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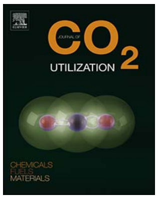

Review article

CaO-based CO_2 sorbents: A review on screening, enhancement, cyclic stability, regeneration and kinetics modelling

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ABSTRACT

This article reviews current developments in metal-based sorbents for carbon capture with emphasis on calcium oxide. A broad overview of carbon dioxide capture with metals in various forms including oxides, hydroxides, carbonates and zirconates is presented. Based on the findings from comparative assessments of these sorbents, CaO appears to be the best solid sorbent for CO_2 capture at high temperatures, and its numerous advantages are discussed in this work. For this reason, a detailed review has been conducted for calcium oxide, which works as a sorbent at temperatures up to 700 °C through carbonation, and desorbs CO_2 above 700 °C by calcination of $CaCO_3$ at atmospheric pressure. A review of studies on kinetics modelling of CO_2 capture with CaO-based sorbents is also included in this work. Decay in activity caused by sintering and attrition is identified as the greatest challenge with CaO-based sorbents. This work also focuses on the available techniques for enhancing performance and cyclic stability. Reactivation of the sorbents by hydration and reduction in decay rate by doping with inert supports and synthetic sorbents are reviewed. Additionally, the use of biomass resources (waste animal shells) as competitive sources of $CaCO_3$ is discussed in this work. The review concludes with recommendations for future studies in carbon capture and sequestration.

1. Introduction

The world is witnessing a rapid growth in population and energy consumption, and is faced with the responsibility of minimizing greenhouse gas emissions. There is a consensus in the scientific world that climate change is a serious issue, with CO_2 emission being one of the prime contributors. This has led to international policies and agreements like the Kyoto protocol and the Copenhagen Accord [1]. Fossil-fuelled power plants are major contributors among anthropogenic sources of CO_2 emissions. Power plants account for more than 33% of the total CO_2 emission globally [2,3], and a coal-powered 500-MW plant can generate approximately 3 million tons/year of CO_2 [4,5]. Although alternative energy sources do not contribute to carbon emissions directly, they are intermittent sources of energy. Furthermore, hydrogen is still considered as fuel for the future and currently, it is produced mostly from fossil fuels, which contributes to CO_2 emissions. It, therefore, appears that fossil fuels are likely to remain as the major source of energy for mankind for the time being [6]. As research progresses on how to shift attention from fossil fuels, carbon capture technologies enable continual usage of fossil fuels, while decreasing CO_2 emission, and thus mitigating climate change. Reduction in CO_2 emission may be achieved in three ways: reduction of energy consumption through the use of energy efficient systems, reduction in carbon intensity by the application of alternative energy sources, and reduction in emission by carbon capture and sequestration (CCS) technologies [7].

Considering their cost-effective performance in reducing carbon emissions, CCS technologies have received significant attention in recent times. The most common industrial technology for CO_2 capture from gas streams is amine-based absorption. However, it is limited to low temperature (40–150 °C) applications [8], requires significant cost and high energy for regeneration [9,10], is susceptible to equipment corrosion and may produce a hazardous waste stream [11]. Although microporous and mesoporous materials like activated carbon, zeolite, and carbon fibre can also capture CO_2 at low temperatures, they are ineffective above 300 °C [12,13]. This limits their applications in processes like gasification for syngas/hydrogen production, where the effluent gases can be more than 500 °C. The use of activated carbon and zeolite, in that case, may require cooling and additional costs. This limitation of application at high temperatures can be solved with the use of alkaline metal-based sorbents for CO_2 capture. Hydrotalcite-like compounds (HTLC) can also be used for CO_2 sorption. Nonetheless,

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their sorption capacities are low [14,15], as compared to alkaline metal-based sorbents.

In this work, an in-depth review is carried out on metal-based sorbents. The work includes a broad overview of metallic sorbents. CO_2 capture, enhancement, and regeneration of CaO-based sorbents are examined in detail, with interest in sorption in combustion and gasification processes. A good sorbent should have certain properties including high CO_2 capture capacity; stability and durability after repeated cycles; good attrition resistance and mechanical strength; good kinetics for CO_2 sorption; availability; competitive cost; and ease of regeneration [12,13,16]. These factors make CaO a good sorbent for CO_2 capture and therefore deserving of special attention in this review.

2. Metal-based sorbents

Metal-based sorbents have been extensively studied for CO_2 capture. They could be in the form of oxides, hydroxides, carbonates, zirconates, bicarbonates, and these salts may occur as hydrates or unhydrates. Some of them are efficient at the pre-combustion carbon capture stage, while others perform better in the post-combustion stage. The use of metal-based sorbents just like other capture technologies is, therefore, dependent on the system for which they are applied. The most widely used forms of metal-based sorbents are oxides and hydroxides. These materials serve as CO_2 sorbents by forming their respective carbonate after undergoing an exothermic reaction with CO_2 at favourable carbonation temperatures specific for each metal. For a metal M, such a reaction with CO_2 can be represented with the expressions in Eqs. (1) and (2).

$$M_a\,O + CO_2 \rightarrow M_aCO_3 \tag{1}$$

$$M(OH)_b + CO_2 \rightarrow M_cCO_3 + H_2O \tag{2}$$

Where, a and c are 1 for alkaline earth metals and 2 for alkali metals, and b = 1 for alkali metals and 2 for alkaline earth metals.

At higher temperatures, the carbonates formed can decompose to form their initial metal-based sorbent by releasing the absorbed CO_2. The decomposition process makes the materials available for further carbonation conversion in a multicycle carbon capture of combustion or gasification processes. In the context of biomass gasification, the carbonation conversion has an additional advantage of enhancing cleaner syngas production through tar removal. This is because the formation of carbonates is exothermic, and in that case, heat is released to the surroundings. The released heat increases the temperature in the gasifier; consequently, the rise in temperature leads to a further tar cracking and a cleaner gas production [17,18].

Metallic oxides have high surface basic sites and, for that reason, they can easily react with CO_2, which is acidic in nature. The factors affecting the degree and rate of CO_2 uptake of metallic oxides can be classified into two categories: (1) the physicochemical properties of the sorbent like presence of additives and water content, and (2) environmental conditions like temperature, pressure, residence time, and initial CO_2 concentration [19,20]. Metallic oxides, especially CaO and MgO, have the capacity to absorb CO_2 at temperatures above 300 °C. The screening of several metal-based sorbents including 11 oxides and 2 carbonates was done by Feng et al. [21]. Their results showed that although Na_2O and K_2O have good capture capacity even above 927 °C, regeneration of the oxides occurs at high temperatures, leading to increasing energy demands as shown in Table 1. Hence, they cannot be considered as excellent sorbents. FeO is also unsuitable due to its poor regeneration property. $FeCO_3$, which is formed after FeO absorbs CO_2, decomposes to Fe_3O_4 at high temperatures. CaO, MnO, MgO and PbO appear to be good materials due to their high sorption capacities and ease of regeneration. The theoretical CO_2 capture capacity of some metal oxides and their regeneration energy are presented in Table 1.

Table 1
Theoretical CO_2 capture and regeneration energy of some metal oxides [21].

Metal oxides	Density (g/cm^3)	Theoretical capacity (g of CO_2/g of sorbent)	Regeneration energy (kJ/g of CO_2)
Ag_2O	7.14	0.189	1.865
BaO	5.72	0.287	6.081
CaO	2.62	0.785	4.042
Cs_2O	4.36	0.156	9.279
K_2O	2.32	0.468	8.895
Li_2O	2.01	1.471	5.146
MgO	3.65	1.092	2.681
Na_2O	2.27	0.709	7.309
Rb_2O	3.72	0.235	9.172
SrO	4.70	0.425	5.249
ZnO	5.47	0.540	1.616

The CO_2 sorption and thermodynamic properties of many metal-based sorbents including oxides and zirconates were also presented in the work of Kumar and Saxena [12]. A pictorial representation of their results is depicted in Fig. 1. It can be seen from the figure that several of the metal-based sorbents have good thermodynamic properties and theoretical CO_2 sorption capacity. However, other factors like regeneration, kinetics, cost, availability, durability and reversibility should also be considered in the selection of a suitable sorbent.

2.1. Alkali metal-based sorbents and support for other sorbents

As far as metal-based CO_2 sorption is concerned, alkali metal-derived sorbents are among the most promising technologies. There is an increase in the affinity for CO_2 by alkali metals from lithium to caesium, with increasing atomic radii and electropositivity in the following order: Cs > Rb > K > Na > Li [22]. This is caused by the improvement in the basicity for CO_2 with an increase in the ionic radii of the elements. According to the results of Reddy and Smirniotis [22], the most electropositive of them, caesium, exhibited the best performance, where CaO doped with Cs demonstrated the highest sorption as compared to CaO doped with the same weight fraction of the other alkali metals. This high sorption is because of the superior basic characteristics of Cs as compared to the other alkali metals. However, the use of caesium as a support material may not be cost-effective due to its relatively high price. Also, the use of Cs_2O as an independent sorbent is limited by its very high regeneration temperature requirement [21]. Li_2O is good for CO_2 capture, but it is not an effective sorbent in multiple cycles. This ineffectiveness is because the decomposition of its carbonate occurs at low CO_2 pressures and/or very high temperatures when Li_2CO_3 is in its liquid phase [23].

Each metal-based sorbent has its equilibrium temperature and pressure at which CO_2 uptake is favourable. An important concept, turnover (maximum) temperature, has been described in previous investigations [12,24,25]. The turnover temperature is the temperature above which the pressure of CO_2 exceeds the pressure in the gas stream from which CO_2 is to be captured [24]. Above this temperature, the sorbent will be unable to capture CO_2, but rather will begin to decompose. An appropriate sorbent is expected to capture CO_2 from a gas stream within the temperature and pressure ranges required for a specific application. For instance, in a pre-combustion process, the temperature typically ranges from 300 − 350 °C, and the gas stream comprises primarily CO_2, H_2O and H_2 at a high pressure (2000–2500 kPa). On the other hand, gases in post-combustion technology are mainly CO_2 and N_2, and are at lower pressures (around 10–20 kPa) and lower temperatures (< 200 °C) [12,24,26]. The maximum temperatures at which alkali metal-based sorbents can capture CO_2 are presented in Table 2, where the partial pressures of CO_2 are 10 and 2000 kPa for the post- and pre-combustion applications respectively. In the table, cases where the temperatures are higher than the maximum temperature of 1500 K are shown [24]. In considering the application of sorbents in a gasification process, where CO_2 capture is pre-combustion, it can be deduced from the turnover temperatures of