

**EFFECTS OF SYNTHESIS METHODS AND
PARAMETERS ON SODIUM ZIRCONATE FOR
HIGH-TEMPERATURE CO₂ SORPTION**

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**EFFECTS OF SYNTHESIS METHODS AND
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HIGH-TEMPERATURE CO₂ SORPTION**

by

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LIST OF SYMBOLS

Δ	heat-treated reaction
ΔH_f	enthalpy of formation
θ	theta
(P/P_o)	relative partial pressure
E_a	activation energy
P_{CO_2}	CO ₂ partial pressure
T	temperature

LIST OF ABBREVIATIONS

AC	activated carbon
APTS	3-aminopropyl-triethoxysilane
aq	aqueous
BET	Brunauer-Emmett-Teller
CA	citric acid/citrate
ca.	approximately/calculated
CNTs	carbon nanotubes
CTAB	cetyl trimethylammonium bromide
DI water	deionized water
DSC	differential scanning calorimetry
EG	ethylene glycol
FTIR	Fourier transform infrared
GHG	greenhouse gas
HTC	hydrotalcite
ICDD	International Centre for Diffraction Data
IEA	International Energy Agency
IPCC	International Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
LDH	layered double hydroxide
MNRE	Ministry of Natural Resources and Environment
MOFs	metal organic frameworks
MS	mass spectrometry
NaCA	trisodium citrate
PSA	pressure swing adsorption
RDS	rate determining step
SEM	scanning electron microscope/microscopy
SESMR	sorption enhanced steam methane reaction
TGA	thermogravimetric analyser/analysis

TSA	temperature/thermal swing adsorption
XRD	X-ray diffraction/diffractometer

KESAN-KESAN PENGUBAHAN KAEDAH DAN PARAMETER SINTESIS TERHADAP NATRIUM ZIRKONAT UNTUK PENJERAPAN CO₂ BERSUHU TINGGI

ABSTRAK

Pemacaran karbon dioksida (CO₂) ialah antara punca-punca pemanasan sejagat. Penangkapan CO₂ secara penjerapan CO₂ telah menjadi salah satu kaedah untuk mengurangkan pemancaran CO₂. Tambahan pula, penjerap yang bercekapan tinggi diperlukan untuk penangkapan CO₂ bersuhu tinggi daripada proses-proses industri hibrid. Natrium zirkonat (Na₂ZrO₃) ialah salah satu bahan penjerap pepejal yang berpotensi dan mempunyai prestasi penjerapan berkisar CO₂ yang tinggi dan stabil, tetapi kapasiti jerapan CO₂ yang lebih dekat dengan kapasiti unggul masih dikehendaki. Tambahan pula, kesan-kesan metodologi yang berbeza terhadap prestasi penangkapan CO₂ dengan penjerap ini belum dilaporkan dalam kajian-kajian terdahulu. Tujuan utama penyelidikan ini ialah menambah baik sintesis dan oleh itu kapasiti jerapan CO₂ untuk penjerapan CO₂ bersuhu tinggi dengan bahan penjerap Na₂ZrO₃. Kesan-kesan keadaan pengkarbonatan dan pengkalsinan, prekursor natrium (Na) yang berbeza dan penambahan asid sitrik (CA) dan etilena glikol (EG) terhadap Na₂ZrO₃ yang disintesis dan oleh itu prestasi penjerapan CO₂ bersuhu tinggi telah disiasat. Ujian pencirian dan prestasi penjerapan CO₂ terhadap sampel-sampel ini dilakukan melalui analisis termogravimetri, pembelauan sinar-X, penjerapan N₂ dan SEM. Semua parameter-parameter tersebut memberi kesan-kesan yang ketara terhadap prestasi penjerapan CO₂ untuk bahan penjerap Na₂ZrO₃ yang disediakan. Kegunaan prekursor Na yang berbeza dan suhu penjerapan CO₂ mempengaruhi kapasiti penjerapan CO₂ sampel-sampel itu. Keadaan kalsinasi yang berbeza juga memperangui ketulenan bahan penjerap Na₂ZrO₃. Penambahan CA dan EG menghasilkan bahan penjerap Na₂ZrO₃ yang lebih tulen, mempunyai morfologi yang lebih berliang dan oleh itu kestabilan penajaan semula penjerap ini yang lebih baik daripada sampel yang disediakan tanpa penambahan CA dan EG. 4.902 mmol/g Na₂ZrO₃, iaitu kapasiti penjerapan CO₂ yang terbaik, telah dicapai

pada suhu pengkarbonatan 550 °C untuk sampel yang disintesis dengan natrium sitrat sebagai prekursor Na serta menggunakan CA dan EG dengan nisbah molar 2:1, dan dikalsin pada 900 °C selama 4 h. Oleh itu, penjerap ini adalah sesuai untuk penangkapan CO₂ bersuhu tinggi. Ujian keberangkapan di bawah keadaan perindustrian untuk bahan penjerap Na₂ZrO₃ ini yang telah bertambah baik adalah dicadangkan.

EFFECTS OF SYNTHESIS METHODS AND PARAMETERS ON SODIUM ZIRCONATE FOR HIGH-TEMPERATURE CO₂ SORPTION

ABSTRACT

Carbon dioxide (CO₂) emission is among the causes of global warming. CO₂ capture by CO₂ adsorption has been one of the methods to reduce CO₂ emission. Moreover, an adsorbent with high efficiency is needed for high-temperature CO₂ capture from industrial hybrid processes. Sodium zirconate (Na₂ZrO₃) is one of the potential solid sorbents with high and stable cyclic CO₂ sorption performance, but CO₂ adsorption capacity closer to its ideal capacity is still desired. Furthermore, the effects of different methodologies on its CO₂ capture performance were not reported previously. The main aim of this research work is to improve the synthesis and thus CO₂ capture capacity of Na₂ZrO₃ for high-temperature CO₂ sorption. Effects of carbonation and calcination conditions, different sodium (Na) precursors, and addition of citric acid (CA) and ethylene glycol (EG) on high-temperature CO₂ sorption performance of synthesised Na₂ZrO₃ were investigated. Characterisation and CO₂ sorption performance of samples were tested using thermogravimetric analysis, X-ray diffraction, N₂ adsorption and SEM. All the above-mentioned parameters significantly affect the CO₂ adsorption performances of the prepared Na₂ZrO₃ sorbents. The use of different Na precursor and CO₂ adsorption temperature influenced the CO₂ adsorption capacity of the samples. Different calcination conditions also affected the purity of Na₂ZrO₃. Addition of CA and EG resulted in producing purer Na₂ZrO₃ with more porous morphology and hence better regeneration stability than the sample prepared without the addition of CA and EG. The best CO₂ adsorption capacity of 4.902 mmol CO₂/g Na₂ZrO₃ was achieved at carbonation temperature of 550 °C, for the sample synthesised with sodium citrate as the Na precursor and CA:EG molar ratio of 2:1, and calcined at 900 °C for 4 h. Hence, this sorbent is suitable for high-temperature CO₂ capture. It is recommended to test the functionality of this improved Na₂ZrO₃ sorbent under industrial conditions.

CHAPTER 1

INTRODUCTION

1.1 Carbon dioxide and its emission

Carbon dioxide (CO₂) is one of the gases present in the atmosphere. It is an important source for photosynthesis and production of useful chemicals, for example cyclic carbonates and organic carbonates (Ma, *et. al.*, 2009; MacDowell *et. al.*, 2010). This gas is produced from natural activities such as respiration of human beings and animals, and anthropogenic sources such as combustion of petroleum and manufacturing industries with CO₂ as one of the secondary products.

CO₂ takes up approximately 0.03% of the total air composition, but this composition has been varying since the Industrial Revolution in mid-18th century due to increasing industrial and human-related activities and thus increasing energy generation from fossil fuel combustion (Wilcox, 2012; Hartmann *et. al.*, 2013). Continuous large emissions of CO₂, which is also a greenhouse gas (GHG), have led to global warming. The International Energy Agency (IEA) reported that global CO₂ emissions reached 31734 million tonnes in the year 2012, which was the last reported year and the highest among all the reported years by IEA (IEA, 2014). The seriousness of the negative impacts of global warming on climate change have led governments, environmental bodies and researchers to put in extra efforts and investigate ways of reducing CO₂ emissions and consequently mitigating GHG effects, namely, melting of glaciers and natural disasters such as drought and floods.

1.2 Current technologies for CO₂ capture

Various solutions have been considered to combat the problems of increasing CO₂ emissions. One of these solutions is CO₂ capture which works on the simple concept of CO₂ sorption from flue gas and other production sources before its emission to the atmosphere. The captured CO₂ will then be desorbed from the sorbents before the gas is either used as a feedstock for conversion to useful raw materials like urea and carbon-based fuels such as methanol and methane, or sequestered in depleted oil and gas reservoirs (Ma *et. al.*, 2009; MacDowell *et. al.*, 2010).

Several methods for CO₂ capture have been studied to reduce CO₂ concentration in waste gas emissions and thus combat the issues of global warming. These methods include CO₂ sorption by amine-based solvent stripping, membrane separation, cryogenic distillation and oxyfuel combustion. These methods have been applied in industrial applications, generally, for feasible reasons such as low operation costs and the removal of CO₂ gas with high purity. However, the presence of impurities such as moisture, NO_x and SO_x gases in the gas stream and fluctuating process conditions lead to corrosion of equipment and deterioration of the medium used for the separation of CO₂ from the gas stream. Besides that, the CO₂ selectivity of these separation processes is still considerably low. The temperature range used for CO₂ absorption and membrane separation is limited to below 500 °C to prevent deterioration of the solvent and membrane respectively (Aaron and Tsouris, 2005; Yang *et. al.*, 2008; Nair *et. at.*, 2009; MacDowell *et. al.*, 2010; Pires *et. al.*, 2011; Wilcox, 2012).

1.3 CO₂ capture by solid-based adsorbents

In addition to the methods as mentioned above, CO₂ capture using solid adsorbents has also been used in several industrial applications such as post-combustion flue gas cleaning and pre-combustion hydrogen gas (H₂) production by sorption enhanced steam methane reaction

(SESMR). Some of the reasons are the lower requirements of energy usage, operating costs, and equipment, and higher and wider operating temperature range from ambient temperature to about 700 °C than the above-mentioned technologies. Furthermore, generation of liquid wastes can be avoided and spent adsorbents can be discarded without environmental concerns (Harrison, 2005; Ochoa-Fernández *et. al.*, 2007; Hao *et. al.*, 2011; Pires *et. al.*, 2011).

Practicability and sustainability of CO₂ capture using solid sorbents is currently among the research fields of interest to improve the efficiencies of CO₂ sorbents. Carbon-based materials such as carbon nanotubes and activated carbons, zeolites and amine-functionalised silica materials are a few examples of solid sorbents. Ideally, a good CO₂ solid sorbent should be a corrosion-resistive material with high CO₂ selectivity, and adsorption and desorption capacities with fast kinetics. It should also exhibit high regeneration stability and durability at industrial operating conditions with low operating pressures and CO₂ partial pressures (Yong *et. al.*, 2002; Deng 2006; Choi *et. al.*, 2009; Sayari *et. al.*, 2011). However, the above-mentioned materials are generally unsuitable for applications in high-temperature or impure gas streams, have low CO₂ adsorption capacities, or could not be regenerated repetitively (Choi *et. al.*, 2009; Hao *et. al.*, 2011; Sayari *et. al.*, 2011; Q. Wang *et. al.*, 2011).

1.4 Sodium zirconate as a potential CO₂ sorbent

Researchers have considered sodium zirconate (Na₂ZrO₃) as one of the most promising materials to effectively remove CO₂ from flue gas. This is due to its reusability and favourable thermodynamics of the whole CO₂ sorption process. Na₂ZrO₃ is one of the known adsorbents that can capture CO₂ gas at high temperatures of above 400 °C, which is applicable for post-combustion reactions and sorption-enhanced H₂ production. It has better regeneration stability than calcium oxide (CaO), higher CO₂ uptake than lithium zirconate (Li₂ZrO₃) and works well in wet gas streams (López-Ortiz *et. al.*, 2004; Santillán-Reyes and

Pfeiffer, 2011; Wang Q *et. al.*, 2011). This alkaline mixed metal-oxide ceramic compound is known to react with CO₂ gas in a reversible exothermic reaction as described in equation (1.1) (López-Ortiz *et. al.*, 2004; Ochoa-Fernández *et. al.*, 2009):



Research studies on this material for CO₂ capture are rarely reported compared to Li₂ZrO₃, which is the other zirconate compound of interest. López-Ortiz *et. al.* (2004) compared the capability of Na₂ZrO₃ with other sodium and lithium-containing oxides, including Li₄SiO₄ and Li₂ZrO₃, for CO₂ sorption and found that Na₂ZrO₃ has better overall CO₂ capture performance than Li₄SiO₄ and Li₂ZrO₃. Besides that, Na₂ZrO₃ prepared with excess sodium precursor can adsorb and desorb a very high amount of CO₂ close to the stoichiometric capacity of 5.400 mmol/g. Its CO₂ sorption rate of 2.348 mmol g⁻¹ min⁻¹ is also the fastest among all the potential CO₂ adsorbents (López-Ortiz *et. al.*, 2004).

1.5 Problem statements

Na₂ZrO₃ solid sorbents were successfully developed for high-temperature CO₂ capture applications. The highest reported CO₂ adsorption capacity of Na₂ZrO₃ thus far was 4.901 mmol/g (Radfarnia and Iliuta, 2012). However, its CO₂ adsorption capacity decreased with increasing number of cycles for 4 cycles. Hence, it is still desirable to produce a Na₂ZrO₃ solid sorbent with CO₂ adsorption capacity that is closer to the theoretical amount of 5.400 mmol/g and is consistent for numerous number of cycles for an even higher removal of CO₂ gas. This could be done by comparison of preparation methods.

Synthesis of Na₂ZrO₃ sorbent has been done, most commonly, by solid-state reaction between the Na₂CO₃ and ZrO₂ precursors. Na₂ZrO₃ has also been developed successfully by simple liquid-state reaction (Zhao *et. al.*, 2007; 2013) and surfactant-template/sonication method (Radfarnia and Iliuta, 2012). Na₂ZrO₃ has also been produced by sol-gel synthesis

for other applications such as coating of metallic biomedical implants (Subrasi *et. al.*, 2002; Devi and Rajendran, 2012). Sol-gel method is known to produce materials with high purity and improved particle characteristics. The Pechini method is the preferred sol-gel method due to its simple and inexpensive methodology (Petrykin and Kakihana, 2005). Currently, the Pechini sol-gel synthesis of Na_2ZrO_3 sorbent for the application of CO_2 capture is yet to be reported.

In this research, development of Na_2ZrO_3 sorbent with improved CO_2 sorption characteristics was attempted. This was done by varying various synthesis and CO_2 sorption parameters, and comparing synthesis methods to investigate their effects on the CO_2 sorption performance of the prepared Na_2ZrO_3 sorbents. It is anticipated that this solid sorbent with improved CO_2 adsorption properties could be produced.

1.6 Research objectives

The aims of this research are:

- 1) To improve the synthesis parameters for the development of Na_2ZrO_3 as a CO_2 solid sorbent with improved characteristics,
- 2) To investigate the CO_2 sorption performance of the above-synthesised Na_2ZrO_3 sorbent, and
- 3) To study the usability and stability of the above-prepared Na_2ZrO_3 for multicyclic high-temperature CO_2 capture.

1.7 Research scope

This research work focuses on the preparation of Na_2ZrO_3 as a CO_2 solid sorbent by liquid-state reaction and Pechini sol-gel synthesis methods for the purpose of improving its CO_2 sorption performance. At the synthesis stage, calcination methods, sodium precursors and

ratios of additional gelling agents were varied. The synthesised Na_2ZrO_3 was then tested for its CO_2 capture performance using the thermogravimetric analyser (TGA) in pure CO_2 gas for every variation of parameters during the preparation and carbonation stages. TGA was used for one-factor-at-a-time screening of the synthesised Na_2ZrO_3 . Finally, the sample with the best CO_2 sorption performance was analysed for its structural characteristics and regeneration stability.

1.8 Thesis outline

The organisation of this thesis starts off with **Chapter 1** to introduce the readers about CO_2 as a greenhouse gas, current statistics of its emission, and issues faced by governments and scientists to combat greenhouse gas effects, particularly CO_2 gas reduction. The concept, current technologies and difficulties of CO_2 adsorption are also briefly discussed in this chapter. With this, the research objectives and scope are outlined here.

Chapter 2 gives readers an insight on the theories and concepts involved in this research work. Various methods and results obtained by different scientists to prepare Na_2ZrO_3 as a CO_2 solid sorbent are also compiled in this chapter.

Details of the experimental and analytical methods done in this work to synthesise and characterise the prepared Na_2ZrO_3 respectively for CO_2 sorption are described in **Chapter 3**, whereas **Chapter 4** discusses the results obtained in this research work and the explanations behind these findings.

Lastly, **Chapter 5** concludes the experimental results and discussions of this research work in this thesis, together with future recommendations of this research study.