Microporous and Mesoporous Materials 243 (2017) 119–129

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Adsorption breakthrough behavior of 1-butanol from an ABE model solution with high-silica zeolite: Comparison with zeolitic imidazolate frameworks (ZIF-8)

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ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
19 December 2016
Accepted 1 February 2017
Available online 4 February 2017

Keywords:
1-Butanol
Hydrophobic materials
Adsorption isotherm
Adsorption kinetics
Breakthrough curve

ABSTRACT

Adsorption breakthrough behavior of 1-butanol was studied on the hydrophobic materials ZSM-5, ZSM-12, and Beta zeolites and compared with the zeolitic imidazolate framework ZIF-8 from an ABE (acetone-1-butnaol-ethanol) model solution. Adsorption equilibrium and adsorption kinetics were analyzed in single-component systems. Our results showed that the equilibrium adsorption amounts for ZIF-8 were much higher than that of the zeolites but zeolites equilibrium time are shorter (10 min) than that of ZIF-8 (60 min). These phenomena were the result of kinetics effects and flexibility in the ZIF-8. We also evaluated the breakthrough characteristics of the fixed-bed in ABE ternary-component systems, and found that the adsorptive separation mechanism of zeolites was the thermodynamic effect, and that of ZIF-8 was a combination of thermodynamic and kinetic effects. We show that zeolite, especially Beta, is a very attractive material because it exhibits shorter equilibrium time for 1-butanol and better separation breakthrough performance for an ABE model solution and more suitable industrial application.

1. Introduction

The rapid growth of economy and the increasing depletion of oil resources have led to an urgent need for cheap, clean, and renewable alternative fuels. 1-Butanol is one such promising substitute for petroleum-based chemicals [1]. It has a higher energy density and is less polar than ethanol, and has a high octane number and calorific value, what is important, it can be blended into gasoline at any proportion [2]. Moreover, 1-butanol have been already utilized as an industrial chemical commonly [3]. One of the most significant challenges in successfully commercialized 1-butanol fermentation is the high cost of 1-butanol recovery from broths due to its low concentration (about 2.0 wt%) and higher boiling point than water [4]. So enrichment and separation of 1-butanol is an expensive and energy intensive process.

Traditional, there are many separation methods, for instance, steam stripping, distillation, pervaporation, gas stripping and adsorption [5]. Among these, the adsorption process has been proven the most energy-efficient, at 1948 kcal/kg 1-butanol compared to the 5789 kcal/kg 1-butanol required for steam stripping distillation and gas stripping and pervaporation require 5220 kcal/kg and 3295 kcal/kg 1-butanol, respectively [6].

High-silica zeolites and ZIF-8 material can provide good adsorptive separation for 1-butanol in comparison with water, and have already been researched extensively. Silicalite was first reported to adsorb 1-butanol from water by Milestone et al. [7]. Subsequently the high-silica Beta and Y zeolites have also been shown to adsorb organic components better than water in single-component systems [8]. However, research of these zeolites just stayed in adsorption isotherm. In a recent study, Saint Remiet et al. investigated adsorption breakthrough behavior on a typical hydrophobic ZIFs material—ZIF-8, for the recovery of 1-butanol from an aqueous solution [9].

Adsorption capacity is an important indicator of the performance of adsorbent materials, and equilibrium time is also an important parameter for evaluating the efficiency of adsorption process. Sufficiently simple, unified guidelines for predicting the adsorption equilibrium time of typical hydrophobic zeolites (ZSM-5, ZSM-12 and Beta) and representative hydrophobic ZIFs (ZIF-8) based on their micropore area, pore size and shape are yet lacking.

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http://dx.doi.org/10.1016/j.micromeso.2017.02.009
1387-1811/

The fixed-bed breakthrough process is commonly used for continuous industrial separation treatment of adsorbates. The breakthrough characteristics of the fixed-bed play an important role in evaluating the separation performance of the column during continuous operations. In previous studies, ZIF-8 was used as adsorbent in the fixed-bed for the removal of 1-butanol but the adsorptive separation properties of high-silica zeolites in the fixed-bed are missing. For these purposes, we selected a panel of high-silica zeolites with different pore sizes and shape: ZSM-5, ZSM-12 and Beta to investigate their adsorptive separation performances as compared to that of ZIF-8.

We used ABE (acetone-1-butanol-ethanol) model solution as adsorbates from the representative molecules of fermentation broth to probe the adsorptive separation properties of the selected materials. The main properties of the adsorbates molecules are summarized in Table 1. The adsorption kinetics of four hydrophobic materials in single-component systems were studied from 2.0 wt% 1-butanol aqueous solution and the adsorptive separation performance was compared in ABE ternary-component systems in a fixed-bed. Furthermore, solid linear force approach (LDF model) [10] was adopted to predict zeolite Beta breakthrough performance in this work.

2. Experimental

Zeolites are classes of crystalline aluminosilicate containing a regular structure of channels and holes [12]. Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal-organic frameworks (MOFs), which consist of imidazolate linkers and metal ions with structures similar to conventional aluminosilicate zeolites [13]. Typical high-silica zeolites and ZIFs possess intrinsically hydrophobic characteristics, high hydrothermal stability, and are easily synthesized.

2.1. Synthesis and brief description of hydrophobic materials

ZSM-5 was prepared by hydrothermal method using Tetrapropylammonium bromide (TPABr, 98%) as the template according to previously published research [14]. ZSM-5 has a three-dimensional 10-ring channel system. The pore diameter of ZSM-5 is 5.1 × 5.5 Å in the [100] plane and 5.3 × 5.6 Å in the [010] plane [15]. ZSM-12 was synthesized by two-silica method in hydroxide medium with tetraethyl ammonium hydroxide (TEAOH, 25% aqueous solution) as the structure-directing agent, according to a previously published method [16]. ZSM-12 has a one-dimensional 12-ring channel (5.6 × 6.0 Å) with linear and non-interpenetrating characteristics [17]. The composite Beta was synthesized according to a previously reported method [18]; with TEAOH as the template. The pore diameter of Beta is 6.6. × 7.7 Å in the [100] plane and 5.6 × 5.6 Å in the [001] plane [18]. ZIF-8 was synthesized based on previously published research, as well [19]. It has a large cage (11.6 Å) structure formed by the intersection of three-dimensional channels. Important characteristics and structure model of the selected four hydrophobic materials are summarized in Table 2 and Fig. 1, respectively.

Table 1
Properties of adsorbate molecules [11].

	Acetone	1-Butanol	Ethanol
Boiling point(K)	329.7	390.7	351.5
Kinetic diameter(Å)	4.6	5.0	4.5
Electric-dipole polarizability(Å^3)	6.15	8.64	4.85

Table 2
Properties of the materials tested in this work.

Materials	ZSM-5	ZSM-12	Beta	ZIF-8
Topology	MFI	MTW	BEA	SOD
Type of Porosity	channel	channel	channel	cages
Type of Channel	3D	1D	3D	3D
Membered Ring	10	12	12	6
Pore Diameter/Aperture (Å)	5.3 5.1	5.6	6.7 5.6	11.6/3.4
BET Surface Area (m^2/g)[a]	375	326	499	1425
Pore Volume (cm^3/g)[a]	0.16	0.13	0.23	0.68

[a] Obtained from nitrogen adsorption/desorption isotherms.

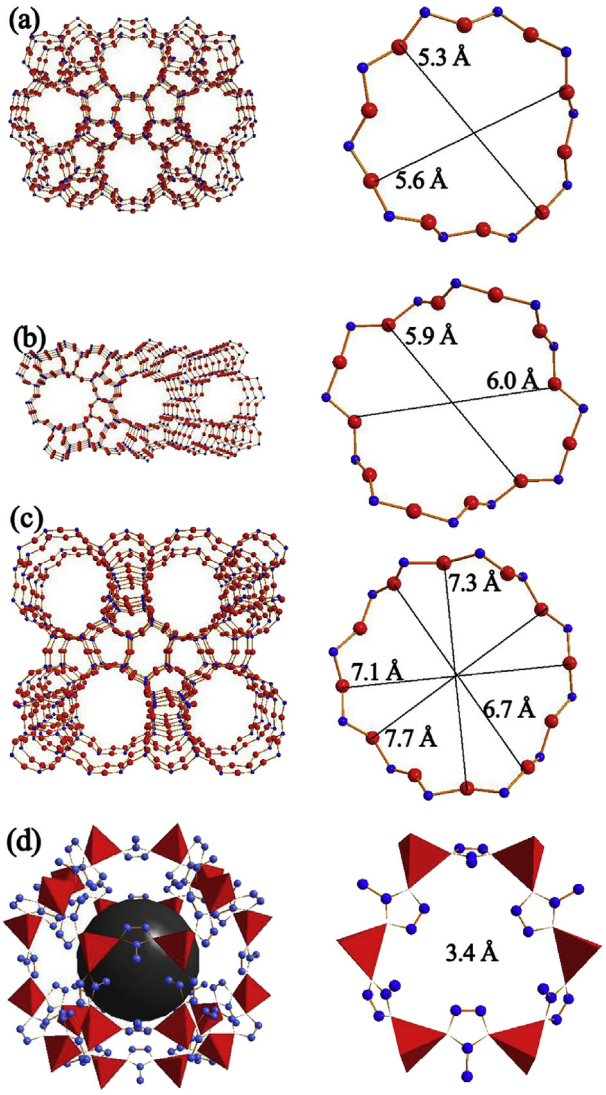

Fig. 1. Model and channels of (a) ZSM-5, (b) ZSM-12, (c) Beta and (d) ZIF-8.

2.2. Characterization of hydrophobic materials

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a Rigaku Mini Flex II. Samples were scanned using CuKα (λ = 1.5418 Å) radiation and diffractograms were recorded in the range 2θ = 3–40°. The morphology of the hydrophobic materials was examined using scanning electron microscopy (SEM) with a Hitachi TM-3000 at an operating voltage of 15 kV. N_2 adsorption/desorption isotherms were determined