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Elevated temperature hydrogen/carbon dioxide separation process simulation by integrating elementary reaction model of hydrotalcite adsorbent

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ABSTRACT

An elementary reaction kinetics model related with Elovich equation is developed to predict the CO_2 adsorption capacity and adsorption kinetic behavior for potassium promoted hydrotalcite-like compound (K-promoted HTlcs). The elementary reaction kinetics model is comprehensively validated by experimental data from both atmosphere pressure thermo gravimetric analysis (TGA) and a high pressure adsorption apparatus. The elevated temperature pressure swing adsorption s(PSA) system modeling framework is then developed on the gPROMS commercial simulation platform by further considering comprehensive coupling effects from mass, momentum and energy transport processes, integrated with dynamic boundary condition and realistic operating procedures. The effects of adsorption time, residence time, purge to feed ratio, working pressure and adsorbents capacity on PSA cycling gas separation performance are studied with the proposed modeling framework based on a four-bed two-pressure-equalization PSA process.

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1. Introduction

The elevated temperature pressure swing adsorption (PSA) based on K-promoted HTlcs solid adsorbent is widely accepted [1–9] as a promising technology for H_2/CO_2 separation in Integrated Gasification Combined Cycle (IGCC) power plant or coal gasification based chemical synthesis plant by taking the advantages of high partial pressure (1.0–2.0 MPa) of CO_2 in the syngas after water–gas shift reaction. In addition, the elevated temperature separation process can save the sensitive heat from the syngas, and the warm hydrogen can be utilized in following chemical synthesis, combustion or high temperature fuel cells. While, the optimal design of PSA bed and system is also significantly crucial for improving the gas separation efficiency and for lowering system costs. Since experimental studies on PSA unit are usually expensive, time-consuming and labor-intensive, quantitative mechanism models for the reactions and transport within the PSA beds and dynamic simulation model for the PSA system are essential for accelerating the technology commercialization.

In fact, a well developed modeling framework by accounting for the adsorbent characteristics, effects of system configuration and operating conditions offers not only the way to understand the complex physical-chemical phenomena which are not readily accessible experimentally; but also can be an useful designing and optimization tool.

Several models for hydrotalcite based solid adsorbent differing widely in terms of the complexity have been developed. Ding and Alpay [4] adopted Langmuir model and revised LDF model based on pore diffusion to describe adsorption and desorption data. Lee et al. [5] found that the isotherm of CO_2 on K-promoted HTlcs below 0.2 atm could be fitted by Langmuir model, but the isotherm deviated remarkably from Langmuir in higher CO_2 pressure region, thus a new equilibrium model based on two-step mechanism was developed together with linear driving force (LDF) model to simulate the breakthrough curve. Oliverira, Grande and Rodrigues [6] used a bi-Langmuir accounted for two different sites of physical adsorption and chemical reaction to fit sorption isotherms below 0.4 bar on K-promoted HTlcs. In most of the models in the published literature, gas adsorption kinetics is usually formulated by the linear driving force (LDF) approximation, and commonly with the detailed reaction and transport mechanisms within the adsorbent particles neglected. Ritter's group [7—11] systematically studied the CO_2 adsorption characteristics of K-promoted HTLcs and developed nonequilibrium model and provided the detailed reaction mechanism for the equilibrium and kinetic behavior of CO_2 in K-promoted HTlcs, and then extended the temperature range of the model to 300—500 °C. However, few adsorbent mechanism model is applied and validated at the high pressure operating conditions for K-promoted HTlcs which is significantly important for the model application for instructing the elevated temperature PSA process design in pre-combustion CO_2 capture.

In the system level, PSA process schedule design has strong influences on separation efficiency and product purity [12—15]. Reynolds et al. [16] simulated six different stripping PSA cycles for concentrating CO_2 from flue gas at 575 K to study the effect of adding concurrent depressurization step and heavy reflux step to a basic 4-bed 4-step stripping cycle with or without light reflux and found that cycles with heavy reflux step outperformed cycles without it and concurrent depressurization step showed disappointing improvement in process performance. While, few of the existing models for PSA process related the mechanism model of K-promoted HTlcs considering direct integration of elementary models for adsorbent reactions and transport processes into PSA system models. And it should be noted that for a given mathematic modeling framework, although most of the model parameters are determined from experiments or from literature, some of the parameters are still needed to be adjusted to ensure good agreement between the model results and the experimental data. The uncertainty in the estimated parameter will surely influence the model reliability and accuracy. The more the parameters are determined independently through experiments or characterization techniques, the more robust the model is.

In this study, an elementary reaction kinetic model related with Elovich equation is developed to predict the adsorbent adsorption capacity and adsorption kinetics which are well validated by TGA at atmosphere pressure and by fixed bed at high pressure. Then, a dynamic modeling framework for the separation of CO_2 and H_2 at elevated temperature using multi-bed pressure swing adsorption process based on hydrotalcite adsorbent is developed in commercial simulation platform gPROMS by considering comprehensive coupling effects of mass, momentum and heat transport processes. The effects of adsorption time, residence time, purge to feed ratio, working pressure and adsorbents capacity on gas separation performance are studied based on a 4-bed, 2-pressure-equalization, 1-adsorption PSA process design for pilot-scale testing in our lab.

2. Experiment

2.1. Adsorbents and gases

Adsorbents used to adsorb CO_2 are 25 wt% potassium carbonate impregnated Mg—Al hydrotalcites (MG70, Sasol Germany GmbH). High-purity H_2, Ar, and He (99.99%), and purity CO_2 (99.99%) are used in experiments. Theoretically, the porosity $å$ is determined by the particle density and tap density of the powder. Since the irregularity of particles of the calcined powder, we take the calculation porosity $å_{cal}$ determined by true density and tap density in our calculation, where the true density is measured by a pycnometer (Micromeritics, AccuPyc 1330). Thus, we take the true density instead of particle density, and calculation porosity $å_{cal}$ instead of porosity $å$ in further calculation.

2.2. Gravimetric adsorption and desorption

A thermo gravimetric analyzer was used to measure the dynamic adsorption and desorption behavior of CO_2 on the K promoted HTlcs. The sample was activated at 400 °C for a specified length of time 6 h in muffle furnace. Then in TGA, the sample was further activated in helium flowing at about 100 mL min^{-1} and 1 atm for 30 min at 400 °C before adsorption experiment at setting temperature. The gas was then switched to CO_2 at 40 mL min^{-1} flow rate and He at 60 mL min^{-1} flow rate at 1 atm in the adsorption tests, and the gas was switched back to helium gas after 30 min for beginning of desorption process. All of the CO_2 adsorption amounts on the adsorbent were based on the weight of the sample at the end of the activation period in TGA.

2.3. Dynamic adsorption capacity tests in a packed-bed reactor

Dynamic adsorption experiments were conducted in a packed-bed reactor, which is capable of keeping a pressure up to 7.0 MPa and a maximum temperature of 700 °C, with a diameter of 5.5 mm and a height of 10 mm. High pressure gas is depressurized by the pressure regulator to the experimental pressure demand. Certain mass flow rate is controlled by a mass flow controller (MFC), whose value is controlled and displayed on the PC terminal. A spiral duct heat exchanger and a gas—liquid separator are set downstream to cool down gas flow. Pressure is detected both before the adsorption