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Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous "molecular basket" adsorbent

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Abstract

A novel nanoporous CO_2 "molecular basket" adsorbent has been developed and applied in the separation of CO_2 from the flue gas of a natural gas fired boiler. The nanoporous CO_2 "molecular basket" adsorbent was prepared by uniformly dispersing polyethylenimine (PEI) into the pores of mesoporous molecular sieve MCM-41. The use of MCM-41 and PEI had a synergetic effect on the CO_2 adsorption. The rates of CO_2 adsorption/desorption of PEI were also greatly improved. Adsorption separation results showed that CO_2 was selectively separated from simulated flue gas and flue gas of a natural gas-fired boiler by using this novel adsorbent. The adsorbent adsorbed very little N_2, O_2 and CO in the flue gas. Moisture had a promoting effect on the adsorption separation of CO_2 from flue gas. The adsorbent simultaneously adsorbed CO_2 and NO_x from flue gas. The adsorbed amount of CO_2 was around 3000 times larger than that of NO_x. The adsorbent was stable in several cyclic adsorption/desorption operations. However, very little NO_x desorbed after adsorption indicating the need for pre-removal of NO_x from flue gas before capture of CO_2 by this novel adsorbent.

Keywords: Adsorption separation; Carbon dioxide; Carbon sequestration; Flue gas; Natural gas-fired boiler; Mesoporous molecular sieve; Nanoporous

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1. Introduction

In the transition towards a more sustainable energy economy, fossil fuels are likely to remain the main source of global energy supply for the foreseeable future [1–3]. However, related CO_2 emissions are a major concern as increasing CO_2 emissions has been identified as a contributor to global climate change, commonly known as the “greenhouse effect”. The continuous use of fossil fuels is dependent on the reduction of CO_2 emissions. Improving the efficiency of energy utilization and increasing the use of low-carbon energy sources are considered to be potential ways to reduce CO_2 emissions [4,5]. Recently, CO_2 capture and sequestration have been receiving significant attention and is being recognized as a third option [4,5]. For carbon sequestration, the cost for CO_2 capture is expected to comprise about 75% of the total costs for geological or oceanic sequestration, with the other 25% costs attribute to transportation and injection [4]. Therefore, the development of techniques for the cost-effective separation and capture of CO_2 is considered to be one of the highest priorities in the field of carbon sequestration.

One of the major sources of CO_2 emissions is the combustion of fossil fuels. In US, fossil fuel-fired electric power plants emit about 2 billion tons of CO_2 every year, of which constitutes about one third of the entire CO_2 emission. With the discovery of increased number of natural gas fields, more electric power plants are converting to the use of natural gas. To date, all commercial CO_2 capture plants use processes based on chemical absorption with alkanolamine such as monoethanolamine (MEA) solvent. An example is the Fluor Econamine process. However, the liquid amine-based processes suffer from high regeneration energy, large equipment size, solvent degradation and equipment corrosion [6]. To overcome these disadvantages, several other separation technologies, such as, adsorption, membrane and cryogenic separation have been studied [7–11]. Because of the low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures, adsorption separation attracts much interest. The key issue for adsorption separation is to develop an adsorbent with high CO_2 adsorption capacity and high CO_2 selectivity.

Recently, a new kind of high-capacity, high-selective CO_2 adsorbents based on a “molecular basket” concept has been developed in our lab [10–12]. The CO_2 “molecular basket” adsorbent can selectively “pack” CO_2 in a condensed form in the mesoporous molecular sieve “basket” and therefore exhibits a high CO_2 adsorption capacity and a high CO_2 separation selectivity. Adsorption separation of a simulated flue gas, which contains 14.9% CO_2, 4.25% O_2 and 80.85% N_2, showed that the CO_2 adsorption capacity was 45 ml (STP)/g-adsorbent, and the CO_2/O_2 and CO_2/N_2 separation selectivity were 180 and >1000, respectively, at 75 °C. The CO_2 adsorption capacity and the CO_2/O_2, CO_2/N_2 separation selectivity of the “molecular basket” adsorbent are all much higher than those of the existing adsorbents, such as zeolites and molecular sieves [13–15]. However, boiler flue gas contains many other gases, such as moisture, SO_2, NO_x, CO. Whether these gases will also be adsorbed by the “molecular basket” adsorbent is not clear. On the other hand, the “basket” material of MCM-41 may not be stable under hydrothermal conditions [16,17]. The preservation of the structure of MCM-41 is critically important for the CO_2 adsorption separation performance of this novel adsorbent [10–12]. In this paper, adsorption separation of CO_2 from flue gas of natural gas-fired boiler, which contains 7.4–