CO\textsubscript{2} adsorption behavior of microwave synthesized zeolite beta

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**Abstract**  
Zeolite beta was successfully synthesized by direct synthesis with addition of seeds under microwave irradiation. CO\textsubscript{2} adsorption properties on the microwave synthesized zeolite beta were investigated at constant temperature 40 °C and absolute pressure 1 atm which compared with zeolite beta synthesized by the conventional hydrothermal method. Microwave synthesized zeolite beta showed higher CO\textsubscript{2} adsorption capacity than that of hydrothermal synthesized zeolite beta. Even the surface area of microwave synthesized zeolite beta (463 m\textsuperscript{2}/g) was similar with hydrothermal synthesized one (482 m\textsuperscript{2}/g), higher aluminum contents and the less hydrophilicity of microwave synthesized zeolite beta contributed to the higher adsorption capacity and selectivity of CO\textsubscript{2} than those of hydrothermal synthesized one, respectively.

**1. Introduction**

Zeolites are crystalline aluminosilicates with diverse framework structures considered as efficient adsorbents with high adsorption capacities for wide variety of adsorbates [1,2]. Moreover, these zeolite-based adsorbents show good regeneration properties with fresh adsorption capacities even after recycling several times [3]. Recently, CO\textsubscript{2} adsorption on zeolites received much attention due to CO\textsubscript{2} as greenhouse gas causing global warming [4-6]. Zeolites showed higher adsorption capacities of CO\textsubscript{2} compared with other adsorbents such as hydrocarbons or metal oxide due to their high affinity for polar molecules at low partial pressures and mild temperatures [3,7]. Various types of zeolites such as LTA [8], FAU [9], MOR [10], and MFI [11] have been applied for CO\textsubscript{2} adsorption studies and are reported earlier.

Zeolite beta is one of typical representative large-pore zeolites having open framework structure with three-dimensional 12-membered ring channels (0.76 × 0.64 and 0.55 × 0.55 nm) which shows large micropore volume, high surface area, tunable Si/Al ratios and ion-exchange capacities [12,13]. Owing to such unique properties, recently zeolite Beta has been demonstrated as a potential adsorbent for CO\textsubscript{2} adsorption. The investigation on zeolite beta for adsorption and separation of CO\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4} was firstly reported by Tezel et al. [14]. They observed that the highest Henry Law constant and good equilibrium separation factors were obtained in the CO\textsubscript{2} adsorption among the gas mixtures over zeolite beta. The similar studies were performed on H-beta, Na-beta and monoethanol amine modified beta reported by Liu et al. [15,16]. Very recently, Ahn et al. [17] investigated the effect of ion-exchanged alkali and alkaline cations such as Li\textsuperscript{+}, K\textsuperscript{+}, Cs\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+} and Ba\textsuperscript{2+} on CO\textsubscript{2} adsorption in zeolite beta. They found that the K\textsuperscript{+}-exchanged zeolite beta showed the highest CO\textsubscript{2} adsorption capacity compared with other cations.

In general, these earlier studies were performed with zeolites synthesized by the conventional hydrothermal method which required longer synthetic times. According to our previous reports, the microwave-mediated synthesis (MW) could provide not only shorter synthetic times but also unique advantages such as uniform morphology, phase control and the enhanced hydrophobicity compared with the conventional hydrothermal synthesis method (HT) [18].

In continuation to our prior studies on microwave mediated synthesis of zeolite beta under fluoride media [19], in this work we report CO\textsubscript{2} adsorption behavior on the microwave synthesized zeolite beta which compared with conventional hydrothermal synthesized zeolite beta.

**2. Experimental section**

**Synthesis of zeolite beta:** Microwave synthesized zeolite beta (beta-MW)—The microwave synthesized zeolite beta was prepared by following procedure. Initially, the tetraethylammonium hydroxide (TEAOH, Aldrich Co., 40 wt %), sodium aluminate (Junsei Co., 37% Na\textsubscript{2}O, 54% Al\textsubscript{2}O\textsubscript{3}), NaOH (Duksan Co., 93%) and seed solution (commercial zeolite Beta from Zeolyst Co. was dissolved in water) were mixed and vigorously stirred for 5 min. To this...
solution, Ludox HS-40 (Aldrich Co., 40% colloidal silica) was slowly added then stirred for 5 min. The molar composition of synthesis mixture was 1SiO₂:0.04Al₂O₃:0.09Na₂O:0.81TEAOH:28.4 H₂O. The resulting mixture was loaded in a microwave oven equipped with a Teflon autoclave (CEM Co., MARS-5) and irradiated at 170 °C for 4 h under 1200 W of microwave power. The resulting product was filtered, washed with distilled water and dried at 80 °C for 24 h in the oven. As-synthesized sample was calcined at 550 °C for 6 h in the air.

**Hydrothermal synthesized zeolite beta (beta-HT)**—The synthesis procedure was same with that of Beta-MW except the heating method, whereby the resulted precursor gel in the pressure vessel was loaded to thermal oven at 170 °C for 48 h instead of microwave irradiation.

**Characterization**—Powder X-ray diffraction patterns (XRD) were obtained using Rigaku Miniflex X-ray diffractometer with CuKα radiation source (λ=0.154 nm) at 30 kV, 15 mA from 5° to 40°. Surface area were determined by the N₂ adsorption–desorption isotherms at 77 K (Micromeritics ASAP2020 analyzer). The Scanning Electron Microscope (SEM) was used for observing morphologies using Hitachi S-4300SE and chemical analysis was done by using Inductively Coupled Plasma Spectrometer (ICP; Optima 7300DV).

**Adsorption isotherms of CO₂ and H₂O**—All samples were pretreated at 140 °C for 4 h under vacuum prior to get CO₂ and H₂O isotherms. The CO₂ isotherms were obtained in Micromeritics ASAP2050 analyzer at constant temperature 40 °C with the absolute pressures range from 1 mmHg to 760 mmHg. For the water adsorption, the isotherms were performed in the same equipment (Micromeritics ASAP2050 analyzer) at constant temperature 25 °C under the relative pressures range from 0.01 to 0.8P/P₀.

### 3. Results and discussion

The XRD patterns of microwave synthesized zeolite beta (Beta-MW) and conventional hydrothermal synthesized zeolite beta (Beta-HT) are shown in **Fig. 1**. Both samples exhibited the typical crystalline structure of beta without impurity phase in XRD patterns from the range 5 to 40°. On the contrary to conventional hydrothermal synthesis required 48 h for getting highly crystalline structure of zeolite beta, the microwave irradiation enabled the synthesis of zeolite beta with high crystallinity in 4 h under 1200 W power by the seeding method. The SEM images of both Beta-MW and Beta-HT revealed well shaped crystals with uniform sized of 400–500 nm which seemed to be formed by aggregation of small crystallites (**Fig. 2**). The N₂ adsorption–desorption isotherms showed typical type I isotherm with rectangular H₄ hysteresis loops at P/P₀ > 0.4 which was the characteristics of typical microporous materials (not shown here) [20]. The surface area of samples estimated employing the Brunauer Emmett and Teller (BET) method from N₂ adsorption isotherm at P/P₀ in the range of 0.1–0.3. The BET surface area and total pore volume of

![Fig. 1. XRD patterns of Beta-MW and Beta-HT.](image)

![Fig. 2. SEM images of (a) Beta-MW and (b) Beta-HT.](image)
Beta-MW were 463 m²/g and 0.28 cm³/g, respectively (Table 1). It was similar with those of Beta-HT (483 m²/g and 0.29 cm³/g).

Generally, the adsorption of CO₂ behavior into zeolites is influenced by the electric field generated by the presence of cation and surface silanol group. Fig. 3a showed the CO₂ adsorption isotherms of both Beta-MW and Beta-HT obtained at constant temperature 40°C with the absolute pressures range from 1 to 760 mmHg. The equilibrium adsorption capacity for CO₂ on Beta-MW (2.16 mmol/g at 760 mmHg) was higher than that of Beta-HT (1.94 mmol/g at 760 mmHg) even having similar surface area and total pore volume as summarized in Table 1. The enhanced adsorption capacity for CO₂ on Beta-MW was mainly attributed to higher Al content which can be seen from lower molar ratio of SiO₂/Al₂O₃. As earlier report by Dunne et al. [21] the adsorption properties of zeolite affected due to higher sodium content. The presence of Al atom in zeolites introduced negative framework charges which require charge-compensating Na⁺ cation which enables zeolites to adsorb acidic gas such as CO₂ [3]. Another more effective enhancement on CO₂ selectivity was resulted from less hydrophilicity property of Beta-MW which was confirmed by water adsorption isotherms at constant temperature 25°C with the relative pressures at P/P₀ from 0.01 to 0.8 as shown in Fig. 3b. The water absorbed amount of Beta-MW was 10.5 mmol/g at relative pressure 0.8 P/P₀ which was lower than that of Beta-HT (11.3 mmol/g) in Table 1. Moreover, the selectivity on CO₂ over Beta-MW (17.1%) was higher than Beta-HT (14.5%). It was indicated that the Beta-MW is relatively less hydrophilic compared with Beta-HT. This observation was in agreement with our previous studies on microwave synthesized zeolites [22].

**Table 1**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area a (m²/g)</th>
<th>Total pore volume b (cm³/g)</th>
<th>CO₂ adsorption capacity c (mmol/g)</th>
<th>H₂O adsorption capacity d (mmol/g)</th>
<th>Selectivity on adsorbed CO₂ e (%)</th>
<th>SiO₂/Al₂O₃ f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta-MW</td>
<td>463</td>
<td>0.28</td>
<td>2.16</td>
<td>10.5</td>
<td>17.1</td>
<td>15.9</td>
</tr>
<tr>
<td>Beta-HT</td>
<td>483</td>
<td>0.29</td>
<td>1.94</td>
<td>11.4</td>
<td>14.5</td>
<td>18.6</td>
</tr>
</tbody>
</table>

| a BET surface area obtained from N₂ adsorption isotherm in the relative pressure range of 0.1–0.3.  
| b Total pore volume was derived at P/P₀=0.97.  
| c The capacity was obtained at absolute pressure 760 mmHg.  
| d The capacity was obtained at relative pressure 0.8 P/P₀.  
| e The selectivity on CO₂ was calculated by CO₂ adsorption capacity/CO₂+H₂O adsorption capacity.  
| f The molar ratio was calculated from Aluminum concentration obtained by ICP.|

4. Conclusion

The zeolite beta with high crystallinity was rapidly synthesized within 4 h under microwave irradiation without fluoride media. The microwave synthesized zeolite beta exhibited enhanced CO₂ adsorption capacity (2.16 mmol/g) and selectivity on CO₂ (17.1%) than those of conventional hydrothermal synthesized zeolite beta (1.94 mmol/g and 14.5%) even similar BET surface area and pore volume. This result was not only attributed to high aluminum content but also less hydrophilicity of microwave synthesized zeolite.

**Acknowledgment**

This work was supported by the Korea Institute of Energy Research (KIER) (No. KIER-B1-2408) and National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 20090083525).

**References**


