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Review

Molten salts-modified MgO-based adsorbents for intermediate-temperature CO_2 capture: A review

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ABSTRACT

Carbon dioxide (CO_2) capture using magnesium oxide (MgO)-based adsorbents at intermediate temperatures has been regarded as a very prospective technology for their relatively high adsorption capacity, low cost, and wide availability. During the past few years, great effort has been devoted to the fabrication of molten salts-modified MgO-based adsorbents. The extraordinary progress achieved by coating with molten salts greatly promotes the CO_2 capture capacity of MgO-based adsorbents. Therefore, we feel it necessary to deliver a timely review on this type of CO_2 capturing materials, which will benefit the researchers working in both academic and industrial areas. In this work, we classified the molten salts-modified MgO adsorbents into four categories: (1) homogenous molten salt-modified MgO adsorbents, (2) molten salt-modified double salts-based MgO adsorbents, (3) mixed molten salts-modified MgO adsorbents, and (4) molten salts-modified MgO-based mixed oxides adsorbents. This contribution critically reviews the recent developments in the synthesized method, adsorption capacity, reaction kinetics, promotion mechanism, operational conditions and regenerability of the molten salts-modified MgO CO_2 adsorbents. The challenges and prospects in this promising field of molten salts-modified MgO CO_2 adsorbents in real applications are also briefly mentioned.

1. Introduction

It is well accepted that the continuous rise of carbon dioxide (CO_2) concentration in atmosphere leads to global warming and extreme climate events [1–3]. Meanwhile, the over discharge of CO_2 from excessive combustion of fossil fuels cannot be addressed immediately [4–6]. At present, pre-combustion capture, post-combustion capture and oxyfuel combustion are the three main approaches to capture CO_2 [7,8]. Among them, pre-combustion CO_2 capture is commonly fit for the integrated gasification combined cycles (IGCC) related processes, e.g. sorption enhanced water gas shift (SEWGS) at intermediate temperatures (200–400 °C) [9–11]. Typically, solid adsorbents show potential application for CO_2 capture in terms of a wide range of operating temperatures, low cost and high uptake capacity [7,12].

Magnesium oxide (MgO) [13] has been wildly considered as a type of promising candidate for CO_2 capture at intermediate temperatures (200–400 °C) [14,15]. The favorable adsorbents have appropriate basic strength and less waste with a rather high theoretical CO_2 capture capacity of 24.8 mmol/g [10]. However, the practical CO_2 capture performance of pure MgO is greatly restricted by low specific surface area, slow kinetics, and poor thermal stability [16]. Therefore, many studies have been devoted to further improving the CO_2 capture capacity of MgO-based adsorbents, such as dispersing on porous supports [17], and synthesizing mixed oxides [18].

During the past few years, we have witnessed a rapid growth of the fabrication of molten salts-modified MgO-based adsorbents. Since Harada and coworkers proposed alkaline nitrates/nitrites coated MgO-based adsorbents with a high CO_2 capture capacity of 15.7 mmol/g in 2015 [19], there have been significant develops in this field. To make a better understanding about the rapid development of the molten salt promoted MgO-based adsorbents, a timely review is highly desired. In this contribution, we try to make a clear clarification about the synthesis method, CO_2 capture capacity, regenerability, and mechanisms of all molten salts promoted MgO-based materials. We hope that this work will assist

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Table 1. Summary of homogeneous molten salt-modified MgO adsorbents and their performance for CO_2 capture.

Adsorbent	Molten salt	Method	CO_2 uptake	Reference
MgO	$LiNO_3$	Aerogel method	1.17 mmol/g, 325 °C	[24]
MgO	$LiNO_3$	Wet impregnation method	1.45 mmol/g, 300 °C	[14]
MgO	KNO_3	Wet impregnation method	0.20 mmol/g, 300 °C	[14]
MgO	KNO_3	Aerogel method	3.16 mmol/g, 325 °C	[24]
MgO	$NaNO_3$	Aerogel method	1.76 mmol/g, 325 °C	[24]
MgO	$NaNO_3$	Supercritical drying method	1.86 mmol/g, 325 °C	[37]
MgO	$NaNO_3$	Wet impregnation method	12.9 mmol/g, 300 °C	[14]

the development of MgO-based adsorbents from fundamental research to practical applications.

2. CO_2 capture performance of molten salts promoted MgO-based adsorbents

Molten salts [20,21], such as alkali metal nitrates, alkali and alkali earth metal carbonates are commonly applied in solar energy utilization due to its advantages such as thermodynamic stability up to high temperatures, low pressure at the operating temperature and wide range of solubility [22]. Considerable research efforts have been devoted to the fabrication of molten salts promoted MgO-based adsorbents due to their outstanding CO_2 capture performance, excellent regenerability and rather higher thermal stability, compared with other modification method. In 2001, a US patent describing alkali molten salts promoted MgO-based adsorbents reported a broad capacity range of 1.1–12.9 mmol/g depending on the conditions of synthesis, with the highest regenerable capacity of 11 mmol/g obtained using pressure swing regeneration at 375 °C [23]. Since then, CO_2 capture using molten salts-modified MgO-based materials at intermediate temperatures has been demonstrated as a very promising way for CO_2 capture, utilization and storage (CCUS) in recent years. Based on the existing methods ever been reported, we have tried to summarize and classify all the possible molten salts-modified MgO adsorbents into four groups, which are (1) homogenous molten salt-modified MgO adsorbents, (2) molten salt-modified double salts-based MgO adsorbents, (3) mixed molten salts-modified MgO adsorbents, and (4) molten salts-modified MgO-based mixed oxides adsorbents.

2.1. Homogeneous molten salt-modified MgO adsorbents

The molten salts modification process combines the benefits of easy handling of solid materials and superior mass transfer with high diffusivity of a liquid solvent. Table 1 lists the preparation method of the homogeneous molten salt-modified MgO adsorbents and their performance in CO_2 capture. In 2014, Vu et al. [24] synthesized a mesoporous KNO_3–MgO adsorbents at a Mg/K molar ratio of 1:0.2 with a four-step calcination process. The developed composites using an aerogel method exhibited a high CO_2 capture capacity of 3.16 mmol/g at 325 °C. It is believed that the KNO_3 liquid interface with the capillaries inside the gel network led to the surface tension force which acted on the wall of the pores, and thus caused a substantial shrinkable owe to the collapse of the gel network and accumulation of the MgO particles [25]. They suggested that KNO_3 offered a liquid “channel” for fast CO_2 diffusion during the adsorption process [24]. Recently, Prashar et al. [26] explored different factors that affect the rate of CO_2 adsorption after partial desorption in $NaNO_3$-promoted MgO composites. They found that some nitrate groups got substituted in the lattice of $MgCO_3$ and thus gave rise to defective phases. And the adsorption in the subsequent cycle appeared to be very fast with no induction period when the desorption process of CO_2 was incomplete [26]. Later on, Jo et al. [27] profoundly studied the mechanism of adsorption and desorption of CO_2 by molten $NaNO_3$-promoted MgO. Their findings indicated that the promoter acted as a reaction medium and dissolved both CO_2 and MgO, facilitating the rather slow reaction kinetics. In the desorption reaction, the introduction of the promoter greatly decreased the relative stability of $MgCO_3$ [27]. Moreover, Zhang et al. [28] assumed that the dissolution of solid MgO in the molten salts overcame the high lattice energy constraints and thus resulted in the extraordinary promoting effects which activated the MgO toward reaction with CO_2. Simplifying molten $NaNO_3$ as a solvent, they have calculated the energy differences for the reaction between MgO and CO_2 with the presence/absence of $NaNO_3$. Fig. 1(a) shows that the energy for the dissociated $[Mg^{2+}...O^{2-}]$ intermediate decreased by 1.77 eV, which displayed a kinetically desirable pathway. It is believed that the molten salt dispersed and partially wet the MgO surfaces. Some solvated ionic pairs $[Mg^{2+}...O^{2-}]$ dissolved into molten salts forming a dissolution/precipitation balance. Gaseous CO_2 weakly adsorbed on the bare MgO surface and migrated to the gas–liquid–solid triple phase boundaries (TPB). The adsorbed CO_2 reacted with the $[Mg^{2+}...O^{2-}]$ to form $[Mg^{2+}...CO_3{}^{2-}]$ and the precipitated $MgCO_3$ was away from the initial dissolution sites

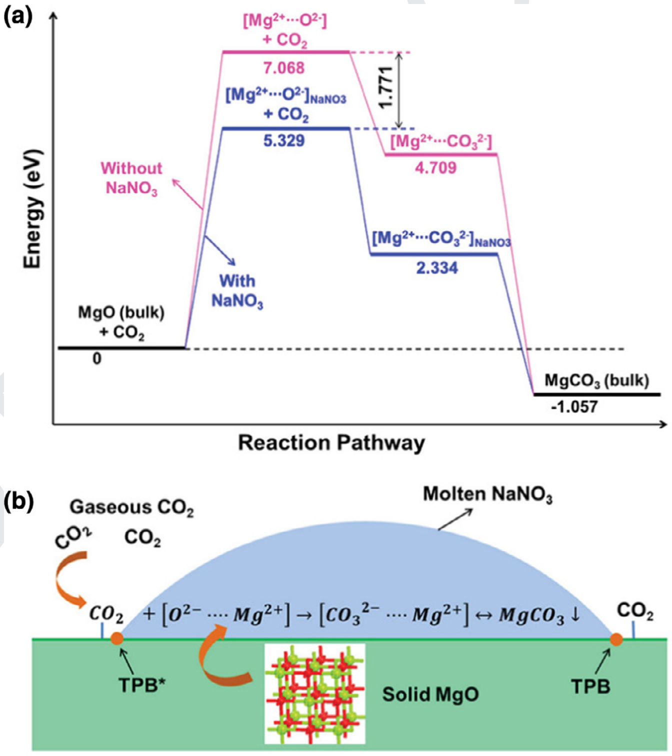

Fig. 1. Proposed reaction mechanism. (a) Proposed Born–Haber cycles, showing the notable enthalpy difference for MgO dissociation in vacuum as compared to that in $NaNO_3$ with solvation effect; (b) Illustrative diagram for the phase transfer catalysis of CO_2 adsorption on MgO with molten $NaNO_3$ (* represents triple phase boundary). Adapted from Ref. [28].

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