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 adsorbents. The extraordinary progress achieved by the coating of molten salts greatly promotes the CO_2 capture capacity of MgO based adsorbents. Therefore, we feel it is necessary to deliver a timely review on this type of CO_2 capturing materials, which will benefits the researchers working in both academic and industrial areas. In this work, we classified the molten salts−modified MgO adsorbents into three categories: (1) homogenous molten salt−modified MgO adsorbents, (2) molten salt−modified double salts−based MgO adsorbents, and (3) mixed molten salts−modified MgO 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.

Keywords: magnesium oxides; CO_2 adsorption; molten salts; intermediate temperatures; regenerability

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] While the over discharge of CO_2 from excessive combustion of fossil fuels cannot be addressed immediately.[4] At present, pre−combustion capture, post−combustion capture and oxyfuel combustion are the three main approaches to capture CO_2.[5, 6] 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).[7, 8] 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.[5, 9]

Magnesium oxide (MgO) has been wildly considered as a type of promising candidate for CO_2 capture at intermediate temperatures (200−400 °C).[10, 11] The favorable adsorbents have appropriate basic strength and less waste with a rather high theoretical CO_2 capture capacity of 24.8 mmol g^{-1}.[8] However, the practical CO_2 capture performance of pure MgO is greatly restricted by low specific surface area, low kinetics, and poor thermal stability.[12] Therefore, many studies have been devoted to further improving the CO_2 capture capacity of MgO−based adsorbents, such as dispersing on porous supports,[13] and synthesizing mixed oxides,[14] etc. In recent years, there has been a rapid growth in fabrication of molten salts−modified MgO 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^{-1} in 2015,[15] there have been significant develops in this field. To make a better understanding about the rapid development of the molten salt promoted MgO 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 salt promoted MgO based materials. We hope this review paper will assist the development of the MgO−based adsorbents from fundamental research to practical applications.

2. CO_2 capture performance of molten salt promoted MgO adsorbents

Molten salts[16, 17], such as alkali metal nitrates, 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, etc.[18] In 2001, a U.S. patent describing alkali molten salts–promoted MgO-based adsorbents reported a broad capacity range of 1.1–12.9 mmol g^{-1} depending on the conditions of synthesis, with the highest regenerable capacity of 11 mmol g^{-1} obtained using pressure swing regeneration at 375 ^{o}C.[19] Since then, CO_2 capture using molten salts−modified MgO materials at intermediate temperatures has been demonstrated as a 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 three groups, which are (1) homogenous molten salt−modified MgO adsorbents, (2) molten salt−modified double salts−based MgO adsorbents, and (3) mixed molten salts−modified MgO 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.*[20] 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^{-1} at 325 ^{o}C. It is believed that the KNO_3 liquid interface with the capillaries inside the gel network leads to the surface tension force acting on the wall of the pores, which caused a substantial shrinkable owe to the collapse of the gel network and accumulation of the MgO particles.[21] They suggested that KNO_3 offered a liquid “channel” for fast CO_2 diffusion during the adsorption process.[20] Recently, Prashar *et al.*[22] 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 appears to be very fast with no induction period when the desorption process of CO_2 is incomplete.[22] Later on, Jo *et al.*[23] 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 $MgCO_3$.[23] Moreover, Zhang *et al*.[24] 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 $NaNO_3$. Figure 1(a) shows that the energy for the dissociated $[Mg^{2+}\ldots O^{2-}]$ intermediate decreased by 1.771 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 $[Mg^{2+}\ldots O^{2-}]$ 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 $[Mg^{2+}\ldots O^{2-}]$ to form $[Mg^{2+}\ldots CO_3{}^{2-}]$ and the precipitated $MgCO_3$ was away from the initial dissolution sites and would not inhibit the continuous reaction (Figure 1(b)).[24]

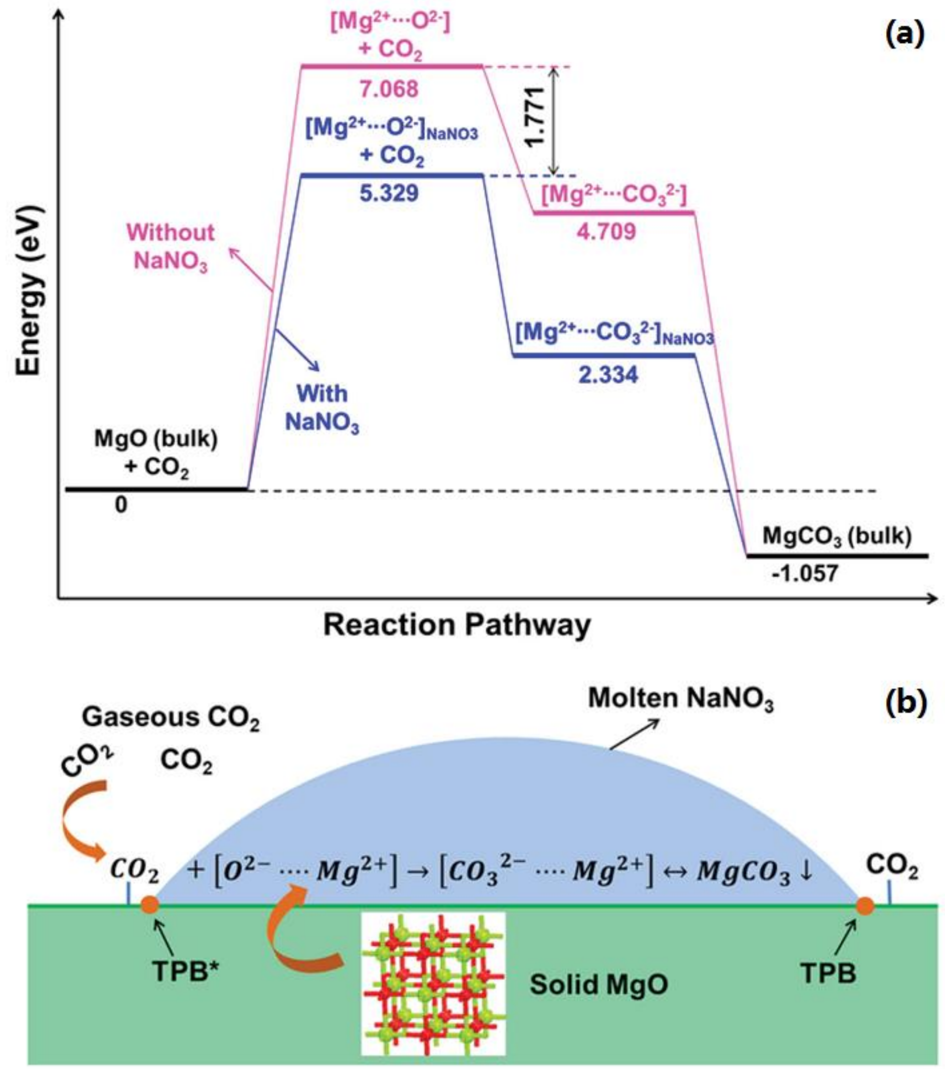

Figure 1. Proposed reaction mechanism. (a) Proposed Born–Haber cycles, showing the notable enthalpy difference for MgO dissociation in vacuum as compared to that in $NaNO_3$ with solvation effect; (b) Illustrative diagram for the phase transfer catalysis of CO_2 adsorption on MgO with molten $NaNO_3$ (* represents triple phase boundary). (Phase Transfer-Catalyzed Fast CO_2 Absorption by MgO-Based Absorbents with High Cycling Capacity)

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

Adsorbent	Molten salt	Method	CO_2 uptake	Reference
MgO	$LiNO_3$	Aerogel method	1.17 mmol g^{-1}, 325 ^{o}C, 1 bar	20
MgO	$LiNO_3$	Wet impregnation method	1.45 mmol g^{-1}, 300 ^{o}C, 1 bar	10
MgO	KNO_3	Wet impregnation method	0.2 mmol g^{-1}, 300 ^{o}C, 1 bar	10
MgO	KNO_3	Aerogel method	3.16 mmol g^{-1}, 325 ^{o}C, 1 bar	20
MgO	$NaNO_3$	Aerogel method	1.76 mmol g^{-1}, 325 ^{o}C, 1 bar	20
MgO	$NaNO_3$	Supercritical drying method	1.86 mmol g^{-1}, 325 ^{o}C, 1 bar	25
MgO	$NaNO_3$	Wet impregnation method	12.9 mmol g^{-1}, 300 ^{o}C, 1 bar	10

2.2 Molten salt−modified double salts−based MgO adsorbents

With the rapid growth in atmosphere CO_2 concentration, there is a growing demand for the further enhancement in CO_2 capture capacity. As the capture performance of homogeneous molten salt−modified MgO adsorbents fails to meet the requirements, recent researches have been focusing on the development of double salts−based MgO adsorbents with the introduction of carbonates. Carbonates commonly have a relatively higher melting temperature and the promotion effect is totally different from nitrates as the solid state (solid phase?) forms double salts system during the CO_2 capture process.

Double salts are salts containing more than one cation or anion, obtained by combing two different salts which are crystallized in the same regular ionic lattice. For instance, Xiao *et al.*[26] prepared K_2CO_3-MgO adsorbents via the wet mixing method. The adsorbent showed an excellent CO_2 capture capacity of 1.94 mmol g^{-1} at 375 ^{o}C when the ratio of Mg/K was fixed at 1:3. It has been found that a new phase of $K_2Mg(CO_3)_2$ was formed after CO_2 adsorption. Furthermore, Byun *et al.*[27] investigated the SEWGS reaction based on a K_2CO_3−MgO adsorbent. The mechanism of the CO_2 capture reaction is proposed to consist of fast hydration of K_2CO_3 and MgO, formation and decomposition of $KHCO_3$, and finally carbonation of $Mg(OH)_2$ to mainly form $MgCO_3$, as described in Figure 2. Acted as a carrying medium, K_2CO_3 promoted the penetration of water vapor and CO_2 into the dense $MgCO_3$ layer and further enhanced the CO_2 capture rate and capacity.[27]

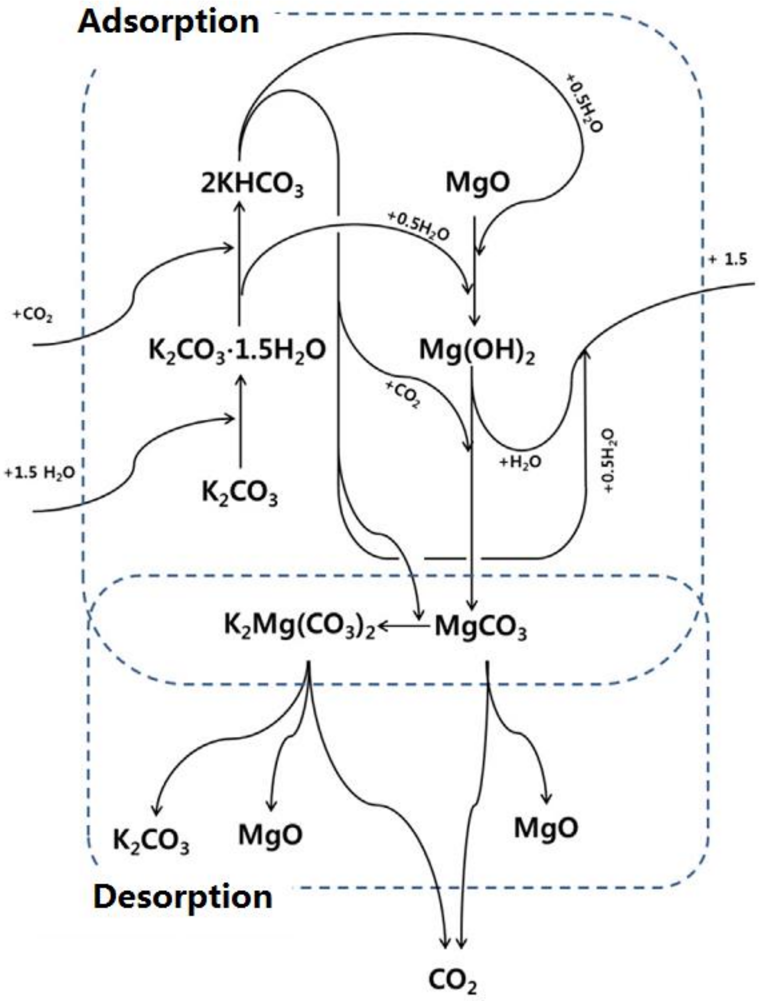

Figure 2. Proposed reaction mechanism for CO_2 sorption by the K−Mg−based sorbent.

(Novel method for investigation of a K-Mg-based CO_2 sorbent for sorption-enhanced water gas shift reaction)

Besides, Liu *et al*.[28] prepared Cs_2CO_3-doped MgO composites with highly dispersed cesium on the surface of MgO particles and yield a high CO_2 capture capacity of 1.9 mmol g^{-1} at 300 ^{o}C. As a reagent, the cesium dopant formed a mixed Mg-Cs carbonate phase alongside MgO and thus reduced the activation energy of the MgO carbonation reaction at moderate temperatures.[28] Moreover, Vogt *et al*.[29] solvothermally developed $CsCO_3$-doped MgO adsorbents with CO_2 capture capacity of 1.14 mmol g^{-1} at 370 ^{o}C. This more uniformed mixture with cesium and magnesium interspersed into the core of the particles accelerated the accumulation of active adsorption sites and led to a higher CO_2 capture performance.[29] Later on, a novel Na_2CO_3-MgO double salt was developed by Lee *et al*.[30] using a precipitation method in aqueous solution. The hexagonal plate shape of the synthesized Na-Mg double salt formed agglomerate clusters with plenty of cracks on their particle surfaces, which thus led to a high CO_2 capture capacity of 3.48 mmol g^{-1} at 375 ^{o}C with rather fast sorption and desorption kinetics. The in-situ X-ray diffraction analysis revealed that $Na_2Mg(CO_3)_2$ was formed during the reaction of CO_2 with MgO and Na_2CO_3.[30] To further investigate the promotion mechanism, Duan *et al*.[31] performed a comprehensive study on the M_2CO_3 (M = Na, K)−modified and $CaCO_3$−modified MgO composites via first-principles density functional theory complemented with lattice phenomenon calculations.[31] The results demonstrated that the maximum allowable CO_2 capture temperatures of the modified adsorbents are shifted to higher temperature ranges by forming double salts ($M_2Mg(CO_3)_2$ and $CaMg(CO_3)_2$).[31] Moreover, Lee *et al*.[32] fabricated MgO−based adsorbents with alkali-metal carbonates by impregnation method. The CO_2 capture capacity of the Na_2CO_3−promoted and K_2CO_3−promoted MgO composites were 0.22 mmol g^{-1} and 1.02 mmol g^{-1}, respectively. Additionally, we have summarized the double salts−based MgO adsorbents and their performances in Table 2.

Table 2. Summary of double salts−based MgO adsorbents and their performance for CO_2 capture.

Adsorbent	Molten salt	Method	CO_2 uptake	Reference
MgO	Li_2CO_3	Aerogel method	1.08 mmol g^{-1}, 325 °C, 1 bar	[20]
MgO	K_2CO_3	Wet mixing method	1.94 mmol g^{-1}, 375 °C, 1 bar	[26]
MgO	K_2CO_3	Aerogel method	0.85 mmol g^{-1}, 325 °C, 1 bar	[20]
MgO	K_2CO_3	Impregnation method	1.02 mmol g^{-1}, 300 °C, 1 bar	[32]
MgO	Cs_2CO_3	Wet impregnation method	1.90 mmol g^{-1}, 300 °C, 0.5 bar	[28]
MgO	Cs_2CO_3	Solvothermal approach	1.14 mmol g^{-1}, 370 °C, 1 bar	[29]
MgO	Na_2CO_3	Precipitation method	3.48 mmol g^{-1}, 375 °C, 1 bar	[30]
MgO	Na_2CO_3	Aerogel method	0.88 mmol g^{-1}, 325 °C, 1 bar	[20]
MgO	Na_2CO_3	Impregnation method	0.22 mmol g^{-1}, 300 °C, 1 bar	[32]
MgO	Na_2CO_3	Supercritical drying method	0.98 mmol g^{-1}, 325 °C, 1 bar	[25]

Later on, much exploration has been concentrating on the realization of combing both the double salts system and the molten salt promotion effect. For instance, Lee *et al.*[32] prepared MgO−based adsorbents modified with both Na_2CO_3 and $NaNO_3$. The binary molten salts-modified MgO composite possessed an excellent CO_2 capture capacity of 2.21 mmol g^{-1} at 200 °C. They found that the desorption temperature was decreased due to the eutectic reaction caused by the alkali−metal nitrates.[32] In addition, Zhang and coworkers[33] designed $NaNO_3$ promoted Na_2CO_3−MgO adsorbent with a CO_2 capture capacity of 3.40 mmol g^{-1} at 380 °C for intermediate temperature CO_2 removal. The reversible formation of the double salt $Na_2Mg(CO_3)_2$ during the CO_2 adsorption process decomposes into Na_2CO_3 and MgO after activation (Figure 3). They proposed that the retained Na_2CO_3 in the adsorbent enables to easily form again during subsequent capture process （修改一下）. And it is possible that $NaNO_3$ penetrates the product double salt grain boundaries and provides a liquid “channel” for fast CO_2 diffusion during adsorption process.[33]

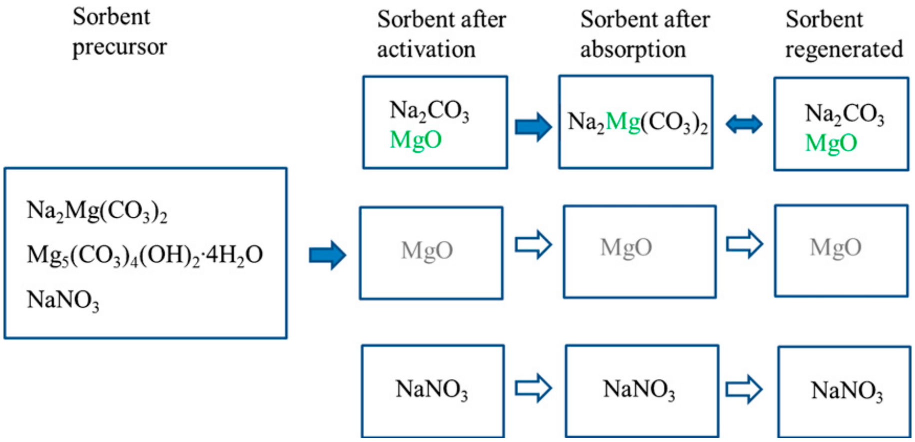

Figure 3. The illustration of the conversions of compounds involved in adsorption and desorption processes. (Roles of double salt formation and $NaNO_3$ in Na_2CO_3-promoted MgO adsorbent for intermediate temperature CO_2 removal)

Later on, Vu *et al.*[25] constructed MgO−Na_2CO_3−$NaNO_3$ compounds with a CO_2

capture capacity of 12.73 mmol g^{-1} at 325 ^{o}C for CO_2 capture at moderate temperatures. When the operating temperatures are fixed near the melting temperature of $NaNO_3$, it appears benefit for both the capture capacity and the adsorption rate. Figure 4 presents the CO_2 adsorption mechanism of $MgO{-}Na_2CO_3{-}NaNO_3$ composites which was governed by the formation of $Na_2Mg(CO_3)_2$ and $MgCO_3$. During the process, Na_2CO_3 functioned as the major CO_2 carrier and $NaNO_3$ worked as a reaction promoter to convert $Na_2Mg(CO_3)_2$ to $MgCO_3$ and $MgCO_3$ to MgO. Under wet conditions, the formation of $Mg(OH)_2$ gave rise to a fast adsorption rate and high CO_2 capture capacity which prevented the composite from stability reductions on account of cyclic phase transitions.[25]

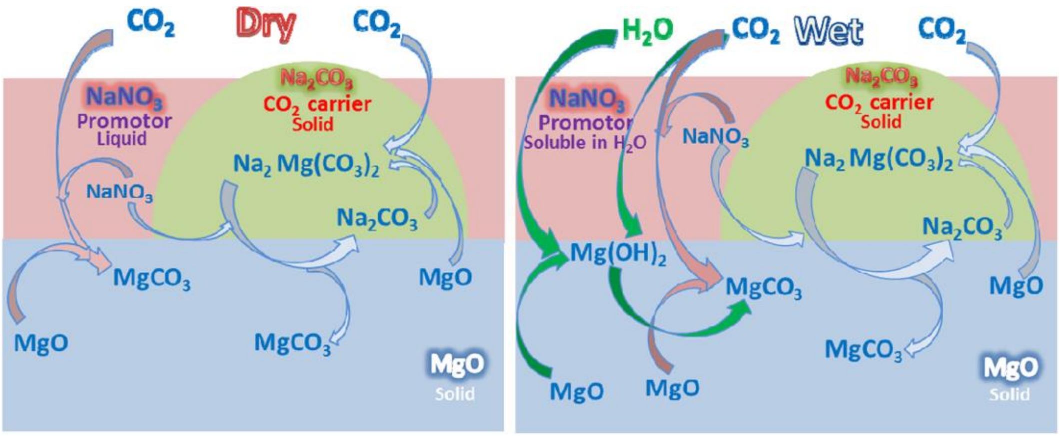

Figure 4. Sorption mechanism of $MgO{-}Na_2CO_3{-}NaNO_3$ under dry and wet gas mixtures at intermediate temperatures. (Double sodium salt-promoted mesoporous MgO sorbent with high CO_2 sorption capacity at intermediate temperatures under dry and wet conditions)

Furthermore, Zhang *et al.*[34] performed a systematical investigation on the double salt adsorbent materials containing MgO, carbonates and nitrates. As shown in Figure 4, MgO dissolves in the molten salt and generates solvated $[Mg^{2+}\ldots O^{2-}]$ ionic pairs, which have much weaker interaction than the strong Mg−O ionic bonds in bulk MgO. Carbonate partially dissolves in the molten salt in similar manner into ionic pairs. The solid reactants are transferred to a liquid medium with the dissolution of solid MgO and the carbonates. Premelting of the nitrates salt occurs in these systems, and thus CO_2 adsorption can take place at temperatures below the melting point of the salt additive.[34]

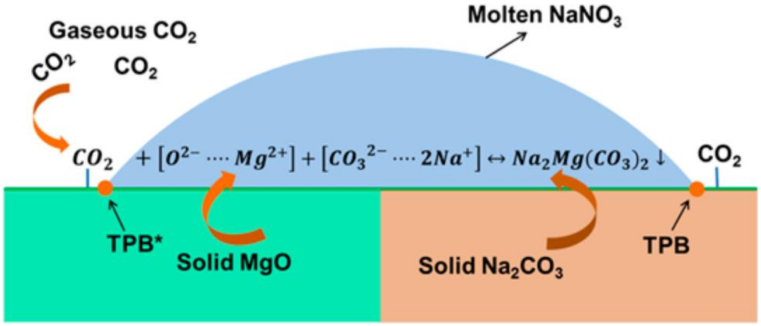

Figure 5. Conceptual diagram showing CO_2 adsorption and reaction with MgO in the presence of Na_2CO_3, with the formation of $MgNa_2(CO_3)_2$ double salt at the triple phase boundary. (Molten Salt Promoting Effect in Double Salt CO_2 Absorbents)

Moreover, Yang *et al.*[35] proposed that the molten $NaNO_3$ may provide a liquid channel for the diffusion of Mg^{2+} during the decomposition process of $MgCO_3$−$CaCO_3$ phase. Their studies demonstrated that the introduction of molten salt declines the decomposition temperature of $MgCO_3$, affects the crystal lattice of the activated adsorbents, and promotes the CO_2 capture performance by accelerating the ion diffusions.[35] In 2017, they performed another study on the promoting effects of $CaCO_3$ on the CO_2 capture capacity of $NaNO_3$−modified MgO adsorbents. The results indicated that alkali or alkali earth metal carbonates have the ability to shift the thermodynamic equilibrium temperature of the modified adsorbents to a higher temperature range and reduce the required equilibrium partial pressure of CO_2 at a certain temperature.[36] In addition, we have summarized the molten salt−modified double salts−based MgO adsorbents and their performance in Table 3.

Table 3. Summary of molten salt−modified double salts−based MgO adsorbents and their performance in CO_2 capture.

Adsorbent	Molten salt	Method	CO_2 uptake	Reference
MgO	Na_2CO_3−$NaNO_3$	Impregnation method	2.21 mmol g^{-1}, 300 °C, 1 bar	[32]
MgO	Na_2CO_3−$NaNO_3$	Precipitation method	3.4 mmol g^{-1}, 380 °C, 1 bar	[33]
MgO	Na_2CO_3−$NaNO_3$	Supercritical drying method	12.73 mmol g^{-1}, 325 °C, 1 bar	[25]
MgO	Na_2CO_3−$NaNO_3$	Ball milling method	3.91 mmol g^{-1}, 400 °C, 8th cycle	[34]
MgO	$CaCO_3$−$NaNO_3$	Ball milling method	4.41 mmol g^{-1}, 400 °C, 8th cycle	[34]
MgO	Na_2CO_3−$LiNO_3$	Ball milling method	4.02 mmol g^{-1}, 400 °C, 8th cycle	[34]
MgO	Na_2CO_3−KNO_3	Ball milling method	3.89 mmol g^{-1}, 400 °C, 8th cycle	[34]
MgO	K_2CO_3−$NaNO_3$	Ball milling method	1.91 mmol g^{-1}, 400 °C, 8th cycle	[34]

2.3 Mixed molten salts−modified MgO adsorbents

Mixed molten salts are considered as a promising medium for both heat transfer and energy storage in solar thermal power because of its many advantages such as large heat capacity, low vapor pressure, low cost, and wide range of temperature in application, etc.[18] Recent developments of mixed molten salts−modified MgO adsorbents have attracted much attention.

The difference in their promoting effect can be attributed to their different melting temperatures and different CO_2 solubility in these salts. The enhancement of CO_2 uptake by MgO particles due to the presence of the nitrates is facilitated at temperatures above the melting points of the nitrates through the dramatic increase of CO_2 solubility on phase transition from the solid to liquid state of the nitrates. In the case of KNO_3−coated MgO particles, the high melting point (=329 ^{o}C) of the nitrate salt result in the solid-state coating at the CO_2 adsorption temperature (=300 ^{o}C). Low CO_2 uptake rates by KNO_3−coated MgO particles may be resulted from the low solubility of CO_2 in the solid KNO_3. Furthermore, it is reported that the CO_2 solubility in molten alkali metal nitrates increases as the ionic radius of the alkali metal cations decreases.[37, 38]

As a typical example, Harada *et al.*[39] fabricated regenerable MgO−based CO_2 adsorbent promoted with mixed molten alkali metal nitrates with high capacity of 10.2 mmol g^{-1} at 300 ^{o}C. The CO_2 uptake by the mixed molten salts−modified MgO materials started from the formation of unidentate carbonates on the MgO surfaces, followed by nucleation of $MgCO_3$ crystals and subsequent growth of these nuclei, and ended with the growth of $MgCO_3$ layers that controlled by the diffusion in the product layer, as presented in Figure 5. It is reasonable to suspect that the dissolution of CO_2 proceeds faster in (Li−Na−K)NO_3 which may induce the highest supersaturation of carbonate ions, and hence to the highest dimensional nucleation and nuclei growth of $MgCO_3$. They suggested that the molten alkali metal nitrates are shown to prevent the formation of a rigid, CO_2−impermeable, unidentate carbonate layer on the surfaces of the MgO particles, and promote the rapid generation of carbonate ions to allow the high rate of CO_2 uptake. It has also been reported that the dissociation of carbonates is accelerated in molten alkali metal nitrates by the favorable solvation of the oxide ion.[40] The molten nitrates may also facilitate the rapid decomposition of $MgCO_3$ at low temperatures, allowing regeneration of the particles without agglomeration, and concomitant excellent cyclic regenerability of these samples.[39]

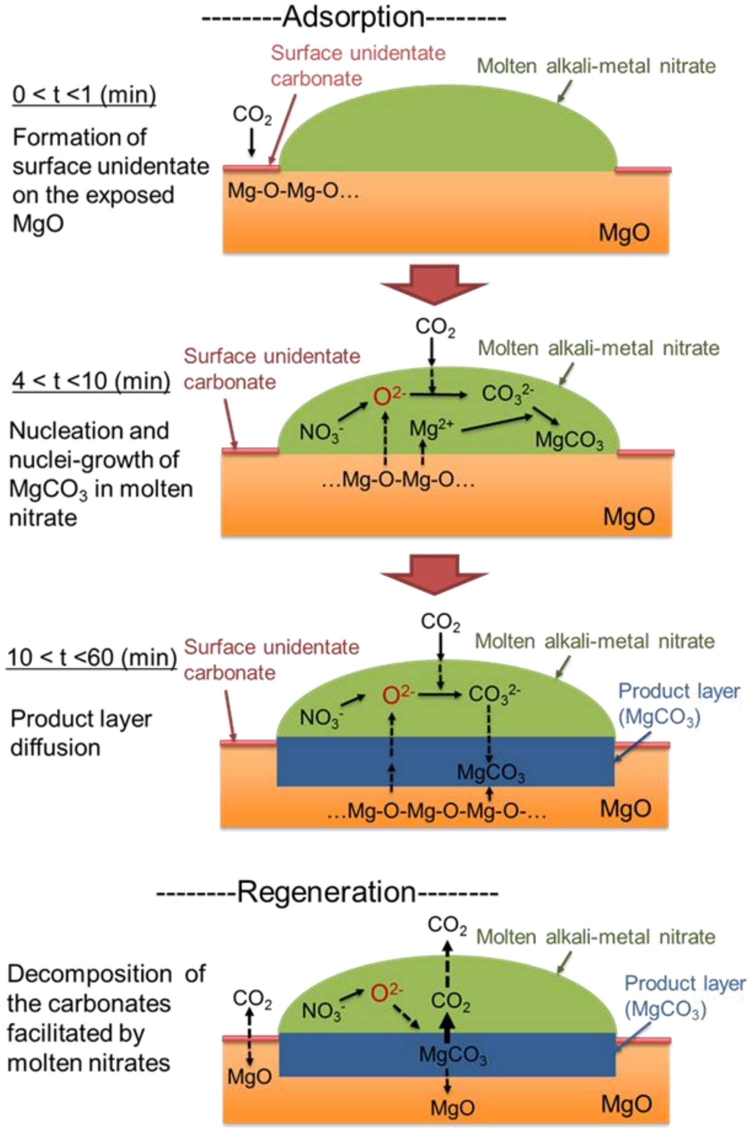

Figure 5. Schematic illustration of the possible reaction occurred in molten alkali−metal nitrate coated MgO. (Alkali metal nitrate-promoted high-capacity MgO adsorbents for regenerable CO_2 capture at moderate temperatures)

As colloidal nanoclusters of metal oxides constitute a promising class of building blocks for a range of advanced functional materials, the same group[15] subsequently proposed a method on the synthesis of colloidal nanoclusters of MgO coated with mixed molten salts. The adsorbent was prepared by a novel non−hydrolytic sol−gel reaction followed by the deposition of alkali metal salts via methanol evaporation−induced surface precipitation, as summarized in Figure 6. The CO_2 uptake of the $LiNO_3$−(Na−K)NO_2 coated MgO sample exceeded 11.7 mmol g^{-1} in 30 min at 340 °C and reached 15.7 mmol g^{-1} in 4 h. Colloidal nanoclusters possessing multiple inner grain boundaries and rough surfaces allowed for a dramatic increase in active surface area of MgO coated with thin layers of alkali metal salts, and enabled the rapid conversion of MgO to $MgCO_3$ with high conversion ratio. The CO_2 adsorption process occurs by the initial dissolution of CO_2 in the coating salt layer in the molten state at the operating temperature for CO_2 adsorption.[37, 38, 41] MgO is also dissolved partially to generate Mg^{2+} and O^{2-} ions in the molten salt coating layers.[42] Subsequently, the dissolved CO_2 reacts with O^{2-} to generate the carbonate ions (CO_3^{2-}) in the salt layer. The concentration of the carbonate ions increases gradually, and when it exceeds a threshold required for the nucleation and growth of the crystals of $MgCO_3$, the uptake increases at an accelerating rate.[43] The uptake rate eventually slows, and does so until the adsorption capacity eventually reaches a constant value without further degradation. The decelerating trend caused by the lowering of the overall reaction rate, is controlled by the diffusion of oxygen anions and carbonate ions through the pre−generated $MgCO_3$ layers.[39, 44] The introduction of mixed molten salts shortens the lag time to the initial increase in uptake, accelerates the uptake rate and elevates the plateau value. The enhancement in uptake loadings may be correlate with the variations in the critical thickness of the product layers.

The surface species on mixed molten salts−modified MgO materials may trigger the generation of defect or grain boundaries in the product layer and increase the critical thickness. They also discovered that the CO_2 uptake and the regenerability of the adsorbents can be enhanced by mixed nitrite salts to the coating layer through the formation of magnesium nitro or nitrate species, which increased the critical thickness of product layers and mitigated the degradation of nanoclusters over the repeated sorption/desorption cycles. (这句话太长了，修改成 2 句吧，更易读些)

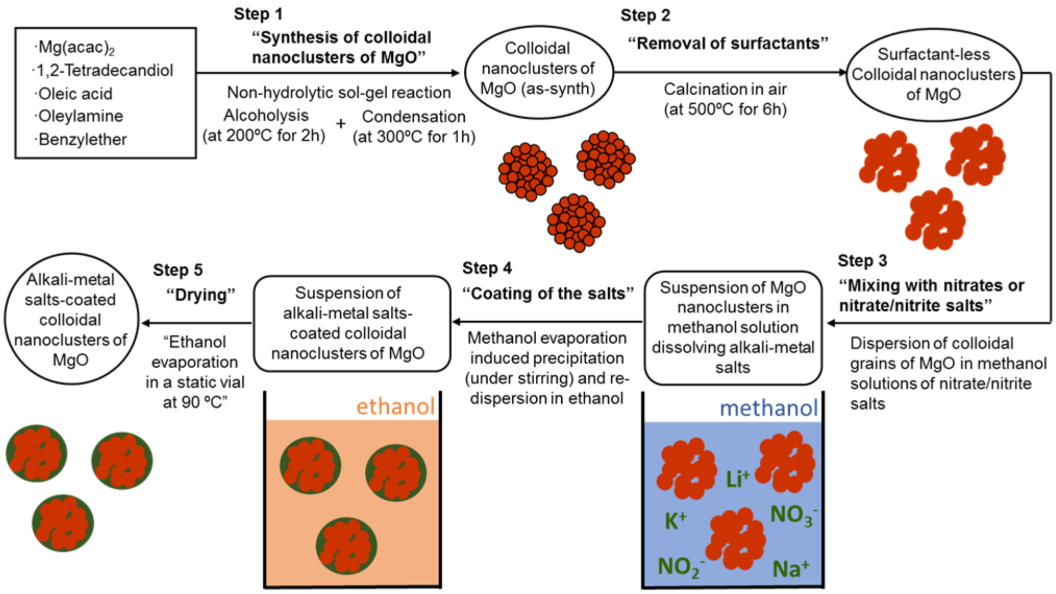

Figure 6. Procedure for the preparation of colloidal nanoclusters of MgO coated with alkali metal nitrates or nitrate/nitrites mixtures. (Molten Salt Promoting Effect in Double Salt CO_2 Absorbents)

Based on the progress mentioned above, Qiao *et al.*[10] optimized the ratio of Li/Na/K nitrates and the loading of the molten salt mixture on the MgO particles in particular, and further evaluated the influence of calcination and adsorption temperatures. Remarkably, the commercial MgO sample doped with 10 mol% $(Li_{0.3}Na_{0.6}K_{0.1})NO_3$ possessing the highest CO_2 uptake (up to 16.75 mmol g^{-1}) is the highest value reported for MgO based adsorbents in literature. Comparison of the CO_2 uptake between neat MgO and 10 mol % $(Li_{0.3}Na_{0.6}K_{0.1})NO_3 \cdot MgO$ adsorbents is shown in Figure 7. Besides, the preparation method of the mixed molten salts−modified MgO adsorbents and their performance in CO_2 capture are summarized and listed in Table 4.

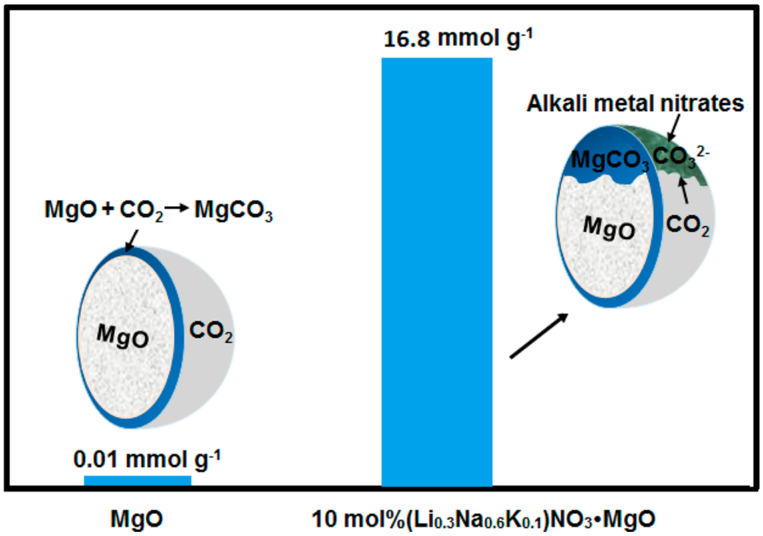

Figure 7. Comparison of the CO_2 uptake between neat MgO and 10 mol % $(Li_{0.3}Na_{0.6}K_{0.1})NO_3 \cdot MgO$ adsorbents. (Alkali Nitrates Molten Salt Modified Commercial MgO for Intermediate-Temperature CO_2 Capture: Optimization of the Li/Na/K Ratio)

Table 4. Summary of mixed molten salts−modified MgO adsorbents and their performance in CO_2 capture.

Adsorbent	Molten salts	Method	CO_2 uptake	Reference
MgO	$(Li{-}Na{-}K)NO_3$	Co-calcination method	10.2 mmol g^{-1}, 300 °C, 1 bar	39

MgO	$LiNO_3$−(Na−K)NO_2	Non−hydrolytic sol−gel reaction method	15.7 mmol g^{-1}, 340 °C, 1 bar	15
MgO	(Li−Na−K)NO_3	Wet impregnation method	16.8 mmol g^{-1}, 300 °C, 1 bar	10

3. Conclusions and Prospects

In this work, the most recent research progress in molten salts−modified MgO adsorbents for CO_2 capture at intermediate temperatures has been thoroughly reviewed. All the molten salts−modified MgO adsorbents are divided into three groups, which include homogenous molten salt−modified MgO adsorbents, molten salt−modified double salts−based MgO adsorbents, and mixed molten salts−modified MgO adsorbents. The first group uses single alkali nitrates as additive, such as $LiNO_3$, KNO_3 and $NaNO_3$. Among them, the $NaNO_3$−MgO sample fabricated through a wet impregnation method possessed the highest CO_2 capture capacity of 12.9 mmol g^{-1} at 300 °C. For second group, we first introduced the double salt formation system with the addition of carbonates, including Li_2CO_3, K_2CO_3, Na_2CO_3, Cs_2CO_3, and $CaCO_3$, etc. Among them, the Na_2CO_3−MgO sample synthesized by a precipitation method exhibited the highest CO_2 capture capacity of 3.48 mmol g^{-1} at 375 °C. For both the carbonates and the nitrates show good potential to improve the CO_2 capture performance, molten salt−modified double salts schemes have been subsequently developed, such as Na_2CO_3−$NaNO_3$, $CaCO_3$−$NaNO_3$, Na_2CO_3−$LiNO_3$, Na_2CO_3−KNO_3, and K_2CO_3−$NaNO_3$, etc. In particular, the Na_2CO_3−$NaNO_3$ modified MgO sample synthesized by a supercritical drying method exhibited the highest CO_2 capture capacity of 12.73 mmol g^{-1} at 325 °C. It is believed that Na_2CO_3 functioned as the major CO_2 carrier and $NaNO_3$ acted as a reaction promoter to convert the intermediate $Na_2Mg(CO_3)_2$ to $MgCO_3$ and $MgCO_3$ to MgO during the adsorption/desorption process.

Additionally, much efforts have been directed towards further enhancing their capture capacity, thermal stability, regenerability, kinetics, etc. Therefore, mixed molten salts−modified MgO adsorbents have been reported to exhibit rather high CO_2 capture capacity of 10.2 mmol g^{-1} at 300 °C. With further optimization of the ratio of Li/Na/K nitrates and the loading of the molten salt mixture on the MgO particles, the commercial MgO sample doped with 10 mol% $(Li_{0.3}Na_{0.6}K_{0.1})NO_3$ showed the highest CO_2 uptake of 16.75 mmol g^{-1}, which is the highest value ever reported for MgO based adsorbents in literature.

Overall, molten salts−modified MgO adsorbents have enjoyed an extended development prospect in CO_2 capture process at intermediate temperatures. Many studies have been dedicated to pushing the application of molten salts−modified MgO adsorbents in real technologies to meet the urgent needs for CO_2 capture. In 2017, Hu *et al.*[45] studied the pelletization of molten salts−modified MgO−based adsorbents using an extrusion−spheronization method. The prepared pellets have splendid mechanical properties which are good for the fluidization in CFBC (Circulating Fluidized Bed Combustion) for the practical applications. The excellent compression, crushing strength and superior attrition resistance of the pellets make it possible for the molten salts−modified MgO−based adsorbents to be applied in the long−term circulation in a fluidized bed. Given that the fabricated molten salts−modified MgO adsorbents exhibit excellent performance for CO_2 capture applications, another promising future direction is to further improve the regenerability of the adsorbents. As the observed decay in CO_2 uptake could be correlated with textural and crystal agglomeration during phase transitional cyclic operation, much effort should be made to overcome the drawbacks. Meanwhile, the mechanisms of the promotion effect by molten salts have not yet been realized.

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