



Full Length Article

High-pressure carbon dioxide adsorption kinetics of potassium-modified hydrotalcite at elevated temperature



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HIGHLIGHTS

- Modified static bed high pressure adsorption kinetics measurement.
- Hydrotalcite sorbent CO₂ adsorption/desorption kinetics at 300–450 °C.
- Elovich type adsorption/desorption behaviors.

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ABSTRACT

A method for characterizing the high-pressure CO₂ adsorption kinetics of potassium-modified hydrotalcite at elevated temperatures based on a modified static bed is proposed. The pressure drop of the adsorption tube with time was measured by a series of high-sensitivity pressure sensors to calculate the CO₂ adsorption curves of the adsorbent. The concept of a hot/cold spot is introduced to eliminate the temperature deviation caused by the dead volume of the pipelines and the temperature disproportion in the tubes. As compared to conventional characterization methods such as thermal gravimetric analysis and fixed bed testing, the proposed method avoids the displacement effect, making it possible to obtain actual adsorption curves above atmospheric pressure. The effect of adsorption temperature (300–450 °C) and CO₂ partial pressure (0.1–2 MPa) and a reversible adsorption isotherm with 30 min adsorption/30 min desorption, as well as desorption performance under vacuum, were investigated. The adsorption/desorption curves of hydrotalcite increased linearly with the logarithm of the adsorption time in almost all tested conditions. The CO₂ uptake reached approximately 0.7 of the total adsorption capacity in less than 0.1 min of adsorption time and exceeded 0.9 after 5 min. A simple one-step kinetic model based on Elovich-type equations is built to describe the adsorption behavior of hydrotalcite at CO₂ partial pressures above atmospheric pressure.

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1. Introduction

Warm gas clean-up (WGCP) refers to the process in which impurities such as CO, CO₂, H₂S, COS, and HCl from syngas are removed at elevated temperatures (200–450 °C) [1]. This process has the potential to be widely used for purification in the petroleum, chemical, metallurgical, and energy industries. In contrast to solvent absorption technologies such as Rectisol[®], Selexol[™], and MDEA, the proposed process (1) reduces equipment investment, (2) avoids sensible heat loss of syngas, and (3) reduces energy consumption for heat regeneration by adopting elevated temperature pressure swing adsorption (ET-PSA) [2,3].

One difficulty in the development of WGCP for CO₂ removal is the synthesis and characterization of CO₂ adsorbents, which require (1) high selectivity and adsorption capacities at elevated temperatures, (2) adequate adsorption/desorption kinetics, (3) stable working capacities, and (4) adequate mechanical strength [4]. Conventional physical adsorbents such as zeolite, activated carbon, and metal–organic frameworks (MOFs) are not applicable for WGCP systems owing to the rapid decrease in adsorption capacity with increasing temperature. Carbon, polymer (COF/POP) based materials attracted extensive attention recently due to their high BET surface area, large micropores and wide utility via choosing different organic functional monomers [5,6]. Hydrotalcite-like compounds (HTIs), which are also known as layered double hydroxide (LDH), exhibit relatively high CO₂ adsorption capacity and nearly infinite selectivity for CO₂ from other molecules through weak-chemisorption in WGCP conditions

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Nomenclature

a	linear regression slope, m^{-3}	t_{lc}	test time for leakage correction, s
A_a	adsorption pre-exponential factor, s^{-1}	T_0	room temperature, K
A_d	desorption pre-exponential factor, s^{-1}	T_1	cold spot temperature, K
b	linear regression intercept, –	\bar{T}_{i1}	assumed cold spot temperature, K
c	pressure factor, –	T_2	test temperature, K
E_a	adsorption activation energy, J/mol	V_{0i}	total volume of standard steel balls, m^3
E_d	desorption activation energy, J/mol	V_1	volume of reference tube, m^3
E_a^0	initial adsorption activation energy, J/mol	V_2	volume of adsorption tube, m^3
E_d^0	initial desorption activation energy, J/mol	V_3	total volume of standard steel balls in correction step, m^3
g	fitting parameter for adsorption activation energy, –	\hat{V}_3	calculated total volume of standard steel balls in correction step, m^3
h	fitting parameter for desorption activation energy, –	V_s	volume of treated K-MG30, m^3
k	kinetic coefficient, s^{-1}	φ_1	cold spot volume ratio of adsorption tube, –
k_i	linear regression coefficient, –	$\hat{\varphi}_{i1}$	assumed cold spot volume ratio of adsorption tube, –
k_a	adsorption kinetic coefficient, s^{-1}	φ_2	cold spot volume ratio of adsorption tube and reference tube, –
k_d	desorption kinetic coefficient, s^{-1}	φ_{i2}	assumed cold spot volume ratio of adsorption tube and reference tube, –
m_s	weight of treated K-MG30, kg	ρ	density of helium, kg/m^3
p_i	gas pressure in the tubes, Pa	$\bar{\rho}$	a series of density of helium, kg/m^3
p_0	atmospheric pressure, Pa	ρ'	density of carbon dioxide, kg/m^3
p_{CO_2}	CO_2 partial pressure, Pa	δ	CO_2 leak rate, Pa/s
q	CO_2 uptake of K-MG30, mmol/g		
$q_{e,a}$	CO_2 uptake of K-MG30 after unlimited adsorption time, mmol/g		
$q_{e,d}$	CO_2 uptake of K-MG30 after unlimited desorption time, mmol/g		
r_a	adsorption rate, s^{-1}		
r_d	desorption rate, s^{-1}		

[7,8]. The adsorption heat of HTIs is between those of zeolite and basic metal oxides [9,10], and thus they could be easily desorbed by pressure swing process.

Yong et al. [4,11,12] systematically investigated the effect of cation, aluminum content, anion type, CO_2 partial pressure (0–0.126 bar), adsorption temperature (20–300 °C), etc. on the CO_2 adsorption capacities of LDH. Wang et al. [13] showed that with the same precipitation agent, the preparation method had little effect on the CO_2 adsorption capacity. Wang et al. [14,15] and Hutson et al. [16] reported that M^{3+} and A^{n-} influenced the thermal stability, morphology, and surface area of LDH and that the Mg–Al– CO_3 type of LDH showed the highest CO_2 adsorption capacity of 0.53 mmol/g at 400 °C and 1 atm. In addition, the effects of steam [17–19], alkali metal modification [20], replacement of interlayer anions [21] and carbon based supports [22–24] on the adsorption capacities and kinetics of LDH was systematically studied.

Several adsorption models have been proposed to understand the adsorption/desorption behavior of LDH. Most studies adopted the Langmuir adsorption isotherm model and the linear driving force (LDF) kinetic model [20,25–27,8]. Lee et al. [8] suggested that a simple Langmuir adsorption model is not adequate to describe the chemisorption isotherms of LDH above 0.2 atm of CO_2 partial pressure. Oliveira et al. [20] adopted a bi-Langmuir model to describe the adsorption isotherms of LDH at 300–500 °C and 0–0.5 atm. Ding et al. [26] included intra-particle diffusion in the calculation of the kinetic coefficient. Different with the above models, Ritter's group [28,29] proposed a reversible non-equilibrium kinetic model (RNEK model) with three temperature-dependent, highly coupled, completely reversible, equilibrium-driven but kinetically limited reactions [29]. The effect of the adsorption temperature (300–500 °C) [30] and CO_2 partial pressure (0–1 atm) [31] were also considered. The concept of a multi-step reaction was also adopted by Zheng et al. [32,33], who developed an elementary reaction kinetic model. The adsorption activation energy was

described by an Elovich-type equation based on the fact that the adsorption activation energy of CO_2 on LDH was related to the coverage ratio [33]. This model was calibrated and validated with experimental data at 250–350 °C and 0.2–0.8 atm of CO_2 partial pressure.

It should be noted that although there have been many experimental tests and models about LDH, most of them have focused on relatively low pressures. The adsorption performance of LDH above 1 atm of CO_2 partial pressure remains unclear. Especially, there are very few studies about the high-pressure adsorption kinetics of LDH, which constrains the further understanding of the adsorption mechanism of LDH and the development of adsorption model that is applicable to high CO_2 partial pressures. In some actual industrial applications, adsorbents need to work in relatively high-pressure environments. For example, in pre-combustion CO_2 capture for coal-fired power plants or in the ammonia synthesis process, the total pressure and CO_2 partial pressure for syngas are 3–5 MPa and 1–1.5 MPa, respectively [34]. An adsorption model built on atmospheric pressure is inapplicable in these conditions.

In this study, a new kind of measuring method based on a modified static bed for high-pressure adsorption kinetics is proposed. The adsorption curve is calculated by the pressure drop of the adsorption tube with time during the adsorption process, which avoids the displacement effect in traditional characterization equipment. The concept of a hot/cold spot is put forward to reduce the measuring error caused by the dead volume in the pipelines and the temperature disproportion in the tubes. The adsorption/desorption kinetics of potassium-modified Mg–Al– CO_3 LDH, as well as the reversible working capacity in a limited time, are systematically investigated under operating conditions of 300–450 °C and 0.1–2 MPa. A simple kinetic model with an Elovich-type activation energy is considered to fit well with the experimental data. The adsorption performance of LDH with temperature/pressure is then explained via the proposed model.

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