Influence of Surface Energetic Heterogeneity of Microporous Adsorbents on Adsorptive Separation of CO$_2$, CO, N$_2$, and H$_2$ from a Controlled-Combustion of Solid Wastes

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Abstract
This study has been concentrated on the effect of the surface nonuniformity of microporous zeolites, activated carbons (AC), and metal-organic frameworks on the adsorption of CO$_2$, CO, N$_2$, and H$_2$ at 25°C and low equilibrated pressures ≤ 850 Torr. The shape of the measured isotherms for the adsorbates strongly depended on themselves as well as on the adsorbents, which could be well correlated with those electronic properties and these surface nonuniformity levels. The selectivity of CO$_2$ to other gases could be explained by different surface nonuniformity among the adsorbents. The zeolites with the most energetically-heterogeneous surfaces yielded high CO$_2$ uptakes and CO$_2$/CO selectivity factors at low pressures. On a surface of the ACs that possessed a moderate surface nonuniformity between the zeolites and a MOF and have minor quadrupole-adsorbent interactions, the adsorption behaviors and the selectivities showed an intermediate feature.

Introduction

Conventional microporous solids, zeolites and activated carbons, have been widely studied for adsorptive separation of CO$_2$ from gas mixtures with other gases, such as CH$_4$, CO, N$_2$, and H$_2$ [1–3], and recently, metal-organic frameworks (MOF) and zeolitic imidazolate frameworks (ZIF) are highlighted as a new outstanding adsorbent because they possess very high surface areas and their textural properties are easily tunable [4–8]. In the case of zeolitic materials, low Si/Al zeolites, such as Y and 13X, are frequently used for such a CO$_2$ adsorption due to a stronger affinity to this gas molecule [1,9]. Activated carbons (AC) have a variety of surface functional groups, such as carbonyl, phenol, carboxyl, lactone, and ether, and these sites after proper thermal excursion play a good role for CO$_2$ adsorption [1,10]. Many types of MOFs can be tailored using different metal-organic building blocks and organic linkers, and some metal centers after guest removal are responsible for CO$_2$ adsorption [4–7,11,12].

Cost-efficient regeneration of porous sorbents is required for adsorptive CO$_2$ separation and has been successfully conducted by using pressure swing techniques, such as vacuum swing adsorption (VSA) and pressure swing adsorption (PSA) [2,3]. Many VSA processes periodically repeat cycles between desorption near 1 bar and desorption around 30 – 100 Torr [13,14], while industrial PSA systems allow adsorption at relatively higher pressures, typically 4 – 6 bar, and then desorption near 1 bar [2,9,15]. Such VSA techniques need a rather much energy compared to PSA ones; however, those provide a better separation efficiency, due to a higher working capacity that is mainly associated to a common feature of microporous materials on which adsorption of light gases with high polarizability and quadrupole moment, such as CO$_2$, usually approaches almost saturated coverage at low pressures [2] and after which, only a small increment occurs. This behavior is more critical for microporous solids with surface sites having high affinity to CO$_2$. This surface energetic heterogeneity also influences the extent of preferential adsorption of CO$_2$ over other gases, usually defined as selectivity.

The difference in the surface nonuniformity among adsorbents should be considered for a better working capacity and selectivity for CO$_2$ adsorption and can be disclosed by comparing its adsorption isotherms collected at low pressure region at which such surface features would prominently appear. Thus, this study has focused on low-pressure adsorption behavior of commercially-available zeolites, ACs and MOFs on which CO$_2$, CO, N$_2$, and H$_2$ were adsorbed at equilibrated pressures ≤ 850 Torr (≈ 1.13 bar). The chosen gases are a predominant component of a well-controlled gasification of biomass-based wastes.

Experimental

Zeolites used were NaY (CBV 100, Zeolyst) and NaX (Z10-08EP, Zeochem) with the respective Si/Al ratio of 2.3 and 1.3 that were independently measured using an ICP (inductively coupled plasma) spectroscopy. A Norit GCN612 and a Kansai Coke and Chemicals MSP-20 were employed as a model AC, designated to “GCN” and “MSP”, respectively. Commercial MOF analogues were purchased from Aldrich: a Basolite A100 isostructural to MIL-53 (Al) and a Basolite Z1200 to ZIF-8 [4,5], designated to “A100” and “Z1200”, respectively.

A Micromeritics ASAP 2020 system was used for collecting N$_2$ sorption data of the adsorbents at -196°C.
For this, an appropriate amount of each sample, ca. 40 mg, was loaded into a BET adsorption cell following evacuation at 200°C in vacuum overnight. Textural properties of the adsorbents, such as BET surface area (S\text{BET}), and micro-/mesopore size and volume, were calculated using the sorption data. The Saito-Foley cylindrical pore model was applied to micropores in all the sorbents, except for those in the ACs which were determined by the original Horvath-Kawazoe slit pore model [16,17]. The mesopores were estimated using the Barrett-Joyner-Halenda (BJH) model.

A stainless steel system with a high dynamic vacuum below 10^{-8} Torr, equipped with an Oerlikon Leybold Vacuum Model TURBOVAC 151 turbomolecular pump with a TurboDrive TD 20 Classic controller backed by a mechanical pump (Kodivac, GHP-340K) was used for volumetrically measuring CO₂, CO, N₂, and H₂ adsorptions on the chosen adsorbents. A single gauge controller (Pfeiffer, Model TPG 261) was employed to display dynamic vacuum levels. Gas pressure was measured using an absolute Honeywell Model Super TJE ultra precision pressure transducer (Type AP112) with a full range of 200 psi connected to a Sensys Model 1300 pressure indicator, and temperature was monitored using a digicator (Hanyoung Nux, BK-6M). Details of such a system have been provided elsewhere [18–20].

Typically 0.5 g each adsorbent was placed in a sample cell in a cylindrical electric furnace equipped with a temperature controller (Misung S&I, TC500P) and evacuated at 300°C overnight under a vacuum using the rotary vane pump following further evacuation for 1 h at room temperature using the TMP high vacuum system. Then, using a Peltier thermoelectric device with a temperature controller (Omega, Model CN 7500), the adsorption cell was controlled to be 25°C at which all adsorption measurements were conducted. During the pretreatment and gas adsorption, temperature of the sample cell was monitored using an Omega Model 410B Digicator. CO₂ (99.999%), CO (99.998%), N₂ and H₂ (99.9999%), Praxair) were further purified by flowing them through moisture traps and Oxytraps (Alltech Assoc.).

### Results and Discussion

All adsorbents used had a common feature of microporous materials, based on the shape of N₂ sorption isotherms (not shown here), and the size of micropores and their occupancy, depending on them, as provided in Table 1. NaY and NaX with a faujasite framework topology has a similar dₘₐ and the former give somewhat higher Sₜₐₛₐₜ value. The two ACs, i.e., GCN and MSP, consist of a microporous structure with a pore size of 5.0 - 5.5 Å and these surface areas are relatively larger. MOFs give the greatest micropore sizes, and the measured surface areas of A100 and Z1200 are very similar to or comparable with those of the respective NaY and GCN. Among the sorbents, the largest Vₘ value is indicated for MSP whose Sₜₐₛₐₜ was also the highest.

### Table 1

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Sₜₐₛₐₜ (m²/g)</th>
<th>dₘₐ (Å)</th>
<th>Pore volume (cm³/g)</th>
<th>Vₘ</th>
<th>V₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>847</td>
<td>7.9</td>
<td>0.31</td>
<td>0.34</td>
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<tr>
<td>NaX</td>
<td>724</td>
<td>7.6</td>
<td>0.27</td>
<td>0.37</td>
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<tr>
<td>GCN</td>
<td>1132</td>
<td>5.0</td>
<td>0.44</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>MSP</td>
<td>2508</td>
<td>5.5</td>
<td>0.99</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>A100</td>
<td>838</td>
<td>10.9</td>
<td>0.36</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>Z1200</td>
<td>1301</td>
<td>12.3</td>
<td>0.55</td>
<td>0.68</td>
<td></td>
</tr>
</tbody>
</table>

Note. dₘₐ: micropore diameter; Vₘ: micropore volume; V₁: total pore volume.

Isotherms of CO₂, CO, N₂, and H₂ adsorptions on zeolites, ACs and MOFs at low pressure region are of particular interest because of their utilization as a VSA adsorbent. Figure 1 shows CO₂ adsorption on the porous solids at 850 Torr. At this pressure, the indicated CO₂ uptake is in the order NaY (7.98) > NaX (5.07) > MSP (4.12) > GCN (3.24) > A100 (2.56) >> Z1200 (0.98 mmol/g). Both the shape of isotherms measured volumetrically and CO₂ adsorption capacity strongly depended on the adsorbent used. Two zeolites, NaY and NaX, display a CO₂ adsorption that steeply increases up to 150 Torr and then occurs with a small increment, which is a typical character of microporous solids with high surface nonuniformity with high affinity sites for binding CO₂ [6,21,22].

![Fig. 1. Isotherms of zeolites, ACs and MOFs for CO₂ adsorption at 25°C.](image-url)

Distinctive response of CO₂ adsorption to equilibrated pressures was indicated for ACs and MOFs. Not that much steep increase at such low pressure region is shown for all these samples. Two ACs and A100 give a weak character of the Langmuir isotherm;
however, Z1200 has an isotherm that is almost linear even up to 850 Torr. It is proposed that the surface of this adsorbent would be homogeneous and has few strong-binding sites even for CO$_2$ [2,23]. Consequently, it is clear that the surface nonuniformity of the sorbents is closely related to their CO$_2$ adsorption capacity.

The NaY, that had revealed the highest CO$_2$ uptake at 850 Torr among the adsorbents studied here, and the two AC all showing higher CO$_2$ adsorption than the Basolites were chosen for adsorbing N$_2$ and H$_2$. As seen in Fig. 3, the carbonaceous materials give a greater CO$_2$ adsorption compared to the zeolite, which is in good agreement with the literature [25], implying a lower CO$_2$/N$_2$ selectivity. This suggests that they may not good adsorbent for VSA applications to gas streams with significant N$_2$ levels.

Fig. 2. Isotherms of zeolites, ACs and MOFs for CO adsorption at 25°C.

Similar behaviors were disclosed for CO adsorption with the six microporous sorbents, as provided in Fig. 2. A shape of the Langmuir adsorption is visible with NaX, while NaY gives a CO adsorption similar to that appeared for GCN and these isotherms suggest weak surface energetic heterogeneity. Whereas, the other adsorbents all show almost linear increase with pressure. These results are mainly due to a lower polarizability (19.5×10$^{-25}$ cm$^3$) and quadrupole moment (25.0×10$^{-25}$ esu·cm$^2$) than those (26.5 – 29.11×10$^{-25}$ cm$^3$ and 43.0×10$^{-25}$ esu·cm$^2$, respectively) for CO$_2$ [2,6,24].

Fig. 3. Isotherms of NaY and ACs for N$_2$ adsorption at 25°C.

The NaY, that had revealed the highest CO$_2$ uptake at 850 Torr among the adsorbents studied here, and the two AC all showing higher CO$_2$ adsorption than the Basolites were chosen for adsorbing N$_2$ and H$_2$. As seen in Fig. 3, the carbonaceous materials give a greater CO$_2$ adsorption compared to the zeolite, which is in good agreement with the literature [25], implying a lower CO$_2$/N$_2$ selectivity. This suggests that they may not good adsorbent for VSA applications to gas streams with significant N$_2$ levels.

Fig. 4. Isotherms of NaY, and ACs for H$_2$ adsorption at 25°C.

H$_2$ adsorption on NaY and ACs at 25°C is displayed against equilibrated pressures in Fig. 4. The extent of its adsorption is much lower than that of CO$_2$ as expected, regardless of adsorbent, which is because of the lowest polarizability (8.0 – 8.042×10$^{-25}$ cm$^3$) and quadrupole moment (6.62×10$^{-25}$ esu·cm$^2$) thereby allowing the weakest adsorbate-adsorbent interactions [2,6,24].

Conclusions

The difference in surface energetic heterogeneity among zeolites, ACs and MOFs gives distinct isotherm shape and performances in the adsorption of adsorbates, particularly CO$_2$ with high quadrupole moment. Zeolitic materials with an energetically wide range of adsorption sites (Na cations) for CO$_2$, such as NaY, may be a better adsorbent for low pressure swing applications.

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References


