Applied Energy 231 (2018) 167–178

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Application of density functional theory in studying CO_2 capture with TiO_2-supported K_2CO_3 being an example

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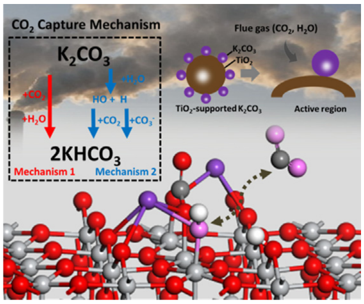
HIGHLIGHTS

- Preadsorbed H_2O makes CO_2 adsorption increase over K_2CO_3/TiO_2 sorbent.
- CO_2 and H_2O prefer to adsorb at the interface of K_2CO_3/TiO_2.
- Carbonation reaction is governed by H_2O dissociation.
- The better K-based sorbent for CO_2 capture is proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Density-functional theory
CO_2 capture
K_2CO_3
Rutile

ABSTRACT

Solid sorbents based CO_2 capture has become increasingly important. Great progress has been achieved with experimental studies in this area. However, the density functional theory based capture study on the function of H_2O in CO_2 capture is lacking. This research was designed to make progress in this important area with TiO_2-supported K_2CO_3 being an example. Due to its high cost-effectiveness, dry K_2CO_3 is a promising sorbent for capturing CO_2. Yet challenges remain in accelerating the rate of the absorption process. The study of mechanism of the effect of H_2O on CO_2 adsorption as well as the carbonation reaction can help select and design better support for the sorbent. Up to now, it is open. In this work, the adsorption and reaction of CO_2 over K_2CO_3 loaded on a rutile (1 1 0) surface have been studied using theoretical calculations. The results show that the CO_2 adsorption is increased when H_2O appears, and carbonation reaction mainly occurs at the interfaces of K_2CO_3/TiO_2 includes bicarbonate formation resulting from the reactions of CO_2 with OH via H_2O dissociation and CO_3 anion with transferred H via H_2O dissociation combining. In addition, H transfer step appears when support TiO_2 exists compared to that on pure K_2CO_3 sorbent. The kinetic modeling indicates that the H_2O dissociation may limit the carbonation reaction. Therefore, H_2O-dissociative or high OH coverage TiO_2 support material can assist CO_2 sorption with the solid K_2CO_3 based CO_2 capture technology. It is expected that the theoretical study sheds light on the preparation of cost-effective CO_2 sorbents in the future.

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https://doi.org/10.1016/j.apenergy.2018.09.114
Received 24 May 2018; Received in revised form 1 August 2018; Accepted 9 September 2018
0306-2619/

1. Introduction

Global warming caused by greenhouse gas emission has, in recent years, been recognized as a major risk to mankind [1–3]. Carbon dioxide (CO_2) is one of the major greenhouse gases, and it has been reported that one-third of CO_2 emissions worldwide come from fossil fuel-based power plants [4]. Hence, capturing CO_2 emitted from the flue gas of power plants has been considered to be a potentially effective approach to controlling atmospheric CO_2 levels.

Methods explored to remove CO_2 from flue gas include membrane separation (separated CO_2 from a CO_2–N_2 mixed gas) [5], absorption with a solvent (CO_2 absorption with aqueous, blends of monoethanolamine and N-methyldiethanolamine, etc.) [6,7], and adsorption on molecular sieves (adsorption–desorption on molecular sieves by pressure or temperature swing) [8,9]. However, these methods are costly and consume large amounts of energy. One of the improved techniques for the removal of CO_2 is the chemical absorption of CO_2 with dry renewable K_2CO_3 sorbents [10,11] and K_2CO_3-promoted hydrotalcite sorbents [12,13]. Hydrotalcites have the unique property of CO_2 sorption at high temperatures (200–600 °C), which can be applied to the direct CO_2 removal from flue gases without cooling process. The equilibrium CO_2 sorption uptake of hydrotalcite could be much more increased by impregnation with K_2CO_3. However, the regeneration temperature is high. Meanwhile, K_2CO_3 sorbents are employed in CO_2 absorption from flue gas of fossil-fueled based thermal power plants at low temperatures (50–90 °C). The use of K_2CO_3 sorbents can be highly cost effective and an energy efficient way to remove CO_2 from flue gas following the reaction $K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3$. In addition, the global carbonation reaction rate for pure K_2CO_3 is rather slow [14]. We therefore suggested that, in preparation support, a promoter or special technique may be needed to modify the structure of the K_2CO_3 surfaces to strengthen the adsorption of CO_2, thereby further improving conversion of carbonate to the bicarbonate based our theoretical calculation.

Some supports such as SiO_2, Al_2O_3, CaO, MgO, TiO_2 and activated carbon (AC) have been used in alkali metal-based sorbents to enhance CO_2 capture. Lee et al. [15–18] and Zhao et al. [19–22] found that sorbents of K_2CO_3/AC, K_2CO_3/TiO_2, K_2CO_3/MgO, and K_2CO_3/Al_2O_3 showed excellent CO_2 capture capacity; on the other hand, those sorbents were completely regenerated above 130, 130, 350, and 400 °C, respectively. However, the CO_2 capture capacities of K_2CO_3/Al_2O_3 and K_2CO_3/MgO decreased during multiple absorption/regeneration cycles (absorption at 60 °C and regeneration at 150 °C), mainly due to the formation of $KAl(CO_3)_2(OH)_2$, $K_2Mg(CO_3)_2$, and $K_2Mg(CO_3)_2{\cdot}4(H_2O)$, which did not completely convert to the original K_2CO_3 phase. However, unlike K_2CO_3/Al_2O_3 and K_2CO_3/MgO, a $KHCO_3$ crystal structure was formed during CO_2 absorption on K_2CO_3/AC and K_2CO_3/TiO_2 sorbent. This phase could easily be converted into the original phase during regeneration, even at a low temperature (130 °C). Meanwhile, Lee et al. [23] investigated the structure effects of potassium-based TiO_2 (anatase) sorbents on CO_2 capture capacity. Under the temperature of calcine, the CO_2 capture capacity of the sorbent was reduced due to the undesired formations of $K_2Ti_2O_5$, $K_2Ti_6O_{13}$, and $K_2Ti_4O_9$. However, the rutile structure of TiO_2 can prevent the formation of new structures such as $K_2Ti_2O_5$ and $K_2Ti_6O_{13}$, thus significantly affect CO_2 capture capacity. In addition, $TiO(OH)_2$ has been found to be a promising catalytic support for not only improving CO_2 capture of solid sorbents [24,25], but dramatically reducing energy consumption [26].

The reaction mechanism for CO_2 uptake by K_2CO_3 and the role of H_2O in the reaction are open. Mahinpey et al. [27] reported that K_2CO_3 hydration to form $K_2CO_3{\cdot}1.5H_2O$ and carbonation occur in parallel, without direct conversion from $K_2CO_3{\cdot}1.5H_2O$ to $KHCO_3$. Further, Mahinpey et al. [28] discussed the kinetic behavior of solid K_2CO_3 under CO_2 capture and brought up that the carbonation reaction are limited by adsorption, not chemical reaction based on proposed Langmuir-Hinshelwood model. However, Zhao et al. [29] and Li et al. [30] suggested that $K_2CO_3{\cdot}1.5H_2O$ can react with CO_2 in a fast kinetic rate. Meanwhile, Li et al. [31] determined that hydration reaction occurred through the reaction between K_2CO_3 and the steam, and approximately 75% of K_2CO_3 were converted to $K_2CO_3{\cdot}1.5H_2O$ in high temperature, however, $KHCO_3$ cannot directly react with the steam to produce $K_2CO_3{\cdot}1.5H_2O$. Although there have been some experimental explorations into the mechanism of carbonation reaction, it is difficult to understand the mechanism completely due to the complexity of CO_2 capture with K_2CO_3 sorbent. Quantum mechanics calculation is a useful tool to help clarify the detail of the reaction. Gao et al. [32] investigated the carbonation reaction only on pure K_2CO_3 with monoclinic structure using the density functional theory (DFT) method, proposing that the carbonation reaction occurs via the single “one-step mechanism”, i.e., the OH group resulting from the dissociation of H_2O attacking the C of CO_2 to form bicarbonate. Also, the same reaction on low index surfaces of pure K_2CO_3 with both cubic and monoclinic structures was studied, and it was confirmed that the carbonation reaction can directly proceed either via the interaction between OH resulting from H_2O dissociation and the C atom of CO_2 on monoclinic and hexagonal K_2CO_3, or between the OH group from H_2O dissociation reacting and gaseous CO_2 on hexagonal K_2CO_3, i.e., the carbonation reaction is both a “one-step” and a “two-step mechanism” [14]. Further, investigating the CO_2 desorption reaction on an anatase-TiO_2 (1 0 1) surface by DFT method, Wu et al. [33] concluded that the formation of the unstable intermediary $TiO(OH)^+$ and OH^- by the adsorption of H_2O on the catalyst TiO_2 surface can accelerate the reaction. However, in their work the initial states are not $KHCO_3$, but rather hydroxyl and carbonyl states. On the other hand, adsorption and carbonation of CO_2 and H_2O on pure rutile or anatase have been investigated extensively. For instance, investigating the co-adsorption properties of CO_2 and H_2O on rutile of TiO_2 (1 1 0) using a dispersion-corrected DFT study, Sorescu et al. [34] found that the co-adsorbed H_2O or OH species slightly increase the CO_2 adsorption energies. Other influence factors, including the solvent effect [35] and the effect of excess electron and hole [36], have also been investigated. However, CO_2 captured by TiO_2-supported K_2CO_3 sorbent still has not been investigated using a theoretical method. Does TiO_2-supported K_2CO_3 capture CO_2 better than pure K_2CO_3 or clean TiO_2? What is the capture mechanism in detail? Where is the active site? The above questions are open.

In order to increase CO_2 capture efficiency, it is imperative to make clear the mechanism by which K_2CO_3/TiO_2 captures CO_2. This work focuses mainly on the mechanisms of the K_2CO_3/TiO_2 (rutile) capture of CO_2 through DFT calculation, due to the relatively simpler capture/regeneration mechanism on rutile-supported K_2CO_3 than other media. At the same time, the results are compared with those using pure K_2CO_3 or clean TiO_2 so that the CO_2 capture mechanism can be comprehended better.

2. Computational details

2.1. Computational methods

The DFT approach has been proved to be very successful in modeling the ground state properties of various structures, and has thus been widely used to predict the structural and energetic properties. DFT with Hubbard U correction is to treat the strong on-site Coulomb repulsion, which is not correctly described by LDA or GGA, mainly employed to calculate and analysis the refined electronic structures. At present, geometric optimization and transition state search cannot yet be carried out using the DFT + U method in the CASTEP code, largely because DFT alone has been considered fairly reliable in most cases for structural optimization, resulting in lattice parameters below 1% level of inaccuracy [37,38].

Previous experimental and theoretical studies have demonstrated that CO_2 molecules interact relatively weakly with the rutile(1 1 0) and K_2CO_3 surface. Thus, one might presume that long-range dispersion