Li-ZSM-5 | 303 | 200 | 1.418 | | |
| 333 | 200 | 1.376 | | |
| Cs-ZSM-5 | 303 | 200 | 1.334 | | |
| 333 | 200 | 1.251 | | |
| Rb-ZSM-5 | 303 | 200 | 1.334 | | |
| 333 | 200 | 1.543 | | |
| K-ZSM-5 | 303 | 200 | 1.209 | | |
| 333 | 200 | 1.501 | | |
| MCM-41 | 323.15 | 101.3 | 0.325 | | |
| 348.15 | 101.3 | 0.195 | | |
| 373.15 | 101.3 | 0.150 | | |
sites in faujasite-type structure are shown in figure 3. In the case of zeolite NaX, the sodium ions that are accessible to CO$_2$ molecules are localized in two sites: the sites II that are strongly bound to zeolite lattice and the sites III that are less bound and responsible of heterogeneous character of CO$_2$ adsorption [17]. In regard with this, Khelifa et al [34, 37] have notably observed a decrease of the CO$_2$ adsorption affinity when Na$^+$ cations of an x-type zeolite are exchanged by the M$^{2+}$ cations (Mg$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, Cu$^{2+}$). However, there is an increase of the CO$_2$ adsorption affinity when the degree of Na$^+$ exchange increases. Khelifa et al [17] have also shown that the CO$_2$ adsorption on the zeolite X exchanged with Ni$^{2+}$ and Cr$^{3+}$ decreases as compared to that of zeolite NaX due to a decrease of the adsorbate-adsorbent interaction. This phenomenon has been associated with a depopulation of sites III and a decrease of electric field in the cavities of zeolite. Nevertheless, it has been shown that the substitution of Na$^+$ cations by the M$^{2+}$ and Cr$^{3+}$ cations changes only the CO$_2$ adsorption affinity when the rate of exchange is superior to 40–50% [17, 37, 38]. A similar effect has also been observed by Khvoshevich and Zverev [39] on the isosteric heat of CO$_2$ adsorption on the dehydrated faujasites (Mg, Ca)-X and (Mg, Ca)-Y following the substitution of a part of the Ca$^{2+}$ ions by the Mg$^{2+}$ ions. The decrease of heat of adsorption achieved during the substitution has been attributed to a greater screening of Mg$^{2+}$ ions by the oxygen atoms electric field of zeolites as compared to that of Ca$^{2+}$ ions. This might be caused by the penetration of Mg$^{2+}$ ions deep within six-membered rings of the framework or to their localization principally outside the cavities of zeolites. Coughlan and Kilmartin [40] and Coughlan and McCann [41] have also showed a decrease of CO$_2$ affinity after an introduction of trivalent cations (Fe$^{3+}$, Y$^{3+}$, Cr$^{3+}$, Co$^{3+}$ and Ti$^3$) in the X, Y, A and L type zeolites. According to these authors, this effect could be generalized to all the polyvalent cations of transition metals [41]. The number of cations which are able to interact with adsorbates has also an importance in the adsorption process. Indeed, a measurement of the heat of CO$_2$ adsorption in faujasites CaY and CaX has indicated that the isosteric heat of CO$_2$ adsorption on the zeolite CaX is higher than that of CO$_2$ on the zeolite CaY. This could be a consequence of a higher CO$_2$ adsorption on zeolite CaX than on the zeolite CaY [39]. Moreover, this difference could also be due to a greater number of Ca$^{2+}$ cations in the zeolite CaX which are able to interact directly with the adsorbed CO$_2$ molecules, than in zeolite CaY.

2.1.3 Influence of the Si/Al ratio. It has been shown that the adsorption capacity and selectivity of zeolites for the polar molecules increases when the Si/Al ratio decreases [10]. This effect is more important when the quadrupole moment of molecules is great. This phenomenon could be due to an increase of electric field in the zeolites pores induced by increasing number of charged sites present at the surface of zeolites. Moreover, the basicity of zeolites framework enhances with the content of Al$^{3+}$ ions due to the presence of a greater amount of exchangeable cations [42]. Hence, at low pressure, the zeolites that possess the more small Si/Al ratios should have the best adsorption capacity and selectivity for the polar molecules such as CO$_2$. This phenomenon might be explained by the fact that the polarity of adsorbed molecules plays a more important role in their adsorption when the electric field into the zeolites pores is great. This is supported by the results of Calleja et al [10] and Harlick and Tezel [11] that have indicated that the CO$_2$ adsorption capacity of H-ZSM-5 vary from 1.869 to 1.279 mmol of CO$_2$ g$^{-1}$ (temperature $= 309$ K; pressure $= 88.75$ and 84.67 kPa) when the Si/Al ratio of zeolite enhances from 15 to 60, as well as 1.24 mmol of CO$_2$ g$^{-1}$ (temperature $= 313.15$ K; pressure $= 101.3$ kPa) with a Si/Al ratio of 280 (table 1). A study of CO$_2$ adsorption on the erionite (ZAPS), mordenite (ZNT) and clinoptilolite (ZN-19) has also indicated that the adsorption of CO$_2$ is greater on erionite than on the mordenite and clinoptilolite while the erionites: 3 $\leq$ Si/Al $\leq$ 3.5, mordenites: 4.17 $\leq$ Si/Al $\leq$ 5.0 and for the clinoptilolites: 4.25 $\leq$ Si/Al $\leq$ 5.25 (table 2) [12, 43].

2.1.4 Influence of the size of pores. The pores size of zeolites is another factor that might influence the capacity and rate of CO$_2$ adsorption. In fact, the size of pores must be appropriate to allow to the adsorbed molecules to penetrate within them. The relationship between the CO$_2$ adsorption capacity of zeolites and the size of their pores depends particularly of the pressure (loading). Indeed, at low pressures, the density of the adsorbate is highest in the smaller pores while that is higher in larger pores at high pressures [44]. At the low pressures, the adsorbed molecules have the tendency to occupy the positions where the adsorbate-adsorbate interactions are less than the adsorbate-pore interactions, corresponding to the energetically most favorable positions. At high pressures, the adsorbed molecules might occupy the central region of the pores and the increase of their packing leads to the greater density [44–46]. This is corroborated by the fact that the affinity of the zeolite NaA for CO$_2$ is highest than that of zeolites NaX and NaY (affinity for the CO$_2$: NaA > NaX > NaY) at low pressures. This might be due in part to small pore diameter of zeolite A [16, 47, 48]. This high affinity of zeolite NaA allows a better selectivity for CO$_2$ in the presence of N$_2$ and O$_2$ than NaX and NaY. Moreover, since the CO$_2$ can also interact
with the pore wall of zeolites, the CO$_2$ adsorption might be limited by the size of zeolites pores at high pressures because the CO$_2$–CO$_2$ interactions might prevent the adsorption of new molecules of CO$_2$ into the pore wall sites that are thus occupied by other molecules of CO$_2$ [12, 19, 21]. The shape of pores also seems to be important for the selective adsorption of CO$_2$. Inui et al [49] have suggested from a study of the CO$_2$ adsorption on the natural and synthetic zeolites (chabazite, clinoptilolite, clinozoisite–smectite–Opal C.T., mordenite, ferrierite, mordenite–ferrierite–pielite, erionite, MS-5A, MS-4A, MS-13X, H-ZSM-5), which have different structures, that the zeolites having three-dimensional pore connection structure are more performing for the CO$_2$ separation.

2.2. Influence of adsorbates characteristics

2.2.1 Influence of the polarity of adsorbates. The affinity of zeolites for some gas is also attributable to the polarity of adsorbed molecules. The molecules that have a great permanent quadrupole moment might interact strongly with the gradient of the electric field induced by the zeolites cations [50]. The quadrupole moment of certain gas varies as following: CO$_2$ > CO > N$_2$ > H$_2$ > CH$_4$ ≈ Ar ≈ Kr [28]. Goj et al [51] have effectively showed that the zeolites ITQ-3 and ITQ-7 adsorb preferentially the CO$_2$ to detriment of N$_2$. This selectivity has been attributed to a strengthening of Coulombic interactions between the CO$_2$ molecules versus N$_2$ and the electric field of zeolites, which might be caused by the quadrupole moment of CO$_2$ (=1.43 × 10$^{-33}$ cm$^3$) that is three times greater than that of N$_2$. Nevertheless, according to Calleja et al [10] and Katoh et al [19] the selectivity of zeolites M-ZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) might be due to fact that all the CO$_2$ molecules are adsorbed on the cations sites while N$_2$ might interact with the wall of ZSM-5. It has also been observed that the zeolites 13X, M-ZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$), ZSM-5, KY, 4A, Na-4A, 5A, clinoptilolite and Na-mordenite, adsorb selectively the CO$_2$ in the presence of N$_2$, O$_2$, He, CH$_4$, H$_2$, C$_2$H$_4$, C$_2$H$_6$, SF$_6$ and Ar [16, 18, 19, 51–56].

2.2.2 Influence of the dimension of adsorbates. Adsorbed molecules dimension seems also to play an important role in their adsorption on the zeolites. Actually, the porosity of zeolites cavities is selective factor for the adsorbed molecules. For example, the erionites, mordenites, clinoptilolites and chabazite can adsorb only the molecules which possess kinetic diameter with a maximum of 4.3, 3.9, 3.5–3.8 and 4.3 Å, respectively, indicating that the CO$_2$ adsorption (diameter = 3.3 Å) is not limited by this steric factor [12, 16, 43, 57]. Moreover, it has been showed by Aguilar-Armenta et al [7] that the require period for reach the middle of the capacity of CO$_2$, O$_2$ or N$_2$ adsorption on Na-clinoptilolite and Ca-clinoptilolite is proportional to diameter of the adsorbed molecules (CO$_2$ < O$_2$ < N$_2$).

2.3. Influence of the carbonates formation on the CO$_2$ adsorption

In the case of several cationic zeolites, the chemical adsorption of CO$_2$ is accompanied by the formation of carbonates including very stable monodentate or unidentate carbonates and bidentate carbonates, at their surface, due to the interaction of CO$_2$ with the oxygen bridging aluminum and silicon atoms [24, 35, 58–62]. Gallei and Stumpf [58] have described the formation of monodentate carbonate at the surface of zeolite CaY by a reaction involving three steps. In the first step, the CO$_2$ is polarized following its interaction with the neighboring Ca$^{2+}$ ions. After this, the atom of carbon of CO$_2$ attacks the oxygen bridging aluminum and silicon atoms, and this results in the rupture of aluminum oxygen bond, and the formation a stable monodentate carbonate species at the surface of zeolite CaY (figure 4) [58, 59]. The presence of these carbonates might decrease the accessibility of CO$_2$ at a great part of the surface of zeolites and thereby contribute to limit its adsorption. This is notably the case of the unidentate surface carbonate species formed during the CO$_2$ adsorption on zeolite CaY that makes inaccessible approximately 20% of the surface cations [59].

2.4. Influence of the presence of water on the CO$_2$ adsorption

Brandani and Ruthven [63] have observed that small amounts of water can inhibited the CO$_2$ adsorption on diverse cationic forms of zeolites X (NaLSX, LiLSX, CaX), notably for zeolites NaLSX at 35 and 70 ℃. According to these authors, this can be due to a reduction of the strength and heterogeneity
of the zeolites electric field caused by a high adsorption capacity of water on the exchangeable cations generated by its strong polarity. The presence of water during the CO\textsubscript{2} adsorption on the zeolites surface seems also to favor the formation of bicarbonates species via hydroxyl group formation [27]. The bicarbonates cause an increase of the CO\textsubscript{2} desorption temperature. As it is shown by Siriwardane et al [27], a strongly bound CO\textsubscript{2} in bicarbonates or bidentate carbonate type species formed on a natural harscheelite-sodium chabazite and two forms of clinoptilolites was desorbed at 115 °C, while the majority of the physically adsorbed CO\textsubscript{2} was desorbed at room temperature.

2.5. Influence of the pressure and temperature on the CO\textsubscript{2} adsorption

Several investigations carried out with diverse zeolites (LaM-10, H-ZSM-5, M-ZSM-5 (M = Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Rb\textsuperscript{+}, Cs\textsuperscript{+}), NaX or 13X, 5A, 4A, NaLSX, MCM-48, erionite, mordenite, clinoptilolite) have shown the effect of pressure and temperature on CO\textsubscript{2} adsorption [10–12, 14, 16, 18, 19, 37, 52, 63–67]. In general, the capacity of CO\textsubscript{2} adsorption on the zeolites enhances when the partial CO\textsubscript{2} pressure increases and decreases with a rise of temperature (table 3). The results obtained by Yucel and Ruthven [68] and Gardner et al [69] have also shown that the diffusion of CO\textsubscript{2} in the zeolite 4A and H-ZSM-5 enhances with the increase of the partial pressure. Moreover, the data obtained by Akten et al [52] have indicated that the Na-4A selectivity for the CO\textsubscript{2} in the presence of N\textsubscript{2} and H\textsubscript{2} decreases slightly when the pressure in the gas phase enhances. This decrease of selectivity is more marked when the molecules of other gas smaller than CO\textsubscript{2} are present in the gas phase. The effect of the pressure on the CO\textsubscript{2} adsorption might be attributed to the fact that the amounts of CO\textsubscript{2} adsorbed are directly proportional to the cationic density in the zeolites pores at low pressures, whereas the volume of pores plays an important role at high pressures [9, 44]. Katoh et al [19] have also attributed this effect of the pressure in the case of the zeolite Li-ZSM-5, to the existence of two types of cations sites species and to the possibility that a rise of the partial pressure might induce a penetration of CO\textsubscript{2} deep into the small channels of zeolite, this allowed to interact more strongly with the Li\textsuperscript{+} cations. In parallel, the decrease of the CO\textsubscript{2} adsorption with the increase of the temperature has been associated with a decrease of adsorbent-adsorbate interactions (site–adsorbate) induced by an increase of the mobility of adsorbed molecules into the zeolites cavities that might be caused by a rise of thermal agitation [34].

3. Conclusions

Zeolites have a high potential for CO\textsubscript{2} capture, reaching an adsorption efficiency of 5.5 mmol of CO\textsubscript{2}/g of zeolite, combined with a degree of irreversible adsorption inferior to 10% (tables 1–3) [9–21]. The CO\textsubscript{2} adsorption is influenced by diverse structural characteristics of zeolites including size, polarizing power, distribution and the number of exchangeable cations in their cavities, the size of the pores and the Si/Al ratio. Moreover, the characteristics of adsorbates such as the size and the polarity, the formation of carbonates species at the surface of zeolites during the CO\textsubscript{2} adsorption, the presence of water and the conditions of adsorption including the gas phase pressure and temperature may also influence the CO\textsubscript{2} adsorption. More specifically, the capacity of CO\textsubscript{2} adsorption on zeolites depends firstly of the basicity and the strength of electric field induced by the presence of exchangeable cations in their cavities as well as the size both of their pores and the adsorbate molecules. Generally, the zeolites, which are very basic and possess a strong electropositivity, show a best capacity of adsorption for the molecules that have an acidic character and a great permanent quadrupole moment such as CO\textsubscript{2}. In fact, this permits to them to strongly interact with the gradient of the electric field of the zeolites. In this case the polarizing power of exchangeable cations represents a very important factor that influences the local electric field and the polarization of the CO\textsubscript{2} molecules on the zeolites. Furthermore, the adsorption is also increased in the presence of small exchangeable cations that can penetrate more easily within the zeolites cavities, and thereby interact stronger with CO\textsubscript{2} as the big cations. Additionally, the adsorption is also influenced by the number of molecules that are able to interact with CO\textsubscript{2}, and their distribution which is responsible of the heterogeneous character of the CO\textsubscript{2} adsorption. The CO\textsubscript{2} adsorption also depends of framework of the zeolites. More particularly, the adsorption capacity and selectivity for the CO\textsubscript{2} are favored on zeolites that possess the small Si/Al ratio due to an increase of number of charged sites and basicity at the surface which is caused by the substitution of Si\textsuperscript{4+} ions by the Al\textsuperscript{3+} ions. On the other hand, the formation of carbonate species at the surface of zeolites during the chemisorption of CO\textsubscript{2} is a factor that can significantly limit the CO\textsubscript{2} adsorption of by the blockade of surface cations. The presence of water can also decrease the CO\textsubscript{2} adsorption capacity of different forms of cationic zeolites by decreasing the strength and the heterogeneity of the electric field. Moreover, the presence of water can support the bicarbonates formation on the zeolites surface and thus generate strongly bound CO\textsubscript{2} (bicarbonate species), which requires a higher temperature for its desorption. Finally, the diffusion of CO\textsubscript{2} in the zeolites generally enhances with the pressure, and this results in an increase of its adsorption. In contrast, the decrease of adsorbent–adsorbate (zeolite-CO\textsubscript{2}) interactions induced through the increase of the temperature is an unfavorable factor for its adsorption.

On the basis of this advanced analysis of the most important studies about the CO\textsubscript{2} adsorption using natural and synthetic zeolites, it appears that the basicity and size of pores of zeolites, as well as the strength of electric field caused by the presence of exchangeable cations in their cavities are the essential factors for the CO\textsubscript{2} adsorption on zeolites. Thus, the consideration of all these factors seems to be necessary for the best choice of an appropriate zeolite for CO\textsubscript{2} adsorption. Hence, the optimization of all these factors and experimental conditions may increase significantly the zeolites adsorption capacities and thus develops efficient technologies to capture the industrial emissions of CO\textsubscript{2}. 

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