



Enhanced mass transfer on hierarchical porous pure silica zeolite used for gas separation



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ABSTRACT

Two types of ultra-high silica silicalite-1 (2000–4400 SiO₂/Al₂O₃) were prepared using a seed crystal synthesis method; silicalite-1-M, which is microporous (0.5 nm) and silicalite-1-H, which is hierarchical porous (0.5 nm and 10–15 nm). From the experimental results, silicalite-1-H/M have almost the same adsorption isotherms for CO₂, CH₄, C₂H₆ and N₂, surface area and equilibrium adsorption selectivity, however, silicalite-1-H has a shorter adsorption equilibrium time when compared with silicalite-1-M at a given pressure, which shows a mass transfer enhancement phenomenon due to its mesoporous structure. A mixed gas breakthrough test and simulation was carried out to verify the mass transfer upgrade theory to determine whether the material could be applied for adsorption separation. Interestingly, their performances on the breakthrough experiment were different; silicalite-1-H has a shorter breakthrough time for CO₂, CH₄, C₂H₆ and N₂ when compared with silicalite-1-M. All the experiment data are consistent with the simulation results. A variety of flow rates were used to investigate and compare the breakthrough time and hold time, and the separation efficiency of CO₂/CH₄, CH₄/N₂ and CH₄/C₂H₆ was improved based on the use of the hierarchical porous sorbent over a certain flow rate range.

1. Introduction

Pressure swing adsorption (PSA) technology has been successfully applied in various operations such as air separation and purification over many years [1,2]. Recently, the rapid development of adsorbents such as synthetic zeolites, porous carbons and new coordination polymers (metal organic frameworks (MOFs) or covalent organic frameworks (COFs)) has aroused more attention in PSA technology [3–10]. For the consideration of energy and the environment, there has been a trend to separate or capture greenhouse gases such as CO₂. CO₂ can be captured from flue gas (CO₂/N₂), biogas (CO₂/CH₄) [11,12], low concentration methane enrichment (CH₄/N₂) [12] and methane/ethane (C₂H₆/CH₄) [13], PSA technology was almost the first choice on account of low energy consumption.

The pursuit of novel porous adsorbents with ultra-high selectivity and adsorption capacity has become a popular research focus. However, some engineering problems in the separation process have prevented the commercialization of these new adsorbents. One of these engineering problems is mass transfer upgrade, which is an important step to improve the efficiency of adsorption [14,15]. There has been a trend

towards increasing the mass transfer rate using hierarchical porous materials as the catalyst [16,17]. In addition, the presence of mesoporous (2–50 nm) or macroporous (> 50 nm) structures may decrease the selectivity and adsorption capacity by reducing the surface area and number of adsorption sites in the sorbent because gas adsorption separation normally relies on micropores with a high adsorption potential and larger differences in selectivity [18–21]. Therefore, whether the hierarchical porous material is suitable or not for gas adsorption separation still needs to be verified.

Even though novel sorbent materials have been rapidly developed over the past few decades, zeolites and molecular sieves are still considered to be the best sorbents for CO₂/H₂/O₂/N₂/CH₄ separation [5,6,22]. Most pure silica zeolites have been abandoned because of their low number of equilibrium ions and adsorption sites. However, as an exception, pure silica ZSM-5 [23], also called silicalite-1 [24] was shown to be an ideal sorbent for CH₄/N₂ separation in our previous research [25,26]. Using the seed crystal synthesis method, two types of ultra-high silica silicalite-1 (2000–4400 SiO₂/Al₂O₃) were prepared with different pore sizes in this work. One has a microporous (0.5 nm) structure and the other has a hierarchical porous (including 0.5 nm

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micropores and 10–15 nm mesopores), and the two types of silicalite-1 have almost the same adsorption isotherms for CO₂, CH₄, C₂H₆ and N₂, Brunauer-Emmett-Teller (BET) surface area and equilibrium adsorption selectivity. Whether mass transfer upgrade technique (MTUT) [16] is applicable or not for zeolite sorbents for enhanced separation efficiency by mesopores enrichment is discussed using adsorption kinetic diffusion on the crystal solids and penetration kinetic diffusion using a mixed gas breakthrough test and simulation on these two types of silicalite-1.

2. Materials and methods

2.1. Materials

2.1.1. Crystal seed (silicalite-1)

Crystal seeds of silicalite-1 were prepared using the method reported by Persson et al. [27] and synthesized according to our previous work [28].

2.1.2. Microporous and hierarchical porous samples

To prepare the **microporous sample** (named silicalite-1-M), the crystal seeds (10 wt% SiO₂) were mixed with SiO₂ (silica-gel filler)/C₂H₇N/TPABr/NaOH/H₂O (with a ratio of 1: 0.1: 0.1: 0.15: 50), stirred for 3 h and then heated at 453 K for 20 h. The prepared silicalite-1-M will obtain a high SiO₂/Al₂O₃ ratio of 2137.

The **hierarchical porous sample** (named silicalite-1-H) was prepared using the same ratio of raw materials and crystal seeds with KF (0.3 of SiO₂) also added to prepare the mesoporous structure. The SiO₂/Al₂O₃ ratio increased to 4424 for silicalite-1-H.

2.2. Characterization

The crystallinity and phase purity of the zeolites were measured using X-ray diffraction (XRD) on a Rigaku (Japan) Mini Flex II X-ray diffractometer with Cu and K α radiation operated at 30 kV and 15 mA. The scanning range was from 5 to 40° (2 theta) at 8°/min. Nitrogen adsorption–desorption isotherms at 77 K were measured on a Micromeritics (USA) ASAP 2020 apparatus. Prior to measurement, the samples were firstly degassed at 573 K under vacuum for 6 h. Scanning electron microscopy (SEM) measurements were performed on a Hitachi (Japan) SU8010 instrument. Transmission electron microscopy (TEM) images were performed using a JEM-2100F (Japan) electron microscope operated at 200 kV. The SiO₂/Al₂O₃ ratio of the zeolites was determined using elemental analysis on an atomic absorption spectrophotometer-S2 (thermo, USA).

2.3. Adsorption measurements

CO₂, CH₄, C₂H₆ and N₂ adsorption isotherms were measured on an Intelligent Gravimetric Analyser (IGA001 series, Hiden Analytical Ltd, UK). The system was degassed at 473 K for 5–6 h until no further weight loss was observed. The system temperature was then switched to 298 K, and the sample cell was kept under vacuum for 30 min. After a stable pressure was obtained, the adsorption equilibrium data were collected and weight was maintained for 30 min at each point along the isotherm.

2.4. Novel mixed gases tests

The samples were extruded, ground, sieved into 40–60 mesh particles (diameter of 0.25–0.425 mm) and then oven-dried for 24 h at 423 K. The samples were then fed into the adsorption bed (9 mm i.d × 150 mm length). Helium (He) was used as the carrier gas to purge the adsorption bed for more than 1 h to ensure the bed was saturated with He and the He flow was then stopped. The raw mixed gases (CO₂: N₂ = 50%: 50%, CO₂: CH₄ = 50%: 50%, CH₄: N₂ = 50%: 50% and C₂H₆: CH₄ = 50%: 50%) at a flow rate of 3–30 cm³/min (STP) were passed through the adsorption bed. The exhaust gas was directed to an

analyser port and analyzed using gas chromatography (Shimadzu, GC-2014C, Japan). The mass of the two samples used was 4.62 g (microporous) and 4.37 g (mesoporous), respectively. The experimental temperature was 298 K and the pressure was 100 kPa. The full experimental setup of these novel gas experiments was described in our previous work [25].

2.5. Mixed gases breakthrough simulation

A simulation program of adsorption breakthrough process on the silica zeolite samples was written in Matlab. The following assumptions were made to simplify the simulation model.

- Gas behaves as ideal gas.
- The system is isobaric during adsorption and desorption steps.
- The flow pattern is represented by the axial dispersion model.
- The porosity of packed bed is assumed to be uniform along the bed.

The simulation package involves a couple of partial differential and algebraic equations (PDAEs) over time and space, including mass, energy, and momentum conservation equations as well as transport and equilibrium equations, as shown below [29]. These PDAEs can be solved by applying corresponding initial and boundary conditions. .

Gas phase mass balance for component i:

$$\varepsilon \frac{\partial (y_i \rho_g)}{\partial t} - \varepsilon D_L \frac{\partial^2 (y_i \rho_g)}{\partial z^2} + \frac{\partial (Q y_i)}{\partial z} + \rho_p \cdot \frac{\partial q_i}{\partial t} = 0 \quad (1)$$

Gas phase overall mass balance:

$$\varepsilon \frac{\partial \rho_g}{\partial t} + \frac{\partial Q}{\partial z} + \rho_p \cdot \frac{\partial q_i}{\partial t} = 0 \quad (2)$$

Solid phase mass balance for component i (mass transfer rates):

$$\frac{\partial q_i}{\partial t} = K_{pi} (q_i^* - q_i) \quad (3)$$

The adsorption isotherm of N₂, CH₄, CO₂, and C₂H₆ on silicalite-1 was predicted by different models depending on the experimental isotherm data.

For N₂ and CH₄, a linear isotherm was used.

$$q_i = K P_i \quad (4)$$

For CO₂ and C₂H₆, Langmuir isotherm was used.

$$q_i = \frac{q_{m0} K P_i}{1 + K P_i} \quad (5)$$

The parameters of the above isotherm equations can be estimated by the fitting method of least squares based on the experimental isotherm data, which are displayed in Table SII-1 to Table SII-3.

Gas phase energy balance [30]:

$$\varepsilon C_g \frac{\partial}{\partial t} [\rho_g \theta_g] = -C_g \frac{\partial}{\partial z} [Q \theta_g] + h a (T_s - T_g) + \varepsilon C_g D_g \frac{\partial^2}{\partial z^2} [\rho_g \theta_g] \# \quad (6)$$

$$\theta_g(z, t) = (T_g - T_0) \# \quad (7)$$

Solid phase energy balance [30]:

$$\rho_b C_s \frac{\partial}{\partial t} [\theta_s] = \rho_b \sum Q_i \frac{\partial q_i}{\partial t} + h a (T_s - T_g) \# \quad (8)$$

$$\theta_s(z, t) = (T_s - T_0) \# \quad (9)$$

3. Results and discussion

3.1. Material synthesis and characterization

The variety of balanced ions in low silica zeolites is the key factor for their multiple functions, however, an increase in the number of

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