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Separation and Purification Technology 52 (2006) 224–231
Separation and Purification Technology
www.elsevier.com/locate/seppur

Multicomponent $H_2/CO/CO_2$ adsorption on BaZSM-5 zeolite

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Received 6 February 2006; received in revised form 7 April 2006; accepted 7 April 2006

Abstract

A step change response method was used to compare the adsorption behavior of CO_2 with that of binary H_2/CO_2, CO/CO_2 and ternary $H_2/CO/CO_2$ gas mixtures on BaZSM-5 zeolite. Experiments were conducted with adsorption temperatures from 323 to 473 K and a total pressure of 1 atm. A comparison between single-component CO and CO_2 adsorption on BaZSM-5 was also made. The CO_2 adsorption capacity was significantly higher than that of CO on BaZSM-5, due to the higher polarity and acidity of CO_2. The CO_2 adsorption capacity of BaZSM-5 for a H_2/CO_2 gas mixture was higher than that for single-component CO_2 adsorption. TPD and FTIR results showed that the quantity of strongly adsorbed species increased significantly for CO_2 adsorption in the presence of H_2, compared to that for single-component CO_2 adsorption. This effect appears to be due to an interaction between H_2 and CO_2 on the surface with the Ba cation to form stronger carbonate species. When the CO partial pressure was increased at constant CO/CO_2 total pressure, a slight decrease in CO_2 adsorption was observed compared to that for single-component CO_2 adsorption. On the other hand, a significant decrease in CO uptake could be seen with increasing CO_2 uptake. Thus, the smaller adsorption capacity for CO/CO_2 gas mixtures compared to each single-component adsorption was probably due to the competitive adsorption of CO_2 and CO molecules on weak physisorption sites. The CO adsorption could be described by a single-site Langmuir model and an extended Langmuir model could be applied to describe the CO/CO_2 adsorption on BaZSM-5.

Keywords: Multicomponent adsorption; BaZSM-5; Step change response; Langmuir adsorption model; FTIR spectra

1. Introduction

Separation of gas mixtures based on differences in adsorbent adsorption capacity is widely used in purification units of numerous practical applications such as gas drying, air separation, synthesis gas production, pollution abatement, etc. Two major commonly used gas adsorption separation processes are: (1) pressure and thermal swing adsorption and (2) supported membrane gas separation. Gas separation by pressure and thermal swing adsorption processes are well-established unit operations in the chemical industry [1,2]. On the other hand, growing attention has been also given to the application of membranes for gas separation, especially zeolite membranes [3–6]. It has been also found that adsorption has a significant effect on selective transport in zeolite membranes and consequently their effectiveness for a separation [4,6]. All of these processes require precise knowledge of multicomponent gas adsorption parameters. Unfortunately, the published data on multicomponent adsorption is scarce.

New potential areas of zeolite applications for separation purposes are removal and recovery of global warming gases, syngas production and hydrogen production for fuel cells. Syngas production includes processing steps such as CO_2 removal, the water gas shift (WGS) reaction, methanation, H_2/CO separation, etc. [7]. Pressure and thermal swing gas adsorption separation is commonly used for these processes since they are typically large scale. Gas sequestration based on pressure swing adsorption separation has been studied widely for CO_2/CH_4, CO_2/N_2 and other CO_2 gas mixtures [8–12]. However, for small-scale hydrogen production, H_2 purification based on in-situ CO_2 removal in the fuel-processing unit is a new potential application [13]. This could be achieved by using an adsorbent in some form to selectively remove CO_2 from the fuel-processing unit, i.e. reformer or water gas shift reactor.

It has been shown that CO_2 is more strongly adsorbed on MZSM-5 (M = Li, Na, Ca, Ba, Sr) than on silicalite-1 [14–19]. BaZSM-5 had a higher CO_2 adsorption capacity and the adsorbed species also had a better thermal stability than for other

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1383-5866/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.seppur.2006.04.009

ion-exchanged zeolites [19]. However, the adsorption behavior studied in the literature has focused more on single-component CO_2 adsorption and the influence of other co-adsorbed species has been mostly neglected [9,11,12]. In this study transient step change response adsorption experiments are carried out to determine the effect of H_2 and CO on the CO_2 adsorption behavior on BaZSM-5 zeolite. Temperature-programmed desorption (TPD) and in-situ Fourier transform infrared (FTIR) spectroscopy were performed to support the adsorption results and to determine the type and quantities of adsorbed species at different temperatures and gas compositions. Multi-site and extended Langmuir models are examined for describing the single- and multicomponent gas adsorptions.

2. Experimental methods

2.1. Material preparation

2.1.1. Gas mixtures

Transient step change adsorption studies were performed with He/CO_2, He/CO, He/H_2/CO_2, He/CO/CO_2 and He/H_2/CO/CO_2 gas mixtures, with He present as an inert diluting gas. The total gas flow rate was 100 mL/min at an ambient temperature of 295 K and atmospheric total pressure. The in-situ FTIR experiments were conducted with Ar/CO_2 and Ar/H_2/CO_2 gas mixtures with Ar as an inert diluting gas. The total gas flow rate was 200 mL/min (ambient). Commercially available carbon dioxide, argon and helium gases with purities greater than 99.999% (AGA, Sweden) were used.

2.1.2. Zeolite sample

The BaZSM-5 sample was prepared by a conventional triple ion exchange method [19,20] from a commercial HZSM-5 sample (Eka Chemicals, Sweden). The composition of the samples was then analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results from the elemental analysis revealed that the BaZSM-5 sample had a Si/Al molar ratio of 27 and a Ba/Al molar ratio of 0.32.

2.2. Step change adsorption and TPD measurements

Experiments were conducted for the BaZSM-5 sample with adsorption temperatures of 323, 373, and 473 K and a total pressure of 1 atm. For comparison purposes control experiments were also conducted under some conditions with the commercial HZSM-5 sample. The adsorption experiments were performed in a flow reactor with the possibility to switch the feed between pure He to He/CO_2, He/CO, He/H_2/CO_2 and He/CO/CO_2 gas mixtures. Temperature-programmed desorption (TPD) with a 15 K/min temperature ramp was conducted to determine the strength of adsorption of species and also to quantify strongly adsorbed species. H_2 pretreatment of the sample prior to CO_2 adsorption was conducted to study whether H_2 could react with and modify surface adsorption sites before exposure to CO_2. This experiment was done by exposing the sample to H_2 with a similar concentration as its concentration in the binary gas adsorption mixtures. When the sample was considered to be saturated, pure He flushing was applied until the outlet H_2 concentration was undetectable by mass spectrometry analysis. The CO_2 was then introduced into the reactor, and the experiment was continued by He flushing and TPD.

Table 1
Inlet concentrations (%) for multicomponent gas adsorption experiments

He/H_2/CO_2		He/CO/CO_2		He/H_2/CO/CO_2[a]	
H_2	CO_2	CO	CO_2	CO	CO_2
20	60[b]	20[c]	60[c]	10	30
30	50	30	50	20	20
40	40[b]	40	40	30	10
50	30	50	30		
60	20[b]	60	20		

[a] $T = 373$ K ($H_2 = 40\%$).
[b] Also conducted for control experiments with HZSM-5 sample.
[c] Not conducted at 373 K.

The outlet gas concentrations from the reactor were detected by a mass spectrometer (MS) as in a previous publication [19]. Tracer experiments using He/H_2 gas mixtures were conducted with the adsorbent samples to measure dispersion and time lag effects in the adsorbent bed and reactor system. Pretreatment of samples involved heating them in a flow of He at 723 K for 4 h. After the sample was cooled to the desired adsorption temperature, the gas feed was switched to the appropriate adsorption mixture. The inlet gas concentrations ranged from 30 to 80% for the single-component adsorption. For the binary and ternary gas mixtures the composition of inlet gases can be seen in Table 1. Powdered samples of 2 g were placed in a quartz glass tubular adsorption bed. Details about the design of the adsorption bed and feed gas manifold were reported in [19].

2.3. Adsorption calculations and modeling

Assuming ideal gas behavior and that the adsorption of H_2 on the zeolite is negligible compared to that of the adsorbate gases CO or CO_2 [16], the amount of gas adsorbed per mass of zeolite (gas loading), q, can be calculated using the differences in the breakthrough curve between the tracer and adsorbed gas as follows:

$$q = \frac{y_0 \left[\int_{t=0}^{t=t_\mathrm{e}} N_\mathrm{tot} F(t)_\mathrm{tracer} \mathrm{d}t - \int_{t=0}^{t=t_\mathrm{e}} N_\mathrm{tot} F(t)_\mathrm{ads} \mathrm{d}t\right]}{w} \tag{1}$$

where N_tot is the total flowrate in mmol/s, y_0 the feed concentration, $F(t)$ the cumulative residence time distribution, t_e the equilibrium time and w is the weight of the zeolite sample. The variation in the total molar flowrate (N_tot) with time due to the adsorption is taken into account by a mass balance based on the assumption that the molar flowrate of inert (He) is constant.

For the single-component gas adsorption, the gas loading data was further analyzed by fitting it to multi-site Langmuir adsorption models [19]. For i adsorption sites, the quantity of gas component j adsorbed (q_j) is

$$q_j = \sum_{i=1}^{\mathrm{ns}} q_{\mathrm{sat},i} \frac{K_i P_j}{1 + K_i P_j} \tag{2}$$