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CO_2 adsorption on silicalite-1 and cation exchanged ZSM-5 zeolites using a step change response method

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Abstract

The adsorption behavior of CO_2 on silicalite-1 and cation exchanged MZSM-5 zeolites (M = H, Na, and Ba) was investigated by a step change response method. Temperature programmed desorption (TPD) and in situ Fourier transform infrared (FTIR) spectroscopy were also performed to study the type of adsorbed species and their thermal stabilities. The adsorption experiments were carried out at temperatures from 323 to 473 K and CO_2 partial pressures were below atmospheric pressure. The results indicated that CO_2 was adsorbed on silicalite-1 and HZSM-5 by one type of adsorption, and on NaZSM-5 and BaZSM-5 zeolites by at least two types of adsorption over the temperature range studied. One was a weak adsorption probably due to interaction with the framework of ZSM-5, and the other was a stronger adsorption caused by interactions with the Na and Ba cations of ZSM-5. The adsorption behavior for silicalite-1 and HZSM-5 was adequately described by a single site Langmuir adsorption model but for NaZSM-5 and BaZSM-5 a dual site Langmuir model was required. FTIR spectra at various elevated desorption temperatures after adsorption of CO_2 at low temperature revealed that CO_2 was adsorbed on MZSM-5 and silicalite-1 in several ways and formed carbonate bands, which seemed to be caused by different adsorption sites. The maximum temperatures at which carbonate species were observed were 473 K for silicalite-1, 573 K for HZSM-5 and NaZSM-5 and 673 K for BaZSM-5. The TPD results indicated that the quantity of irreversibly adsorbed CO_2 on silicalite-1 and HZSM-5 was undetectable.

Keywords: CO_2 adsorption; ZSM-5; Step change response; Langmuir adsorption model; FTIR spectra

1. Introduction

Recently, attention has been given to CO_2 adsorption for separation purposes. Two example applications of environmental importance are CO_2 sequestration and fuel reforming for PEM fuel cells. CO_2 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 [1–5]. However, CO_2 removal from the fuel processing unit for hydrogen production for PEM fuel cells is a new potential application. A process for hydrogen production for a PEM fuel cell might consist of the following parts; a reforming reactor, one or more water-gas shift (WGS) reactors and finally a CO oxidation reactor. The equilibrium limitations of the reactions pose an important hinder against achieving a high yield of hydrogen and a low concentration of CO in the product. Breaking the reforming or WGS reaction equilibriums by CO_2 removal could reduce the required size of these reactors, reduce the differences in their operating temperatures or eliminate the need for a CO oxidation reactor. This could be achieved by using an adsorbent in some form to selectively remove CO_2 from the reaction zone of the reforming or WGS reactors.

Effective CO_2 adsorbents are required for the processes discussed. Thus, the choice of adsorbent becomes the most crucial design consideration for separation methods based on adsorption processes. One of the most widely used

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adsorbents for CO_2 separation are zeolites especially the MFI type, i.e., silicalite-1 and ZSM-5. Highly crystalline zeolites with a high surface area and a three-dimensional pore structure are expected to be a high-performance adsorbent for CO_2 removal. Silicalite-1, with its pure SiO_2 framework, has no exchangeable cations, whereas the framework charge of ZSM-5 must be balanced by positive charged cations. These cations are exchangeable and influence the adsorption capacity and transport properties of the zeolite. There are many publications concerning CO_2 adsorption over zeolites [6–8]. It has been shown that CO_2 is more strongly adsorbed on MZSM-5 than on silicalite-1 [9–17]. However, the temperature and pressure ranges studied in the literature have been lower than those typical for a fuel processing system. In this study slightly higher temperature and partial pressure were used. The present work also combines experiments and modeling to fit adsorption isotherms that quantify the types of adsorbed species which has not been dealt with in the cited literature.

In this study transient step change response experiments are carried out to determine the effect of cation exchange on CO_2 adsorption behavior on silicalite-1 and ZSM-5 zeolites. This method offers the possibility for determining both the single and multi-component gas adsorption behaviors and studying mass transport and diffusion of components in zeolite particles with a relatively short observation time. In situ FTIR spectroscopy and temperature-programmed desorption (TPD) measurements determined the nature, stability and quantities of adsorbed species at different temperatures and gas compositions. Multi-site Langmuir adsorption models could describe how the exchanged cations affect the adsorption strength of different species.

2. Experimental methods

2.1. Material preparation

2.1.1. Silicalite-1 powders

The samples were prepared by crystallization from a TPA-silicalite-1 precursor sol prepared by hydrolyzing TEOS with a dilute TPA solution at room temperature on a shaker for 24 h. The molar composition of the solution was $9TPAOH{:}25SiO_2{:}480H_2O{:}100ethanol$. The silicate solution was then heat-treated for 72 h under reflux and without stirring in a polypropylene container submerged in a silicon oil bath preheated to 373 K. Then the crystals were purified by repeated centrifugation and dispersion. The samples were steadily heated in a furnace from room temperature up to 823 K over 5 h. The furnace was held constant at 823 K for 6 h to complete the calcination. After the calcination the samples were cooled to room temperature [18,19]. Based on the preparation method used for the sample, the silicalite-1 framework is free of alumina.

2.1.2. Cation-exchanged ZSM-5 zeolites

The Na and BaZSM-5 adsorbents were prepared by a conventional triple ion exchange method [20] from a commercial HZSM-5 sample (Eka Chemicals, Sweden). This material was ion-exchanged in 0.5 mM solutions of $NaNO_3$ or $Ba(NO_3)_2$ at 333 K for 3 h for each ion-exchange stage. For every stage a fresh solution was used. Also, after each stage samples were filtered and washed with distilled and deionized water for three times at room temperature. Finally they were dried overnight at 383 K and calcined at 773 K for 6 h. A 10 K/min temperature ramp was used to reach the calcination temperature. 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 all ZSM-5 samples had Si/Al molar ratios of 27, the NaZSM-5 sample had Na/Al molar ratio of 0.73, and the BaZSM-5 sample had Ba/Al molar ratio of 0.32. Assuming that one Na^+ and half of a Ba^{2+} cation replaces one H^+ proton in the original sample, the fractional degrees of ion-exchange achieved were approximately 73% for NaZSM-5 and 64% for BaZSM-5 samples.

2.1.3. Gas mixtures

Transient step change adsorption studies of CO_2 on zeolites were performed with He/CO_2 gas mixtures (He as an inert gas). The total gas flow rate was 100 mL/min (ambient). The in situ FTIR experiments were conducted with Ar/CO_2 gas mixtures (Ar as an inert 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.

2.2. Step change adsorption and TPD measurements

Experiments were conducted with adsorption temperatures of 323, 373 and 473 K and a total pressure of 1 atm. The adsorptions were performed in a flow reactor with the possibility to switch the feed between pure He to a He/CO_2 gas mixture. The inlet CO_2 gas concentrations ranged from 10% to 80%. Temperature-programmed desorption (TPD) was conducted to determine the strength of adsorption of species and also to quantify strongly adsorbed species. The temperature ramp used was 15 K/min. Outlet gas concentrations from the reactor were detected by a mass spectrometer (MS). The mass spectrometer was a triple filter quadrupole gas analyzer, equipped with a dual filament ionizer assembly (thoriated iridium), and dual detectors for a fast response (<100 ms). Tracer experiments using He/Ar 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.

Powdered samples of 1.5–2 g were placed in a quartz glass tube reactor with an inside diameter of 25 mm and supported by a quartz glass frit. The feed gas flowed down through the adsorbent bed. Inside the quartz tube