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EFFECTS OF SYNTHESIS METHODS AND PARAMETERS ON SODIUM ZIRCONATE FOR HIGH-TEMPERATURE CO_2 SORPTION

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2015

EFFECTS OF SYNTHESIS METHODS AND PARAMETERS ON SODIUM ZIRCONATE FOR HIGH-TEMPERATURE CO_2 SORPTION

by

OOI KHIM MAY

Thesis submitted in fulfillment of the requirements for the degree of Master of Science

October 2015

ACKNOWLEDGEMENTS

First of all, my utmost appreciation goes to my main supervisor from Universiti Sains Malaysia (USM), Prof. Dr. Abdul Rahman bin Mohamed, and co-supervisor from Monash University Malaysia, Dr. Chai Siang Piao, for accepting me as their postgraduate student. Without their supervision and guidance, I would have been lost in direction in undertaking my research activities.

Furthermore, I would like to acknowledge the financial supports given by USM through the Research University-Postgraduate Research Grant Scheme (USM-RU PRGS) (1001/PJKIMIA/8035017) and Research University Team (RUT) (1001/PJKIMIA/854001), and the Ministry of Higher Education (MOHE) Malaysia through the Long-term Research Grant Scheme (LRGS) (203/PKT/6723001) and MyMaster scholarship. These grants and scholarship have been a great help throughout my whole postgraduate studies in reducing the financial burden for self-support and to perform my research activities.

I am very grateful to the administrative staff and laboratory technicians from School of Chemical Engineering, School of Materials and Mineral Resources Engineering, and School of Physics in USM, and School of Engineering in Monash University Malaysia for their technical support and assistance. My utmost gratitude also goes to Mr. Karunakaran and En. Mohamed Mustaqim from the X-ray Crystallography Lab in School of Physics in USM for the discussions and guidance in analysing the XRD results.

Last but not least, my sincere gratitude goes to all of my family members and friends, of whom too many are to be named here. Their endless moral support, company, motivation, guidance and assistance in research and non-research related issues have led me to persevere to the very end of my research studies.

TABLE OF CONTENTS

ACKNOWLEDGEMENT ii
LIST OF TABLES vi
LIST OF FIGURES viii
LIST OF PLATES xi
LIST OF SYMBOLS xii
LIST OF ABBREVIATIONS xiii
ABSTRAK xv
ABSTRACT xvii

CHAPTER 1: INTRODUCTION 1
1.1 Carbon dioxide and its emission 1
1.2 Current technologies for CO_2 capture 2
1.3 CO_2 capture by solid-based adsorbents 2
1.4 Sodium zirconate as a potential CO_2 sorbent 3
1.5 Problem statements 4
1.6 Research objectives 5
1.7 Research scope 5
1.8 Thesis outline 6

CHAPTER 2: LITERATURE REVIEW 7
2.1 Definition and general process description of CO_2 adsorption 7
2.2 Statistics of CO_2 emission sources 9
2.3 Current technologies for CO_2 capture 12
2.4 CO_2 capture by solid adsorbents 16
2.5 Sodium zirconate and its application for CO_2 capture 24
2.6 Synthesis and CO_2 adsorption performance of Na_2ZrO_3 28
2.6.1 Solid-state reaction 28
2.6.2 Liquid-state synthesis 29
2.6.3 Surfactant-template/sonication synthesis 33
2.6.4 Sol-gel synthesis 36
2.6.5 Variations of combinations of precursors for synthesis of Na_2ZrO_3 39

2.6.6 Modifications of Na_2ZrO_3 sorbent with additives 41
2.7 Influence of CO_2 adsorption parameters on the CO_2 adsorption process of Na_2ZrO_3 49
2.8 Regeneration performance of Na_2ZrO_3 53
2.9 Summary 57

CHAPTER 3: RESEARCH METHODOLOGY 61
3.1 Flow chart of research methodology 61
3.2 Synthesis methods of Na_2ZrO_3 65
3.2.1 Simple liquid-state synthesis of Na_2ZrO_3 65
3.2.2 Liquid-state synthesis of Na_2ZrO_3 with addition of ethylene glycol and citric acid 69
3.2.3 Solid-state synthesis of Na_2ZrO_3 70
3.3 CO_2 sorption performance and regeneration studies of synthesised Na_2ZrO_3 71
3.3.1 Determination of CO_2 sorption capacity of synthesised Na_2ZrO_3 71
3.3.2 Regeneration studies of synthesised Na_2ZrO_3 72
3.4 Characterisation of synthesised Na_2ZrO_3 73
3.4.1 BET surface area and porosity measurements 73
3.4.2 Fourier transform infrared (FTIR) spectroscopy 73
3.4.3 Scanning electron microscopy (SEM) 74
3.4.4 X-ray diffraction (XRD) analysis 74

CHAPTER 4: RESULTS AND DISCUSSION 75
4.1 Screening of synthesised Na_2ZrO_3 for CO_2 sorption performance 75
4.1.1 Effects of different carbonation temperatures during CO_2 sorption process 76
4.1.2 Effects of different calcination conditions during synthesis of Na_2ZrO_3 78
4.1.3 Effects of different sodium precursors 87
4.1.4 Effects of addition of citric acid and ethylene glycol as gelling agents 95
4.1.5 Effects of different synthesis methods 98
4.2 Regeneration studies of synthesised Na_2ZrO_3 with highest CO_2 capture capacity 99
4.3 Characterisation of synthesised Na_2ZrO_3 101
4.3.1 XRD analysis of synthesised Na_2ZrO_3 101

4.3.2 SEM analysis of synthesised Na_2ZrO_3 107
4.3.3 BET surface and porosity measurements of synthesised Na_2ZrO_3 115
4.4 Summary and comparisons with literature results 118

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS 120
5.1 Conclusions.....120
5.2 Future recommendations.....121

REFERENCES 123

LIST OF PUBLICATIONS 134

APPENDICES
Appendix A Lists of chemicals and gases utilised for synthesis and CO_2 sorption performance tests of Na_2ZrO_3
Appendix B Sample calculations to determine stoichiometric ratios of reactants
Appendix C N_2 adsorption-desorption isotherms of Na_2ZrO_3

LIST OF TABLES

		Page
Table 2.1	Methods of regeneration in cyclic-batch fixed bed adsorption systems (Geankoplis, 2003).	8
Table 2.2	Various technologies for CO_2 capture and their advantages and disadvantages.	14 – 15
Table 2.3	Temperature range in which CO_2 adsorption by various solid adsorbents are effective (Wang Q *et. al.*, 2010).	17
Table 2.4	CO_2 sorption capacities of various adsorbents.	17
Table 2.5	Solid adsorbents produced for CO_2 capture and their advantages and disadvantages.	18 – 21
Table 2.6	CO_2 adsorption and regeneration properties of Na_2ZrO_3 synthesised at different Na:Zr molar ratios (López-Ortiz *et. al.* 2004).	29
Table 2.7	Combinations of sodium and zirconium precursors for synthesis of Na_2ZrO_3.	39
Table 2.8	Comparison of Li- and K-modified Na_2ZrO_3 adsorbents with the same molar ratio of binary alkali metals.	46
Table 2.9	Comparison of synthesis and carbonation methods and their effects on the CO_2 sorption capacity of Na_2ZrO_3-based sorbents.	58 – 60
Table 3.1	List of synthesis parameters to study the effects of different calcination temperature and time.	66
Table 3.2	List of synthesis parameters to study the effects of different Na precursors.	66
Table 3.3	List of modifications of this research study from Zhao *et. al.* (2007).	67
Table 3.4	List of synthesis parameters to study the effects of different CA:EG ratios.	70
Table 3.5	List of parameters for solid-state synthesis of Na_2ZrO_3.	71
Table 3.6	List of analyses for characterisation of prepared Na_2ZrO_3 with highest CO_2 sorption capacity.	73
Table 4.1	Molecular weights of reactants in Equation (4.3) (Silberberg, 2006).	76

Table 4.2	K_a and pK_a values of weak acids possibly formed (Silberberg, 2006).	91
Table 4.3	CO_2 capture capacities of Na_2ZrO_3 solid sorbents synthesised from various sodium precursors. Operating conditions: carbonation temperature, 550 ℃; carbonation pressure, 101.3 kPa; carbonation duration, 60 min.	95
Table 4.4	CO_2 sorption capacities of Na_2ZrO_3 sorbents prepared with different synthesis methods.	98
Table 4.5	Average crystallite sizes of prepared samples 1_900C-4h and CA2_EG1 before and after carbonation.	104
Table 4.6	BET surface area, porosity and pore size of samples 1_900C-4h and CA2_EG1 before CO_2 adsorption.	115
Table 4.7	The parameters required for preparation of Na_2ZrO_3 with highest CO_2 sorption amount.	118
Table 4.8	Comparison of CO_2 sorption capacity of solid sorbent synthesised in this study with others available in the literature.	119
Table A.1	List of chemicals for synthesis of Na_2ZrO_3.	Appendix A
Table A.2	List of gases utilised for CO_2 sorption performance tests.	Appendix A

LIST OF FIGURES

		Page
Figure 2.1	CO_2 emissions in the world from year 1971 to 2012 (IEA, 2014).	10
Figure 2.2	CO_2 emissions in Malaysia from year 1971 to 2012 (IEA, 2014).	10
Figure 2.3	CO_2 emissions by different sectors from fuel combustion globally from the year 2008 to 2012 (IEA, 2010; 2011; 2012; 2013; 2014).	11
Figure 2.4	CO_2 emissions by different sectors from fuel combustion in Malaysia from the year 2008 to 2012 (IEA, 2010; 2011; 2012; 2013; 2014).	12
Figure 2.5	Schematic diagram of the CO_2 adsorption mechanisms of Na_2ZrO_3 adsorbent.	27
Figure 2.6	Simplified flowchart of sol-gel synthesis (Pierre, 1998).	37
Figure 3.1	Flow chart of overall research methodology.	63 – 64
Figure 3.2	Schematic diagram of experimental setup for synthesis of Na_2ZrO_3 sorbent.	68
Figure 4.1	CO_2 sorption profiles of sample 1_900C-4h tested at different isothermal carbonation temperatures. Operating condition: carbonation pressure, 101.3 kPa.	77
Figure 4.2	CO_2 sorption profiles of Na_2ZrO_3 sorbents calcined at different conditions during synthesis. Operating conditions: carbonation temperature, 550 ℃; carbonation pressure, 101.3 kPa.	79
Figure 4.3	FTIR spectrum of sample Na2ZrO3_SS.	81
Figure 4.4	FTIR spectrum of sample 1_600C-4h.	82
Figure 4.5	CO_2 sorption profiles of Na_2ZrO_3 sorbent prepared with different sodium precursors. Operating conditions: carbonation temperature, 550 ℃; carbonation pressure, 101.3 kPa.	88
Figure 4.6	CO_2 sorption profiles of Na_2ZrO_3 prepared via sol-gel synthesis with addition of different CA:EG molar ratios. (Inset) A zoom-in of CO_2 sorption profiles of samples prepared with CA:EG molar ratios of 1:1 to 2:1. Operating conditions: carbonation temperature, 550 ℃; carbonation pressure, 101.3 kPa.	96

Figure 4.7	CO_2 sorption profiles of samples CA2_EG1, 1_900C-4h and Na2ZrO3_SS. Operating conditions: carbonation temperature, 550 ℃; carbonation pressure, 101.3 kPa.	98
Figure 4.8	CO_2 sorption capacities achieved in regeneration stability test of samples 1_900C-4h and CA2_EG1. Operating conditions: carbonation temperature, 550 ℃; carbonation duration, 40 min; regeneration temperature, 750 ℃; regeneration duration, 30 min; operating pressure, 101.3 kPa.	100
Figure 4.9	XRD patterns of sample 1_900C-4h before and after 1 cycle of CO_2 adsorption. The following labels correspond to different chemicals and phases: (▼) monoclinic Na_2ZrO_3 (ICDD file 00-035-0770), (♦) hexagonal Na_2ZrO_3 (ICDD file 00-021-1179), (■) monoclinic Na_2CO_3 (ICDD file 00-019-1130), (●) tetragonal ZrO_2 (ICDD file 01-079-1769).	101
Figure 4.10	XRD pattern of sample CA2_EG1 before and after 1 cycle of CO_2 adsorption. The following labels correspond to different chemicals and phases: (▼) monoclinic Na_2ZrO_3 (ICDD file 00-035-0770), (♦) hexagonal Na_2ZrO_3 (ICDD file 00-021-1179), (■) monoclinic Na_2CO_3 (ICDD file 00-019-1130), (●) tetragonal ZrO_2 (ICDD file 01-079-1769).	103
Figure 4.11	XRD pattern of samples 1_600C-1h, 1_600C-4h, 1_700C-1h and 1_700C-4h after calcination at different conditions. The following labels correspond to different chemicals and phases: (▼) monoclinic Na_2ZrO_3 (ICDD file 00-035-0770), (♦) hexagonal Na_2ZrO_3 (ICDD file 00-021-1179), (■) monoclinic Na_2CO_3 (ICDD file 00-019-1130), (●) tetragonal ZrO_2 (ICDD file 01-079-1769).	106
Figure 4.12	SEM images of sample 1_900C-4h before carbonation at (a) 5 kx, (b) 10 kx, (c) 15 kx, and (d) 20 kx magnifications.	108
Figure 4.13	SEM images of sample 1_900C-4h after one cycle of carbonation at (a) 5 kx, (b) 10 kx, and (c) 15 kx magnifications.	109
Figure 4.14	SEM images of sample 1_900C-4h after 3 cycles of carbonation at (a) 5 kx, (b) 10 kx, (c) 15 kx, and (d) 20 kx magnifications.	110
Figure 4.15	SEM images of sample CA2_EG1 before carbonation at (a) 5 kx, (b) 10 kx, and (c) 15 kx magnifications.	112
Figure 4.16	SEM images of sample CA2_EG1 after one cycle of carbonation at (a) 5 kx, (b) 10 kx, and (c) 15 kx magnifications.	113

Figure 4.17 SEM images of sample CA2_EG1 after 7 cycles of carbonation at (a) 5 kx, (b) 10 kx, (c) 20 kx, and (d) 30 kx magnifications. 114

Figure C.1 N_2 adsorption-desorption isotherms of samples 1_900C-4h and CA2_EG1. Appendix C

LIST OF PLATES

		Page
Plate 3.1	Photograph of experimental setup for synthesis of Na_2ZrO_3 sorbent.	69
Plate 4.1	Samples calcined at (a) 600 ℃ for 1 h, (b) 600 ℃ for 4 h, (c) 700 ℃ for 1 h, and (d) 700 ℃ for 4 h.	80

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_{CO2}	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 CO_2 BERSUHU TINGGI

ABSTRAK

Pemacaran karbon dioksida (CO_2) ialah antara punca-punca pemanasan sejagat. Penangkapan CO_2 secara penjerapan CO_2 telah menjadi salah satu kaedah untuk mengurangkan pemancaran CO_2. Tambahan pula, penjerap yang bercekapan tinggi diperlukan untuk penangkapan CO_2 bersuhu tinggi daripada proses-proses industri hibrid. Natrium zirconat (Na_2ZrO_3) ialah salah satu bahan penjerap pepejal yang berpotensi dan mempunyai prestasi penjerapan berkitar CO_2 yang tinggi dan stabil, tetapi kapasiti jerapan CO_2 yang lebih dekat dengan kapasiti unggul masih dikehendaki. Tambahan pula, kesan-kesan metodologi yang berbeza terhadap prestasi penangkapan CO_2 dengan penjerap ini belum dilaporkan dalam kajian-kajian terdahulu. Tujuan utama penyelidikan ini ialah menambah baik sintesis dan oleh itu kapasiti jerapan CO_2 untuk penjerapan CO_2 bersuhu tinggi dengan bahan penjerap Na_2ZrO_3. Kesan-kesan keadaan pengkarbonanatan dan pengkalsinan, prekursor natrium (Na) yang berbeza dan penambahan asid sitrik (CA) dan etilena glikol (EG) terhadap Na_2ZrO_3 yang disintesis dan oleh itu prestasi penjerapan CO_2 bersuhu tinggi telah disiasat. Ujian pencirian dan prestasi penjerapan CO_2 terhadap sampel-sampel ini dilakukan melalui analisis termogravimetri, pembelauan sinar-X, penjerapan N_2 dan SEM. Semua parameter-parameter tersebut memberi kesan-kesan yang ketara terhadap prestasi penjerapan CO_2 untuk bahan penjerap Na_2ZrO_3 yang disediakan. Kegunaan prekursor Na yang berbeza dan suhu penjerapan CO_2 mempengaruhi kapasiti penjerapaan CO_2 sampel-sampel itu. Keadaan kalsinasi yang berbeza juga memperanguhi ketulenan bahan penjerap Na_2ZrO_3. Penambahan CA dan EG menghasilkan bahan penjerap Na_2ZrO_3 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 Na_2ZrO_3, iaitu kapasiti penjerapan CO_2 yang terbaik, telah dicapai

pada suhu pengkarbonatan 550 ℃ untuk sampel yang disintesis dengan natrium sitrat sebagai prekursor Na serta menggunakan CA dan EG dengan nisbah molar 2:1, dan dikalsin pada 900 ℃ selama 4 h. Oleh itu, penjerap ini adalah sesuai untuk penangkapan CO_2 bersuhu tinggi. Ujian keberangkapan di bawah keadaan perindustrian untuk bahan penjerap Na_2ZrO_3 ini yang telah bertambah baik adalah dicadangkan.

EFFECTS OF SYNTHESIS METHODS AND PARAMETERS ON SODIUM ZIRCONATE FOR HIGH-TEMPERATURE CO_2 SORPTION

ABSTRACT

Carbon dioxide (CO_2) emission is among the causes of global warming. CO_2 capture by CO_2 adsorption has been one of the methods to reduce CO_2 emission. Moreover, an adsorbent with high efficiency is needed for high-temperature CO_2 capture from industrial hybrid processes. Sodium zirconate (Na_2ZrO_3) is one of the potential solid sorbents with high and stable cyclic CO_2 sorption performance, but CO_2 adsorption capacity closer to its ideal capacity is still desired. Furthermore, the effects of different methodologies on its CO_2 capture performance were not reported previously. The main aim of this research work is to improve the synthesis and thus CO_2 capture capacity of Na_2ZrO_3 for high-temperature CO_2 sorption. Effects of carbonation and calcination conditions, different sodium (Na) precursors, and addition of citric acid (CA) and ethylene glycol (EG) on high-temperature CO_2 sorption performance of synthesised Na_2ZrO_3 were investigated. Characterisation and CO_2 sorption performance of samples were tested using thermogravimetric analysis, X-ray diffraction, N_2 adsorption and SEM. All the above-mentioned parameters significantly affect the CO_2 adsorption performances of the prepared Na_2ZrO_3 sorbents. The use of different Na precursor and CO_2 adsorption temperature influenced the CO_2 adsorption capacity of the samples. Different calcination conditions also affected the purity of Na_2ZrO_3. Addition of CA and EG resulted in producing purer Na_2ZrO_3 with more porous morphology and hence better regeneration stability than the sample prepared without the addition of CA and EG. The best CO_2 adsorption capacity of 4.902 mmol CO_2/g Na_2ZrO_3 was achieved at carbonation temperature of 550 ℃, for the sample synthesised with sodium citrate as the Na precursor and CA:EG molar ratio of 2:1, and calcined at 900 ℃ for 4 h. Hence, this sorbent is suitable for high-temperature CO_2 capture. It is recommended to test the functionality of this improved Na_2ZrO_3 sorbent under industrial conditions.

CHAPTER 1

INTRODUCTION

1.1 Carbon dioxide and its emission

Carbon dioxide (CO_2) 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 CO_2 as one of the secondary products.

CO_2 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 CO_2, which is also a greenhouse gas (GHG), have led to global warming. The International Energy Agency (IEA) reported that global CO_2 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 CO_2 emissions and consequently mitigating GHG effects, namely, melting of glaciers and natural disasters such as drought and floods.

1.2 Current technologies for CO_2 capture

Various solutions have been considered to combat the problems of increasing CO_2 emissions. One of these solutions is CO_2 capture which works on the simple concept of CO_2 sorption from flue gas and other production sources before its emission to the atmosphere. The captured CO_2 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 CO_2 capture have been studied to reduce CO_2 concentration in waste gas emissions and thus combat the issues of global warming. These methods include CO_2 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 CO_2 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 CO_2 from the gas stream. Besides that, the CO_2 selectivity of these separation processes is still considerably low. The temperature range used for CO_2 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 CO_2 capture by solid-based adsorbents

In addition to the methods as mentioned above, CO_2 capture using solid adsorbents has also been used in several industrial applications such as post-combustion flue gas cleaning and pre-combustion hydrogen gas (H_2) 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 CO_2 capture using solid sorbents is currently among the research fields of interest to improve the efficiencies of CO_2 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 CO_2 solid sorbent should be a corrosion-resistive material with high CO_2 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 CO_2 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 CO_2 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 CO_2 sorbent

Researchers have considered sodium zirconate (Na_2ZrO_3) as one of the most promising materials to effectively remove CO_2 from flue gas. This is due to its reusability and favourable thermodynamics of the whole CO_2 sorption process. Na_2ZrO_3 is one of the known adsorbents that can capture CO_2 gas at high temperatures of above 400 °C, which is applicable for post-combustion reactions and sorption-enhanced H_2 production. It has better regeneration stability than calcium oxide (CaO), higher CO_2 uptake than lithium zirconate (Li_2ZrO_3) 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 CO_2 gas in a reversible exothermic reaction as described in equation (1.1) (López-Ortiz *et. al.*, 2004; Ochoa-Fernández *et. al.*, 2009):

$$Na_2ZrO_3 + CO_2 \leftrightarrow Na_2CO_3 + ZrO_2 \quad (1.1)$$

Research studies on this material for CO_2 capture are rarely reported compared to Li_2ZrO_3, which is the other zirconate compound of interest. López-Ortiz *et. al.* (2004) compared the capability of Na_2ZrO_3 with other sodium and lithium-containing oxides, including Li_4SiO_4 and Li_2ZrO_3, for CO_2 sorption and found that Na_2ZrO_3 has better overall CO_2 capture performance than Li_4SiO_4 and Li_2ZrO_3. Besides that, Na_2ZrO_3 prepared with excess sodium precursor can adsorb and desorb a very high amount of CO_2 close to the stoichiometric capacity of 5.400 mmol/g. Its CO_2 sorption rate of 2.348 mmol g^{-1} min^{-1} is also the fastest among all the potential CO_2 adsorbents (López-Ortiz *et. al.*, 2004).

1.5 Problem statements

Na_2ZrO_3 solid sorbents were successfully developed for high-temperature CO_2 capture applications. The highest reported CO_2 adsorption capacity of Na_2ZrO_3 thus far was 4.901 mmol/g (Radfarnia and Iliuta, 2012). However, its CO_2 adsorption capacity decreased with increasing number of cycles for 4 cycles. Hence, it is still desirable to produce a Na_2ZrO_3 solid sorbent with CO_2 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 CO_2 gas. This could be done by comparison of preparation methods.

Synthesis of Na_2ZrO_3 sorbent has been done, most commonly, by solid-state reaction between the Na_2CO_3 and ZrO_2 precursors. Na_2ZrO_3 has also been developed successfully by simple liquid-state reaction (Zhao *et. al.*, 2007; 2013) and surfactant-template/sonication method (Radfarnia and Iliuta, 2012). Na_2ZrO_3 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.