CO₂ adsorption on LTA zeolites: Effect of mesoporosity

Chao Chen a,b, Wha-Seung Ahn a,*

a Department of Chemistry and Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea
b College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, Henan Province, China

A R T I C L E   I N F O

Article history:
Received 2 April 2014
Received in revised form 30 April 2014
Accepted 30 April 2014
Available online 10 May 2014

Keywords:
Mesoporous
Microporous
LTA zeolite
CO₂ adsorption

A B S T R A C T

Highly mesoporous LTA zeolite (Meso-LTA) was prepared using an organosilane surfactant, dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride, as a mesopore-generating agent. Meso-LTA was characterized by X-ray powder diffraction, N₂ adsorption–desorption isotherm at 77 K, scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy, and then investigated for CO₂ adsorption at 298 K. Compared to a solely microporous LTA zeolite (Micro-LTA), Meso-LTA showed faster CO₂ adsorption kinetics at 1 bar and higher CO₂ adsorption capacities under high pressure conditions (>10 bar).

1. Introduction

Anthropogenic CO₂ emissions, largely caused by fossil fuel combustion, have raised serious concerns about global warming [1]. Compared to conventional sorption processes that use basic liquid amine species [2], CO₂ capture based on adsorption principle is considered to be more convenient and energy-efficient [3]. Various types of solid adsorbents such as zeolites [4–7], carbons [8,9], and metal–organic frameworks (MOFs) [10–12] are being considered, and among them, synthetic zeolites, especially low silica zeolites, such as zeolite A, 13X, and zeolite Y have been widely used in commercial adsorption processes.

It has been demonstrated that the presence of mesopores in zeolite crystals alleviates diffusional limitations in catalytic reactions [13]; Ryoo and co-workers reported that the molecular diffusion inside a mesoporous LTA zeolite is much more rapid compared with that of a solely microporous counterpart [14]. As far as we know, there have been very few reports using mesoporous zeolites for CO₂ adsorption, and this advantage of accelerated diffusion by the mesopores can also be very effective for applications in adsorption processes. In this work, we report for the first time CO₂ adsorption carried out over a highly mesoporous LTA zeolite (Meso-LTA) under 1–30 bar conditions at 298 K. Microporous zeolite 4A (Micro-LTA) was also tested for comparison.

2. Experimental

2.1. Preparation of Meso-LTA

Meso-LTA was prepared following the procedure reported by Cho et al. [14]. Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC, 60% in methanol, ACROS) was used as an organosilane surfactant to form mesoporosity. In a typical synthesis, a homogenous solution of Na₂SiO₃ (6.10 g), NaOH (5.96 g), TPOAC solution (3.31 g) in H₂O (120 g) was quickly mixed with a solution of NaAlO₂ (6.45 g) in H₂O (60 g). The mixture was vigorously shaken for 10 min, and heated for 4 h at 373 K with stirring. Products were filtered, washed with water, dried at 373 K, and calcined at 823 K for 4 h. For comparison, commercial zeolite 4A (Aldrich) was used.

2.2. Characterization methods

Powder X-ray diffraction (XRD) patterns were measured on a Rigaku diffractometer using Cu Kα (λ = 1.54 Å) radiation. Nitrogen adsorption–desorption measurements were carried out on a Belsorp(II)-max at 77 K. Surface area and total pore volume were calculated by the BET (Brunauer, Emmett, and Teller) method, and the pore size distribution was estimated based on the BJH (Barrett–Joyner–Halenda) model. The morphological features and chemical composition of zeolite samples were examined by scanning electron microscopy (SEM, Hitachi S-4300) equipped with an energy dispersive X-ray spectroscopy (EDX)). The powder
sample densities were measured by a gas pycnometer (Micromeritics AccuPyc 1330).

2.3. CO2 adsorption measurement

TGA unit (SCINCO thermal gravimeter S-1000) connected to a flow panel was used to study the CO2 adsorption kinetics at 1 bar 298 K conditions. Samples were pretreated at 573 K for 2 h in He before the CO2 adsorption measurement. The feed flow rate to the sample chamber was controlled to 30 mL/min using a mass flow controller. Both CO2 and He were of ultra-high purity grades (99.999% U-Sung, Korea).

High pressure CO2 adsorption isotherms (1–30 bar) at 298 K were obtained using a magnetic suspension balance (Rubotherm, Germany) with in situ density measurement in a closed system. Samples were initially conditioned at 523 K under vacuum overnight. Prior to commencing measurement of the CO2 adsorption capacity, buoyancy was corrected in He.

3. Results and discussion

3.1. Characterization

Both Meso-LTA and Micro-LTA showed identical XRD patterns with high crystallinity (Fig. 1a). As shown in Fig. 1b, Meso-LTA showed a type IV N2 adsorption–desorption isotherm with a hysteresis loop, which is characteristic of a mesoporous material [14], whereas the N2 adsorption isotherm for Micro-LTA showed practically no adsorption; N2 becomes essentially excluded at temperatures below 173 K for microporous 4A zeolite [14,15]. Consequently, N2 adsorption–desorption measurement at 77 K cannot characterize the microporosity of Micro-LTA in terms of BET surface area and micropore volume due to its narrow aperture size. The pore size distribution curve of Meso-LTA (inserted) shows a peak centered upon ca. 9 nm, confirming its mesoporous structure. Physical and chemical properties of zeolite samples are summarized in Table 1. Both zeolite samples showed close Si/Al ratios. As shown in Fig. 1c, Meso-LTA exhibited a very distinctive morphology from that of Micro-LTA in SEM images, but both were made of particles having a similar average particle size (ca. 2 μm).

3.2. CO2 adsorption measurement

As shown in Fig. 2a for CO2 adsorption at 1 bar 298 K conditions, Meso-LTA achieved higher amounts of adsorbed CO2 than Micro-LTA during early 2 min of the adsorption process (inserted small figure) and a practical CO2 adsorption equilibrium was reached before 7 min, while CO2 adsorption by the Micro-LTA was still ongoing till ca. 30 min. This indicates that Meso-LTA shows faster CO2 adsorption kinetics than that of Micro-LTA. Since both LTA zeolite samples showed similar particle sizes and close Si/Al ratios, the faster CO2 adsorption kinetics of Meso-LTA must be attributed to its mesoporosity, which led to rapid gas transport inside the zeolite framework. The final equilibrium amount of CO2 adsorbed with Meso-LTA was, however, less than that with the Micro-LTA, since...
CO₂ adsorption under ambient condition is mostly taking place inside the micropores. CO₂ adsorption isotherms by Meso-LTA and Meso-LTA from 1 to 30 bar conditions measured by Rubotherm are shown in Fig. 2b. Meso-LTA exhibited less CO₂ uptake than that of Micro-LTA at 1 bar as observed in Fig. 2a, but the gap in adsorption capacity gradually decreased as the pressure increased, and CO₂ uptake by Meso-LTA surpassed that of Micro-LTA at CO₂ pressures greater than 10 bar. Further increases of CO₂ pressure to 30 bar resulted in continuous increases in the amount of CO₂ adsorbed by Meso-LTA, while CO₂ adsorption by Micro-LTA seemed saturated beyond 15 bar. The advantage of Meso-LTA in CO₂ adsorption capacity at high pressure conditions became more pronounced when the capacities were estimated in a volume basis using the zeolite densities given in Table 1. The higher adsorption capacity exhibited by Meso-LTA for CO₂ adsorption in the high pressure ranges can be attributed to its larger effective pore size, which can hold more bulk gas present in the pore volume [16], and large pore volume that can accommodate larger amount of CO₂. A similar trend has been reported for MOF (MOF-177) [17], mesoporous silica (MCM-41) [18], and mesoporous carbon (CMK-3) [19] materials.

4. Conclusions

Highly mesoporous LTA zeolite was prepared and investigated for CO₂ adsorption. Owing to its mesopores (average ca. 9 nm), rapid gas transport inside the zeolite framework was achieved, leading to faster CO₂ adsorption kinetics than that of microporous 4A at 298 K 1 bar conditions. Mesoporous LTA zeolite also showed CO₂ uptake surpassing that of a microporous zeolite 4A under high pressure ranges (>10 bar), which was attributed to a combined effect of mesopores and larger pore volume.

Acknowledgement

This work was supported by Inha University (2014).

References


Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sa (m²/g)</th>
<th>Vtotal¹ (cm³/g)</th>
<th>Vmicroporous² (cm³/g)</th>
<th>Density (g/cm³)</th>
<th>Si/Al ratio³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-LTA⁴</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.91</td>
<td>1.0</td>
</tr>
<tr>
<td>Meso-LTA</td>
<td>140</td>
<td>0.35</td>
<td>0.05</td>
<td>2.06</td>
<td>1.1</td>
</tr>
</tbody>
</table>

¹ Vtotal = total pore volume calculated from nitrogen adsorption at P/P₀ = 0.995.
² Vmicroporous = micropore volume calculated from nitrogen adsorption at P/P₀ = 0.1.
³ By SEM-EDX.
⁴ Textural properties of Micro-LTA cannot be determined by N₂ adsorption at 77 K [14,15].

Fig. 2. (a) CO₂ adsorption kinetics of Micro-LTA and Meso-LTA at 25 °C, 1 bar; (b) high pressure CO₂ adsorption isotherms (1–30 bar) by Micro-LTA and Meso-LTA at 25 °C.