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Low temperature carbon dioxide capture by PEI-modified mesoporous silica: synthesis and adsorption performance analysis

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Chemical Engineering
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PREFACE

This master thesis has been conducted during the spring semester in 2021 at the Norwegian University of Science and Technology. This project is supported by SINTEF - the largest research organization in Europe

Due to personal health reasons and the effects due to COVID-19 pandemic, the research of this thesis is faced with huge difficulties and challenges. Therefore, I do feel grateful on receiving plentiful help from my supervisor professor De Chen. Without his encouragement and support, it would not be possible to achieve such good results of this thesis research.

In addition, I would like to thank my supervisor professor De Chen, co-supervisor Dr. Kumar Ranjan Rout, for their academical guidance during this thesis research. Also, I would like to sincerely thank Dumitrita Spinu (PhD candidate) and Jørgen Lausund Grinna (M.Sc in Chemical engineering) for valuable guidance and experimental supports.

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Hereby, I declare that this is an independent work according to the exam regulations of the Norwegian university of science and technology (NTNU)

Trondheim, 04 June 2021

Yun Liu

ABSTRACT

Mesoporous silica sorbents were prepared at different synthesis conditions by conventional sol-gel methods. The rigid spherical silica sorbents of high surface area and high porosity in narrow distribution were tuned by varying initial gel composition and operation condition and studied Physical properties and morphology studies were carried out by nitrogen adsorption / desorption and SEM techniques. The surface area, pore volume and pore size of synthesis silica sorbents in this study were up to 700 m^2/g, 1.5 cm^3/g and 7 nm, respectively. These mesoporous silica particles had a size in range of 4 to 10 µm.

CO_2 adsorption and desorption performance of synthesized sorbents were studied via TGA after amine modification at different loading concentrations. Both equilibrium and working CO_2 capacity of PEI-modified mesoporous silica were discussed in this work. As per unit amine mass, the optimum and practical CO_2 of solid sorbents were up to 6.02 and 5 mmol/g, respectively within a 5 vol.% of CO_2 inlet gas condition at 75 °C adsorption temperature. The cycle stability of solid sorbent in a pure N_2 regeneration environment obtained an outstanding result as 99.1 % and 95.4 % under mild and harsh condition, respectively.

In addition, studies of amine loading check and comparison with previous master student's work were also discussed in this thesis research.

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LIST OF ABBREVIATIONS

Abbreviation*:*

Ads.	Adsorption
BET	Brunauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
CTAB	Cetyltrimethylammonium bromide
CCS	Carbon dioxide capture and storage
CO_2	Carbon dioxide
Des.	Desorption
EtOH	Ethanol
HCl	Hydrochloride acid
H_2O	Water
PEI	Polyethylenimine
PEI_SiO_2	Mesoporous silica impregnated with polyethylenimine
P123	Poly(ethylene oxide)–block–poly(propylene oxide)–block–poly(ethylene oxide)
SEM	Scanning Electron Microscope
Temp.	Temperature
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
Vp	Pore volume

1. INTRODUCTION

It is well known that the CO_2, as the greenhouse gas, mainly contribute to the global warming and climate change (Association, 2015). Reduction on the emission of CO_2 to the atmosphere has become as a common mission in the world and CO_2 capture and storage (CCS) has been researching for several years (Association, 2015). 80% of CO_2 in the world are emitted from the flue gas exhausted after extensive combustion of fossil fuels in the coal-fired power plants (De Coninck et al., 2009). Post-combustion flue gas is typically composed of 70% of N_2 and 15% of CO_2 with moisture and other impurities at ambient pressures (1 bar) and temperatures (298 K),but the CO_2 volume percentage could be even lower to 5% after desulfurization (Hu et al., 2015).

Therefore, efficient post-combustion CO_2 adsorbents fitted for power plant flue gas condition is interesting to be developed (Hu et al., 2015). Due to several withdraws of the amine liquid absorption process, like amine degradation, a high energy penalty, corrosion of setup and secondary environmental pollution (Kim et al., 2017). Nano-porous solid sorbents have been widely investigated for the application of CCS in terms of its high CO_2 adsorption capacity and low energy input for sorbents' regeneration (Fisher and Gray, 2015, Verdegaal et al., 2016). Amongst them, mesoporous silica materials feature high surface area, thermal stability as well as large pore volume, which allow for amines group immobilisation in turn to an outstanding performance on CO_2 capture at low temperatures (Sanz-Pérez et al., 2016a, Lee and Yavuz, 2016). The most common methods used for mesoporous silica adsorbents are derived from alkoxide based precursors such as Tetraethylorthosilicate (TEOS) by sol-gel process (Minju et al., 2017).

According to the literature review and previous work done by other students in IKP group, solid sorbents synthesis to expected properties with high surface area and large pore volume

with narrow distribution is still employing aim to optimum CO_2 capture performance of high adsorption capacity as well as good thermal stability during long-term CO_2 adsorption and desorption runs. Therefore, this research work focused mainly on the two aspects: developing silica adsorbents with stable pore structures as mentioned above; and evaluating CO_2 adsorption performances of various silica composites with amine impregnations as per the simulation of flue gas condition from post-combustion.

2.   LITERATURE REVIEW

2.1. Outlines of carbon capture processes

According to different industrial conditions and the purpose of reduction anthropogenic carbon dioxide emission, several CO_2 capture process routs has been developed as cost/effective and scalable techniques and adopted practically in various industrial applications: 1) post-combustion capture; b) pre-combustion capture and c) oxy-fuel combustion. The separation of each type of process has been shown in an outline sketch, given in Figure 1 (Modak and Jana, 2019).
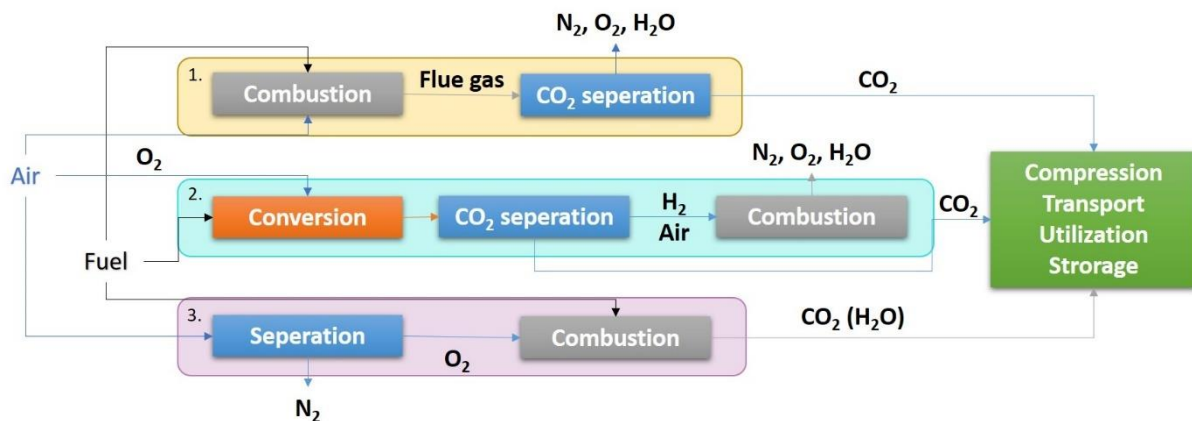
Figure 1: Schematic representation of three different CO_2 capture technologies

2.1.1. Post-combustion CO_2 capture (CO_2 /N_2 at low pressure)

For most applications of the post/combustion CO_2 capture process, N_2 seperation is a must when tail gas emits the atmosphere after combustion of fossil fuels. In common, the flue gas produced by fossil fuels combustion, which consists of generally 15% CO_2, 70% N_2 along with other minor components (H_2O, CO, NOx, and SOx) with total pressure of 1 bar and the temperature

between 40 and 60 °C (Demessence et al., 2009). CO_2 can be captured and separated by passing through a suitable adsorbent, and then the adsorbed CO_2 is compressed for transportation and storage or further utilization. To be noticed, the high purity of captured CO_2 is benefit for its compression, transportation and storing underground from cost-effective perspective consideration. However, researches indicated that the CO_2 concentration, normally, is around 4 vol% after desulfurization which increases the difficulty of adsorption, it is quite inevitable to explore high-effective adsorbents (Demessence et al., 2009).

2.1.2. Pre-combustion CO_2 capture (CO_2 /H_2 at high pressure)

In the pre-combustion technology, fuel reacts with air/O_2 to produce synthesis gas which is a mixture of CO and H_2. With further converter reaction, the CO reacted with steam to produce CO_2 (25%–35%, by volume) and additional H_2 (30%–50%, by volume) at high pressure (5–40 bar) in the catalytic reactor, then the pre-combustion capture process is applied to separate CO_2 from H_2 at elevated pressures (~30 bar) and temperatures (~40 °C) with an adsorbent bed (Change, 2005). Application of pre-combustion capture process is a part of purification of natural gas and/or syngas, it provides, meanwhile, suitable feeds regarding energy generation, CO_2 separation, steam reforming process and gasification of coke or oil residues (Demessence et al., 2009). By decreasing pressure, the adsorbents can be recycled. Compared with the post-combustion technology, the availability of ~15% CO_2 makes CO_2 seperation convenience in this process, whereas severe problem could be occurred due to high reaction temperature and H_2-rich turbine fuel (Change, 2005).

2.1.3. Oxy-fuel combustion (O_2/N_2 at low pressure)

As shown in above sketch, the combustion of fossil fuel, in the conventional oxy-fuel combustion line, is carried out under nearly pure O_2 atmosphere in purpose of minimizing NOx generation. O_2 is fed into the power generator and diluted to a partial pressure of 0.21 bar with CO_2 in the combustion process, and the emitted gaseous products are mainly composed of CO_2 (55%–65%, by volume) and H_2O (25%–35%, by volume) (Passé-Coutrin et al., 2005). Compared with post-/pre-combustion capture technologies, CO_2 captured by oxy-fuel combustion process can be directly subjected to sequestration after dehydration, and it is easily implanted into industry regarding to its simplicity in the seperation of flue gas and high purity

of CO_2 adsorbed, whereas the rigorous requirement for nearly pure O_2 combustion chamber is both technical and economical challenge of implementation of oxy-fuel combustion process.

2.1.4. Post-combustion CO_2 capture technology chosen for this thesis research

Fossil fuel-fired power plants are the main contributors to the world energy resources at the moment and it is increasing in future as illustrated in Figure 2. Since this demand will mainly be satisfied producing power from fossil fuels, the emissions of greenhouse gases will continue to increase, to solving this problem, among several CO_2 capture technologies introduces above, the post-combustion carbon capture processes technique with secure energy supply, as the only option for the retrofitting of existing power plants, can be ensured from fossil fuels reducing the emission of CO_2 to atmosphere and mitigating the global warming effect.
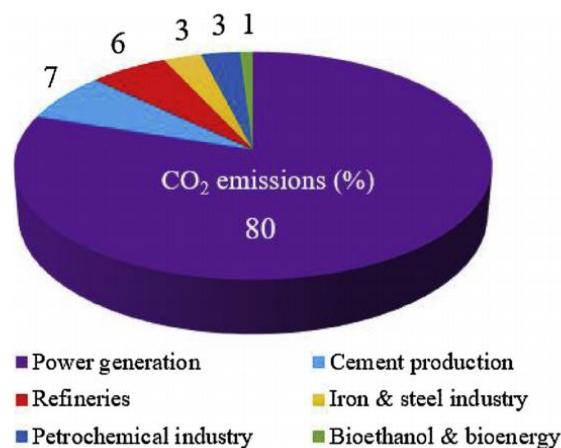
Figure 2: Percentage of total amount of annual CO_2 emissions from different industries (De Coninck et al., 2009)

2.2. Promising adsorbents for post-combustion CO_2 capture

Many different technologies of post-combustion CO_2 capture has been proposed and some of them have commercial demonstration and application for several years, such as absorption, membranes, cryogenic carbon dioxide, and adsorption. The most commonly implemented in industry is chemical absorption technology and the absorbents it deployed from single amines like MDEA, DEA, MEA, and TEA to mixed amines like PZ/MDEA, MEA/MDEA, SULFOLANE/MDEA, etc. to absorber carbon dioxide from other gases (Ooi et al., 2020, Abd and Naji, 2020, Naji and Abd, 2019). In Figure 3, it presents a pictorial representation of

aqueous amine-based coal-fired power plant for CO_2 adsorption and separation from acidic gas mixtures to enhance oil recovery operation.
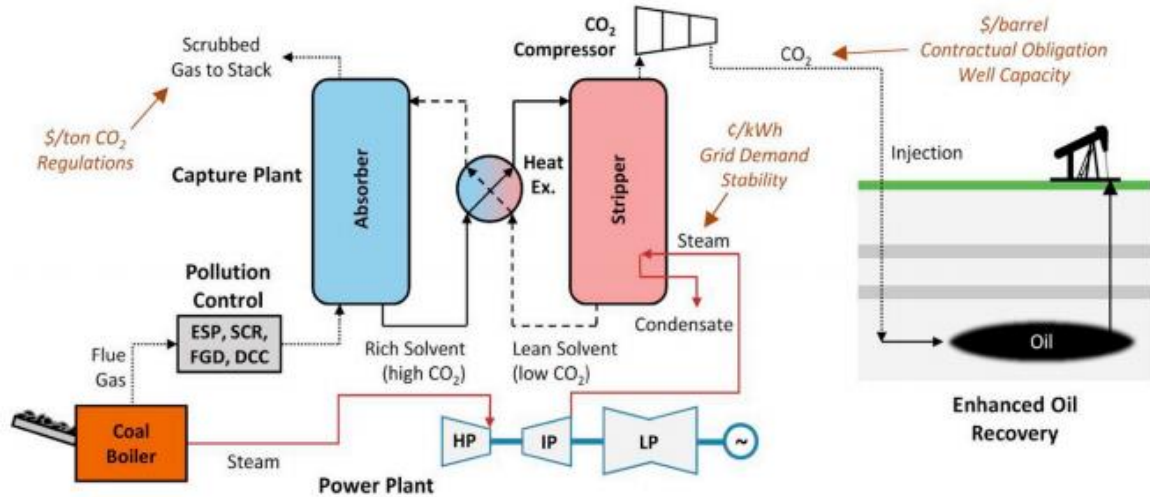
Figure 3: Schematic representation for flue gas CO_2 capture from coal-fired power plant (Walters et al., 2016)

Although the amine-based absorption technology is the state-of-art of post-combustion CO_2 capture process, it has several serious drawbacks, in which the main drawbacks of employing absorption technology are the extensive energy demand especially in the regeneration stage. Take the most widely used absorbent at present, MEA as an example, its regeneration energy consumption is between 3.2~5.5 GJ/ton CO_2. It is an attempt to reduce the energy consumption of absorbent regeneration to 2.0 GJ/ton CO_2 (Abd and Naji, 2020). Steam is main heat source used for absorbents regeneration as shown in Figure 4.
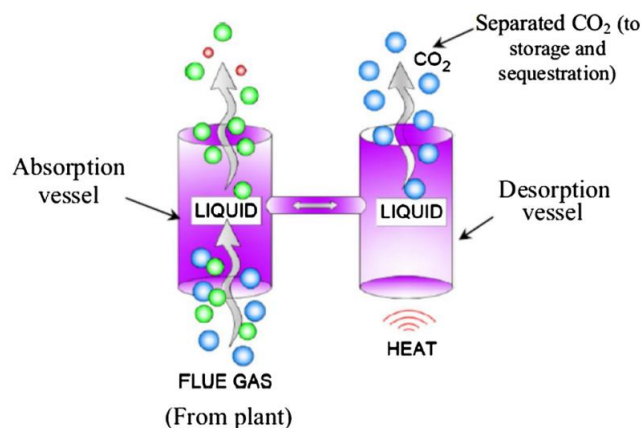
Figure 4: Graphical diagram of aqueous amine scrubbing technology (Ben-Mansour et al., 2016)

Besides the energy consumption issue, due to the corrosive nature and degradation of absorbents, as well as secondary environmental pollution caused by discharging of absorbent, use of aqueous amines as CO_2 absorbent in the existing power plants caused the corrosion issues of the plant facilities, accompanying with the requirement of costly design and high longevity of the system in order to keep them for safe running (Sanz-Pérez et al., 2016b).

As the chemical absorption method still has unresolved problems, in recent years research has also been carried out in the direction of solid adsorption. The mechanism of carbon dioxide removal on the adsorbent surface can be envisaged as (Ben-Mansour et al., 2016):

$$CO_2 + Surface \iff (CO_2) \cdot (Surface)$$
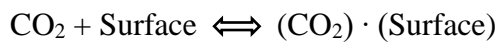
Because of van der Walls attraction of carbon dioxide molecules and the adsorbent surface, as well as, via pole/ion and pole/pole interactions between the quadruple of carbon dioxide and the ionic and polar sites of the solid adsorbent surface, selection for carbon dioxide is obtained (see Figure 5). Advantages of carbon dioxide removal using solid adsorbents are included but not least: high carbon dioxide uptake, high recovery and stability materials, efficient under humid conditions, and low cost in contradiction to absorption processes (Satyapal et al., 2001, Kapdi et al., 2005).
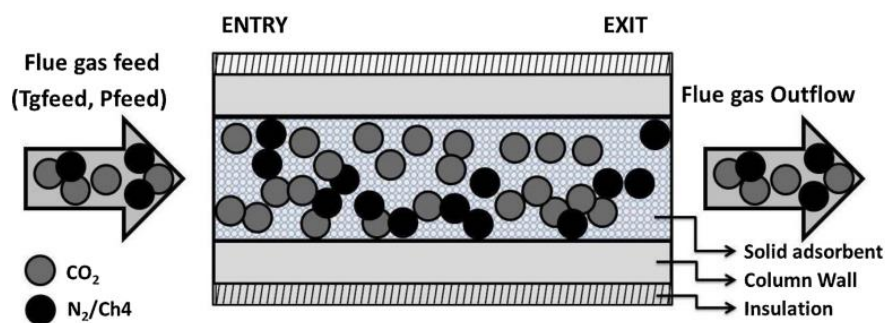
Figure 5: Graphical diagram of carbon dioxide capture by solid adsorbents (Ben-Mansour et al., 2016)

2.3. Solid adsorbents selection for physical adsorption CO_2 capture

For convenience and cost-effective adsorption and desorption of CO_2, porous solid adsorbents (see Figure 6) are much better candidates as: a) they can support facilitates better adsorption sites; b) they have high accessibility for CO_2 molecules; and 3) they can be easily recycled many times (Abd et al., 2020).
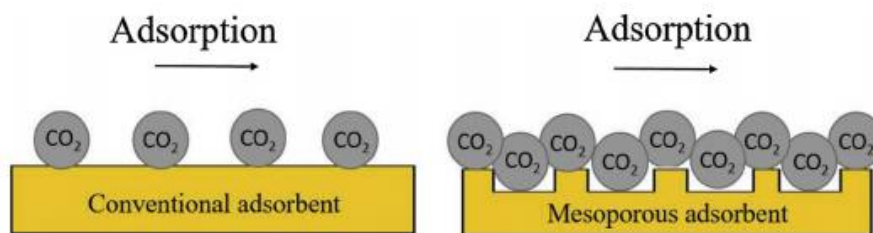
Figure 6: Schematic differences between conventional adsorbent and porous adsorbent during the adsorption process

The International Union of Pure and Applied Chemistry defined porous solid adsorbent by three types based on the pore size as:

- Micropores, < 2 nm
- Mesopores, in-between 2 and 50 nm, and
- Macropores, > 50 nm

Besides the pore size, a lot of factors impact on the adsorption capacity, for instance, the shape of pores like silts, cylinders and/or other cross-linked shapes is valuable to manage the adsorption performance (Derouane, 1998). Thus, the adsorbent material should meet some necessary criteria to be satisfied in both economical and operational for carbon dioxide capture as summarized by several researches:

- <u>CO_2 uptake</u>

The most critical factor for adsorbent is its adsorption performance to the capital cost of the adsorption process. The CO_2 adsorption capacity determines the required amount of adsorbent which turns in the sizing of relevant adsorption column. Higher uptake of carbon dioxide minimizes both adsorbent amount and setup size (Gray et al., 2008).

- CO$_2$ selectivity

The ratio of CO$_2$ capacity to N$_2$ capacity which has a direct impact on the entrapped carbon dioxide in post-combustion capture process. Efficient adsorbent should show high carbon dioxide selectivity, as well as the adsorbents must offer high capacity for CO2 in humid conditions (Gray et al., 2008).

- Adsorption/desorption kinetics

Fast adsorption/desorption kinetics for carbon dioxide produce a sharp carbon dioxide breakthrough curve and key to control the cycle time to enhance the efficiency of adsorbents accordingly. The carbon dioxide adsorption kinetics on the porous adsorbents influenced by the reaction kinetics of carbon dioxide with the functional group on the adsorbent surface, besides the mass transfer through the adsorbent surface(Gray et al., 2008).

- Mechanical strength

The high kinetics can be maintained by better mechanical strength of adsorbents. Besides, adequate mechanical strength leads less adsorbent consumption and results in achieving a cost-effective CO$_2$ capture process (Gray et al., 2008).

- Adsorption heat

Low energy required for adsorbents regeneration is an essential factor to judge the competitive of CO$_2$ capture technology. Recommended value given by some studies indicated that for physisorption cases, the heat of adsorption is ranging between −25 to −50 kJ/mol, whereas it is much low than absorption technologies with amine solvents (Samanta et al., 2012).

- Adsorbent cost

A baseline of 10$ per kg of the adsorbent is resulted from a sensitivity economic analysis conducted for reference over two dozen years ago for amine modified adsorbents (Tarka Jr et al., 2006). Till now, lots of researches are still carrying out on reducing adsorbent costs while maintaining satisfied CO$_2$ capture capacity.

2.4. Different types of solid adsorbents

As shown in the Figure 7, solid sorbents developed nowadays can be categorized in tow big parts based on original materials chosen: 1) carbonaceous adsorbents and 2) non-carbonaceous adsorbents.
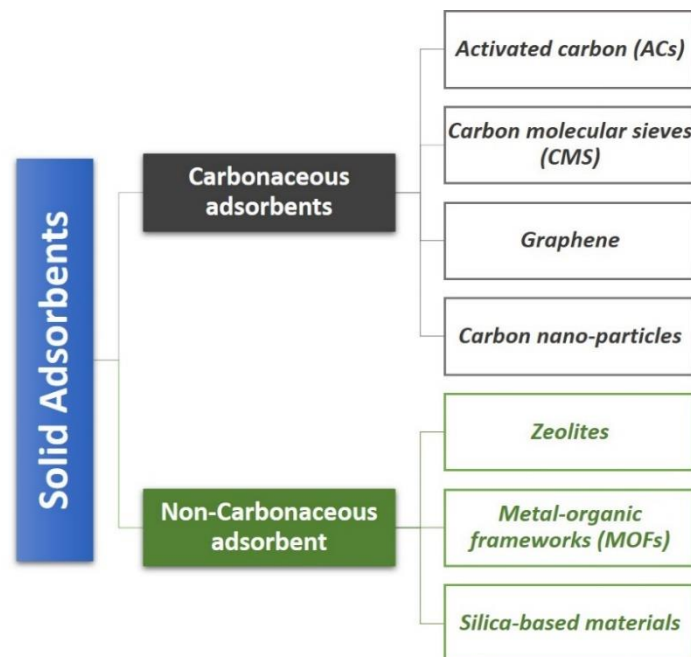
Figure 7: Physical solid adsorbents for carbon dioxide adsorption

2.4.1. Carbonaceous adsorbents

Carbonaceous adsorbents are usually consisting of carbon and other associated material, many types used for CO_2 capture research are studied such as porous activated carbons, molecular carbon sieve, carbon nanoparticles, and graphene. Due to their advantages of cheap, easily consisted of natural sources, high specific surface area, large pore volume, and lightweight, those types of solid adsorbents generally are considered as excellent sorbents with properties of eco-affinity, thermal and chemical stability, heat and electrical conductivity, or high strength (Lozano-Castelló et al., 2002, Bilalis et al., 2014).

▪ **Activated carbon materials (ACs)**

Activated carbons synthesize from carbonaceous materials via pyrolysis at elevated temperature and specific pressure through the activation furnace where high surface area and

complex pore structure are formed. The carbonization stage employs inert gas like nitrogen or argon to remove the volatile matters and/or impurities and produce enriched carbon samples. After purified by inert gas like N_2 and Ar, the carbonized sample will react with CO_2 to complete the physical activation process under high temperature (up to 1273 K) as illustrated in below equations (Xu et al., 2018):

$$C + CO_2 \rightarrow 2CO \; \Delta H = +173 \, kJ/mol$$

$$C + H_2O \rightarrow CO + H_2 \; \Delta H = +132 \, kJ/mol$$
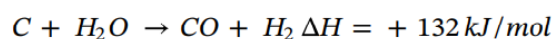
The chemical activation process involves impregnation of raw materials with a dehydrating agent before the carbonization/activation process is used broadly to overcome the main drawbacks of the physical activation of energy requirements and low carbon yield to match the industrial specifications scale (20–40 wt.%) (Xu et al., 2018).

Activated carbons are low-cost adsorbents with a fast adsorption process and low desorption energy penalty as well as high thermal stability (Seo and Park, 2010). However, they have several disadvantage under post-combustion capture conditions, like 1) the activated carbons are highly sensitive for moisture that water negatively affected the carbon dioxide adsorption at low pressure; 2) low CO_2 selectivity with negative impacts of the presence of impurities (Wang et al., 2008, Tong et al., 2017); and 3) poor mechanical strength that may cause high attrition in the bed and more adsorbents replacement from negative impacts on cost perspective consideration (Wang et al., 2014).

- **Carbon molecular sieves adsorbents (CMS)**

CMSs are microporous carbon adsorbents with molecule-sized pores by synthesized through four steps 1) carbonization of raw material, 2) surface activation, 3) deposition usually via chemical vapor, and 4) subsequent carbonization of aromatic molecules (Abd et al., 2020). Its property of narrow pore size distribution which leads to a high adsorption performance and selectivity on carbon dioxide adsorption (Foley, 1995). Although the carbon dioxide uptake decreased as the temperature increased, CMSs was still reported that they have equivalent adsorption capacity with other carbon-based adsorbents or even better (Silvestre-Albero et al., 2011).

- **<u>Graphene</u>**

It is basically a flat single layer of sp2 hybridized carbon atoms, densely packed into an ordered two-dimensional honeycomb network (Abd et al., 2020). Since 2012, many literature researches have been carried out to investigate the employing of graphene/graphite as carbon dioxide adsorbent owing to the large active surface area and low preparation cost. Results showed that graphite has a low affinity for carbon dioxide to some extent and low surface area in comparison to other carbon-based adsorbents (Zhang et al., 2011). Besides, the CO2 uptake reduces as the temperature increases due to the exothermic nature of the adsorption process, low selectivity and recyclability are challenge for this material as well (Chowdhury and Balasubramanian, 2016).

- **<u>Carbon nanotubes</u>**

Carbon nanotubes are generally considered as efficient adsorbent for carbon dioxide separation. Research on comparison the performance of purified single walled carbon nanotubes adsorbent to activated carbon adsorbent (See Figure 8) to demonstrate that the nanotube adsorbent exhibited double carbon dioxide adsorption capacity than activated carbon (Cinke et al., 2003). But the CO_2 uptake decreases as temperature increases from study reported (Su et al., 2011).
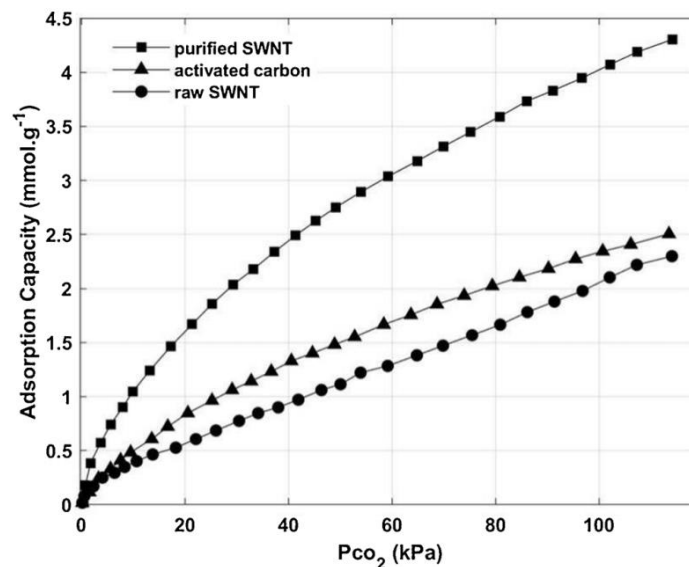
Figure 8: Comparison of carbon dioxide uptakes of arrived carbon and carbon nanotubes adsorbent (Cinke et al., 2003)

2.4.2. Non-Carbonaceous adsorbents

In addition to carbon-based adsorbents, there are many non-carbon-based materials that have been extensively studied in post-combustion carbon capture technology, such as zeolites, MOFs, silica materials, etc., which are considered to be better solid adsorbents for post-combustion carbon dioxide capture application..

- **Zeolites**

Zeolites are available naturally microporous (pore size is range from 0.5 to 1.2 nm) crystalline framework materials, which consisting of a chain of channels to capture CO_2 (Chester and Derouane, 2009). As it can also be synthesized in the research laboratory, zeolites have been broadly studied for carbon dioxide removal in the interest of their molecular sieving impact and the robust dipole–quadrupole (electrostatic) interactions between carbon dioxide and alkali metal cations in the zeolite frameworks (Zhang et al., 2008).

Common types of synthesized zeolites for carbon dioxide adsorption are well known as zeolite A, X, and Y, natural zeolite like chabazites, ferrierites, and mordenites are also applied (Siriwardane et al., 2001, Siriwardane et al., 2003). Researches on the carbon dioxide adsorption capacity and selectivity by comparing G-32H activated carbon, zeolite 13X, and 14A molecular sieves conducted that 13X performed relatively better CO_2 capacity than the ACs adsorbents, with high selectivity in the mixture gases of N_2 and H_2 (Siriwardane et al., 2001). However, zeolite adsorbents of carbon caputure is typically employed at high regeneration temperature (573 K) and pressure (> 200 kPa), it turns in therefore a huge energy loss (Harlick and Sayari, 2006). Besides, small content of moisture could greatly reduce the CO_2 loading of zeolites adsorbent due to its high H_2O affinity, formed film blocked the access for carbon dioxide molecules turn in less CO_2 uptake (Chester and Derouane, 2009).

- **Metal-organic frameworks (MOFs)**

Metal-organic frameworks are solid adsorbents materials that are produced by the combination of metal ions linked by coordination bonding as shown in Figure 9. Two types are classified in the metal-organic frameworks: 1) Rigid MOFs with strong frameworks that create permanent pores similar to zeolite materials; 2) Dynamic MOFs with soft frameworks whose structures change by external impacts like pressure, temperature, and guest molecules (Li et al., 2011). Researched conducted that the high heat of adsorption in some MOFs like HKUST-1, MIL-

100/101, and the MOF-74 group can be achieved to create a bare-metal site lining the pore by liberation of a coordinating solvent (typically water) molecule (Plant et al., 2007, Llewellyn et al., 2008, Caskey et al., 2008). Generally, metalorganic frameworks possess high capacity to adsorb carbon dioxide at high pressures, whereas their adsorption capacity, at atmospheric pressures, is lower in comparison to other physical adsorbents (Abd et al., 2020).
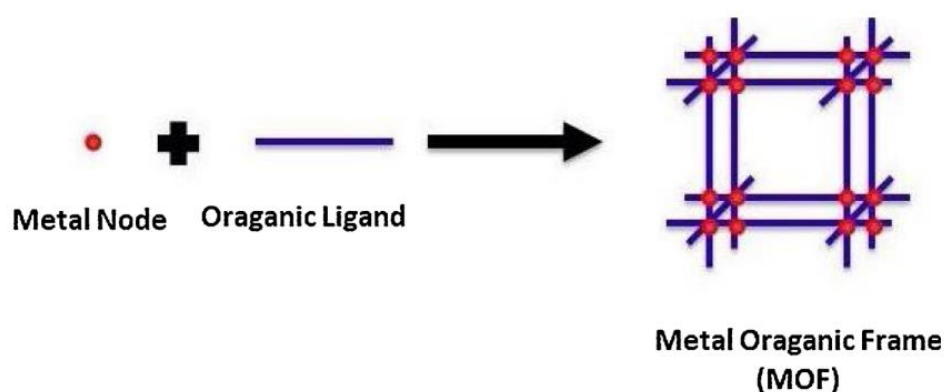
Figure 9: Graphical diagram of producing MOFs materials (Abd et al., 2020)

- **Silica**

Mesoporous silica materials commonly are considered as a thermal and chemical stable material with tunable structure, its morphological flexibility and porosity allows these nanoparticles be able to functionalize with suitable organic and inorganic groups (Kumar et al., 2017). Large micropores and mesopores on silica surfaces is one of the advantages to be utilized as an adsorbent in CO_2 capture and the adsorption can be carried out with moderate temperature at 298 K and 1 bar. Therefore, lots of studies has been employed on Mesoporous silica materials, among of them, there are two classical types widely applied as support material for post-combustion CO_2 capture technology as:

- **SBA-15** (Santa Barbara Amorphous No. 15)

  An attractive mesoporous silica material having well-ordered and relatively large hexagonal pores in the range of 4.6−30 nm (Kruk et al., 2000).

- **MCM-41** (Mobil Crystalline Material No. 41)

  it constitutes a structure of the class of ordered mesoporous silica materials with uniformly ordered honeycomb like pores with diameter in the range of 2–6.5 nm (Trewyn et al., 2007).

However, silica as an adsorbent without any modification is not recommended as the regeneration difficulties of silica nanoparticles with huge energy penalty during CO_2 desorption turns in undesirable economic feasibility as a distinct disadvantages, concluded by researches (Lee and Park, 2015). Therefore, most of the research efforts on silica-based adsorbents are mainly interested in modifying various types of silicas and deploying appropriate amines types. Heretofore, many studies reported the use of silica materials-based adsorbents for carbon dioxide (Abd et al., 2020).

2.4.3. Comparison of various physical solid adsorbents for carbon dioxide adsorption

It is has been concluded by many researches that the adsorption of carbon dioxide using solid adsorbents is a promising technology that can minimize the energy requirements for the regeneration process compared to the other commonly used absorption capturing technologies, and the efficient solid adsorbents used in post-combustion CO_2 capture process should offer high thermal stability, good mechanical strength, high selectivity, low synthesis cost, resistance in humid conditions (Abd et al., 2020). Pro and cons of various solid adsorbents summarized in Table 1 stated that neither carbon-based adsorbents nor non-carbonaceous (zeolites and MOFs), their features cannot fully satisfy the CO_2 capture condition from flue gas of post-combustion power plant with low CO_2 pressure after desulfurization, low temperature and humid condition, to achieve high CO_2 adsorption performance and economic efficiency (Abd et al., 2020).

Table 1: Comparison of pro and cons among carbon-based adsorbent, zeolites, and MOFs for carbon dioxide adsorption

Feature	Carbonaceous adsorbents	Zeolites	MOFs
Major application	High pressure CO_2 adsorption	H_2 enrichment	CO_2 seperation
CO_2 selectivity	Medium	Low	High
CO_2 capacity	Better at high pressure but reduce at low pressure	Medium	High
Stability (humid condition)	Stable	Unstable	Unstable
Materials cost	Acceptable cost	Low cost	Expensive
Advantages	• High conductivity ▪ High stability • Large surface area and pore volume, • Light weight	• Large micro-/mesopores • Medium CO_2 uptake at ambient conditions • Low energy penalty	• Ability of tuning the pore volume • High surface area
Disadvantage	• Low adsorption and regeneration temperatures • Low adsorption capacity among those three tye sold sorbents	• High affinity with water • High energy penalty • Difficult readiness	• Low CO_2 uptake at low pressures • Low economic efficiency • Difficulty on synthesis • Sensitive to humid • Morphological destroyed at high temperature

2.5. Amine functionalization on mesoporous solid adsorbent for CO_2 capture

the capability of capturing CO_2 by amino groups as well as the stable and high porosity to promote accessibility of functional groups and adsorption kinetics can be enhanced by loading or grafting amine species into or onto the inner mesopore surface of mesoporous materials (see Figure 10, as the N-containing groups can be designed and fabricated through loading or grafting linear or hyperbranched amine group into the mesopores. Amine modified adsorbents are acknowledged with high CO_2 adsorption capacity, fast adsorption kinetics, as well as easy regeneration with stable cycling performance recently (Azmi and Aziz, 2019).

According to the synthesis methods, amine-based materials are of different types, as shown in Figure 10 for instance the amine functionalization on mesoporous silica (Modak and Jana, 2019). The pros and cons of each synthesis method and their applications are summarized in Table 2.

(i) **Class 1 (Impregnation)** materials which are prepared by impregnation of amines into the pores,

(ii) **Class 2 (Grafting)** consisting of amines which are covalently bonded to the walls of porous materials, and

(iii) **Class 3 (In-situ polymerization)** where amine monomers are in-situ polymerized to polyamines inside the framework.
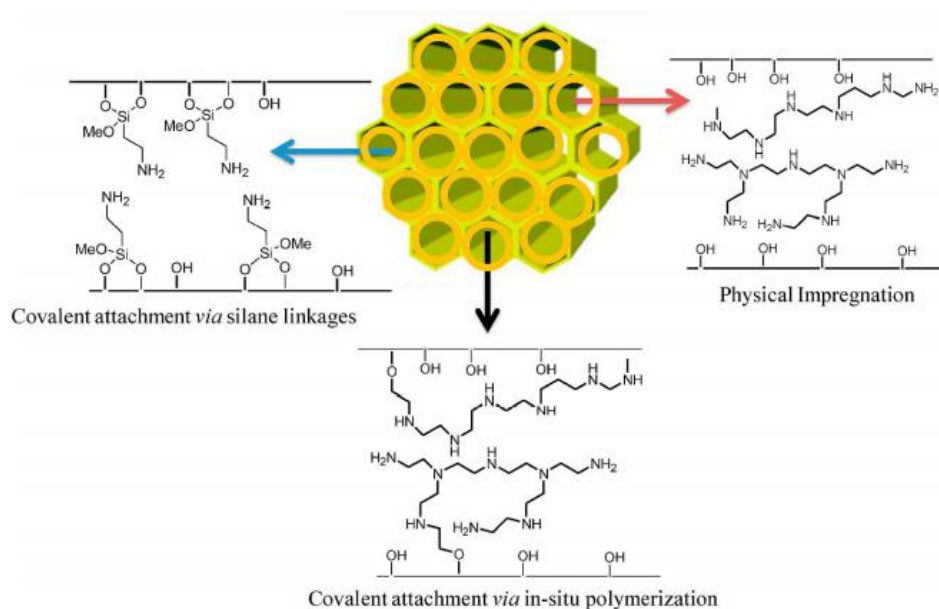
Figure 10: Schematic representation of the formation of several amine-functionalized mesoporous silica
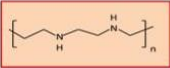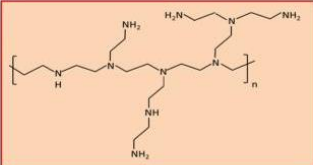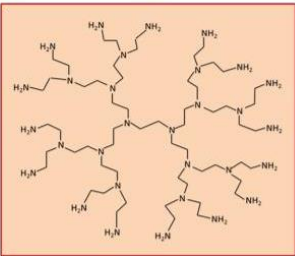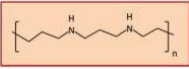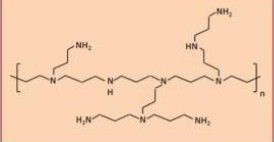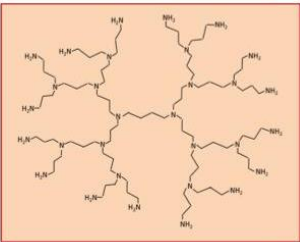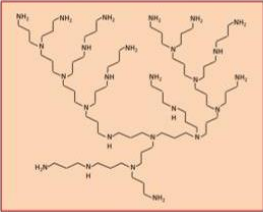
Table 2: Summary of N-loading methods onto adsorbents and their characteristics (Hu et al., 2020)

Method	N source	Advantages	Disadvantages
Impregnation	Monomeric or polymeric amine, amino acid, amino-containing ionic liquid, other amino-containing organic material except alkoxysilanes	• Higher amine loading than grafting • Usually higher CO_2 adsorption capacity than grafting sorbents • Repeatable synthesis method • Mild synthesis conditions	• Weak connection between aminomaterial and substrate mate • Weak thermal stability • Surface amine aggregation with high amine loading
Grafting	Amine-containing alkoxysilanes	• Linkages between amino-material and substrate material are bonds • Stable under a higher temperature (above 200 °C) • Better amine dispersion degree • Repeatable synthesis method • Mild synthesis conditions	• Amine loadings largely subject to substrate's silanol group number • Usually lower CO_2 adsorption capacity than impregnation sorbents
In-situ polymerization	N-containing precursor	• One-step synthesis method • Reported adsorbents usually have high adsorption performance	No regular synthesis method

Modifying of mesoporous silica-based materials with amines can efficiently enhance the adsorption capacity for CO_2 by virtue of the primary and secondary amines have a high affinity for carbon dioxide and react strongly by hydroxyls on the surface as following (Lee and Park, 2015). Typical amine chosen for Mesoporous silica materials modifications are summarized as Table 3 given below.

Table 3 - Details of polymeric amines reported for CO_2 capture applications (Varghese and Karanikolos, 2020)

| 3. | Polyallylamine | | • Primary amine at the side chain.
• Better thermal and oxidation stabilities.
• Capable to bind strongly with other material surfaces. |
| 4. | Polyaniline | | • Secondry amines in the backbone.
• Superior thermal stability. |

Commonly, flue gas of power plant combustion consists high amount (up to 15 vol%) of water (Xu et al., 2004). For instance, silica-based adsorbent is rich with OH groups usually with water affinity during adsorption which causes the moisture content to increase, in other words, H_2O molecules will occupy the active site of silica surface and turns in reduction of the CO_2 capture performance of the silica-based adsorbent. Theoretically, by elevating the adsorption temperature, the water molecules expand and evaporates away from the support. Therefore, the accessibility of CO_2 to support surface increases, as displayed in Figure 11 (Azmi and Aziz, 2019).
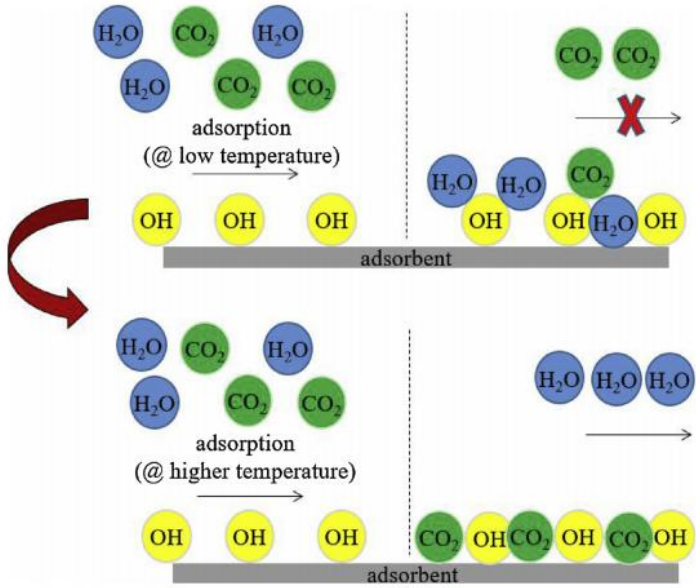
Figure 11: Illustration of water impacts on CO_2 adsorption capacity

To be noticed, the adsorption temperature tuning will impact on overall adsorbents properties and is limited by power plant flue gas condition. With amine modification on mesoporous silica adsorbents, theoretically, the water content through carbon dioxide capture should enhance the amine adsorption performance because of the formation of carbonates and bicarbonates. However, due to the competitiveness of CO_2 and water adsorb, the moisture content can turn in amine leaching (Quang et al., 2017).

2.6. PEI-modified mesoporous silica materials chosen for post-combustion CO_2 capture studied further in this thesis research

Due to the advantages of high surface area, large pore volume, tunable pore size and excellent mechanical stability, many researches on CO_2 capture by silica materials mainly on the following three aspects: 1) novel synthesizing method of amine modified silica composite materials; 2) development of new pore structures silica adsorbents; and 3) evaluation of CO_2 adsorption performances of various silica composites (Lee and Park, 2015, Choi et al., 2016). As above mentioned, silica is not recommended without modification due to huge energy requirement for its regeneration. Therefore, with modifications methods like amine functionalization and enhancing the textural properties improve the carbon dioxide adsorptive performance, mesoporous silica nanoparticles with narrow pores distribution with carbon dsioxidephilic heteroatoms are compatible with carbon dioxide removal technologies, to exhibit competitive CO_2 capacity with good selectivity and stability for achieving scaled-up industrial application for realizing post-combustion carbon dioxide capture technology.

Compared with as-synthesized silica, amine-impregnated porous silica not only have higher CO_2 adsorption kinetics, but also showed advantages of high amine loading (Chen and Bhattacharjee, 2017). Besides, the CO_2 capture performance of the amine-impregnated mesoporous silica nanoparticles is also closely related to the properties of introduced amine types, which should have a high boiling point to prevent amine leaching and high N concentration to achieve a higher CO_2 capture capacity (Subagyono et al., 2011), therefore PEI becomes one of the most used for Mesoporous silica materials amine modification worldwide (N contents of ca. 33%) and high boiling point (see Table 3).

The temperature of the post-combustion CO_2 flue gas usually falls in the range of 50–75 °C (D'Alessandro et al., 2010), which is close to the optimal temperature range of CO_2 capture by PEI-modified Mesoporous silica materials at 75 °C, as researches concluded. At this adsorption temperature, the improved mobility of amine species and the facilitated diffusion of CO_2 within the pore channels lead to a high CO_2 uptake of PEI-modified Mesoporous silica materials (Subagyono et al., 2011).

3. THEORY

3.1. Synthesis mechanism for mesoporous silica materials

Mesoporous silica materials are synthesized by modified Stober's method, i.e., "sol-gel process", was widely used. Sol-gel chemistry is a mature developed process for many inorganic materials syntheses. Theoretically, reaction involves the alkoxide monomers hydrolysis and condensation into a colloidal solution (normally called as 'sol'), which would be aging to form an ordered network (normally called as 'gel') of polymer (Danks et al., 2016).

A typical sol-gel process can be accomplished in basic or acidic conditions according to the catalysts. The alkoxide group gets hydrolysed in aqueous environment first and it is experimentally proved that the hydrolysis rate of silicon precursor is faster in basic conditions compared to acidic. Subsequently condensation followed by the hydrolysis step, the schematic representation of the hydrolysis and condensation reactions are shown in follow equations (Danks et al., 2016):

$$\text{Hydrolysis}: Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$$

$$\text{Polycondensation}: \quad \equiv Si - OH + HO - Si\equiv \rightarrow \equiv Si - O - Si\equiv + H_2O$$
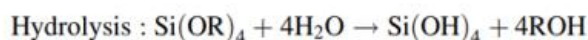
Sol-gel process used in this thesis research mainly based on action of the micelle which forms organic-inorganic phase between surfactant and target production, in other words the synthesis of Mesoporous silica materials occurs wherein hydrolysis and condensation of silica on the surface of surfactant micelles takes place. The liquid silica (e.g, TEOS) transforms to solid silica. Due to the aggregation by weak intermolecular or intramolecular interaction creates a certain structure of space, as illustrated in Figure 12 (Agudelo et al., 2020).
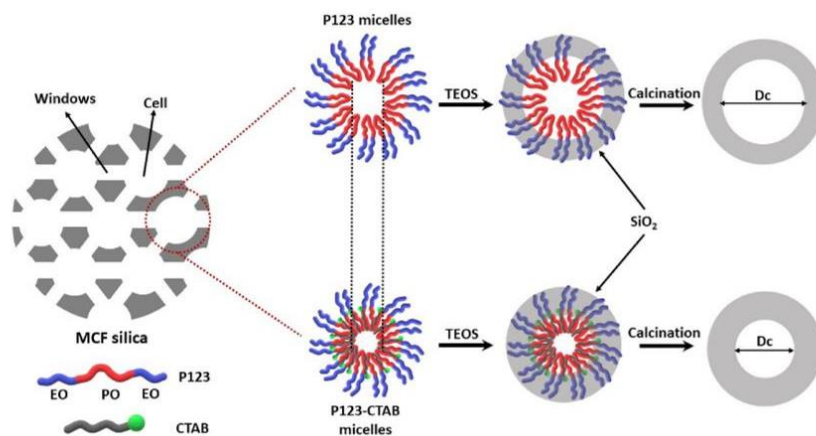
Figure 12: Scheme of the formation of Mesoporous silica materials with and without CTAB with TEOS as silicon precursor

3.2. Polyethylenimine (PEI) impregnation to Mesoporous silica materials

Due to the easy synthesis and large amount of amine introduced to the silica support, amine–modified porous silica synthesized by physical impregnation method have been the most practical adsorbents for large-scale gas separation applications in all types of amine–silica combinations (Choi et al., 2009).

After dispersing the amine into methanol evenly by stirring, a certain amount of porous is added into the amine solution continuously while stirring usually at room temperature for a certain time to help the amine molecules disperse into the pores of the support materials (Ahmed et al., 2017), as illustrated in Figure 13. The adsorption sites for capturing CO_2 are formed by the bond between amine molecules, the surface and within the pores of the support. The loading of amine on the support substrate depends on the pore volume of the support, in other words, functionalized adsorbents with higher adsorption capacities can be obtained from porous supports with large pore volumes (Chen et al., 2016). As there is no substantial chemical bond between the dispersed amines and the supports, the as-obtained adsorbents have similar thermal stabilities to the origins of the amines (Anbia et al., 2012).
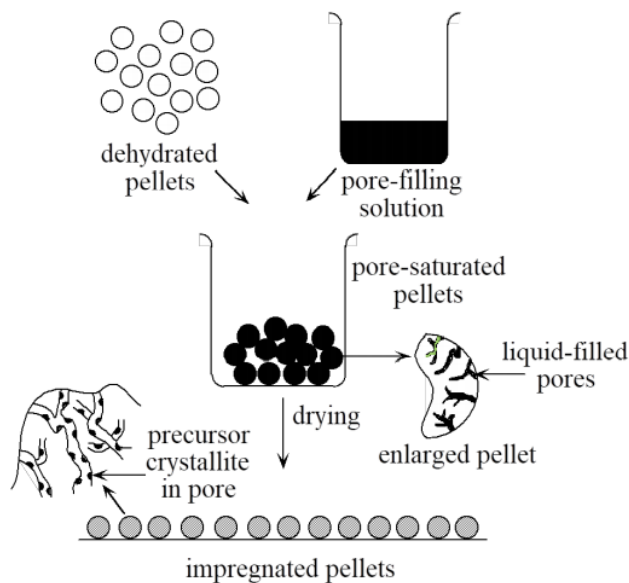
Figure 13: Physical impregnation illustration

3.3. CO$_2$ caputure by PEI-modified Mesoporous silica materials

It is understood that the interaction mechanism of CO$_2$ with the amine-functionalized mesoporous silica sorbents is of paramount importance for the development of prospective adsorbents, which will turn in a reduction of emitting the anthropogenic emissions. Based on the absorption mechanism achieved by aqueous amine solutions, research on the adsorption mechanism of CO$_2$ over amine-based mesoporous silica and its performance of CO$_2$ capture were exploring over decades. Researches demonstrated that CO$_2$ was captured in the forms of ammonium carbamates through the two-step zwitterion mechanism in case of primary and secondary amines (Caplow, 1968). CO$_2$ was firstly attracted by the lone electron pair of the nitrogen atom giving rise to the formation of the zwitterionic intermediate which was then converted into an ammonium carbamate ion pair through deprotonation by a base molecule that is usually a neighbouring amine to the zwitterionic intermediate (Sartori and Savage, 1983). Carbamate could not be formed but leading to the production of bicarbonate once the amine was sterically hindered or tertiary (Davran-Candan, 2014, Yamada et al., 2011). Figure 14 indicates a schematic of functionalization of porous materials with polymeric amines and their CO$_2$ capture.
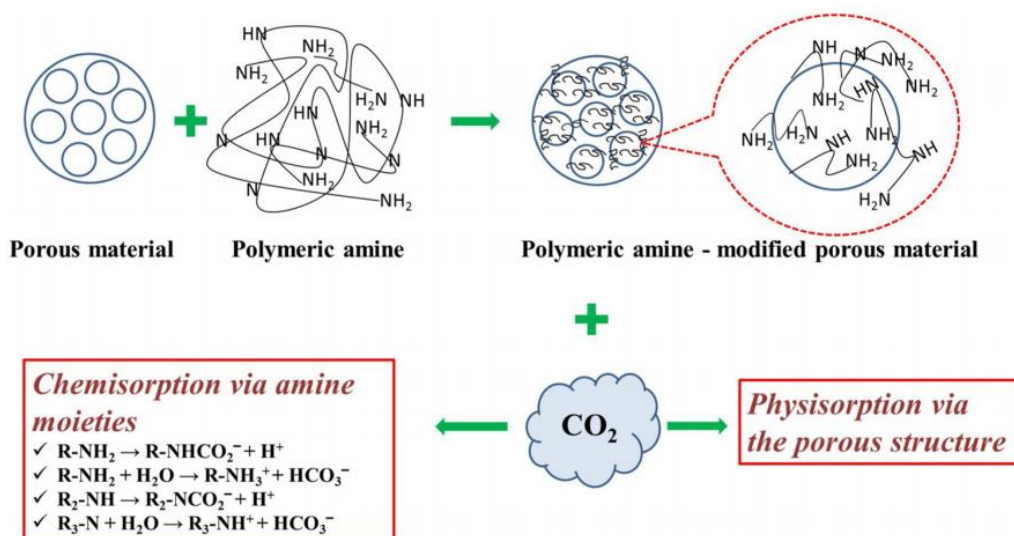
Figure 14: Schematic of functionalization of porous materials with polymeric amines and their CO_2 capture action (Varghese and Karanikolos, 2020)

3.4. Characterization

3.4.1. Nitrogen adsorption and desorption

Nitrogen adsorption and desorption is commonly understanding to be applied for analysing materials' textural properties such as surface area, pore volume, pore size distribution and etc. by most using commonly the Brunauer-Emmet-Teller theory. According to the BET method, the surface area is obtained by measuring the volume of the gas adsorbed at the surface, at a constant temperature (77K liquid nitrogen), as a function of the equilibrium pressure. The pressure is demonstrated as a relative pressure: actual pressure p divided by the vapor pressure. Meanwhile, pore diameter, volume and distributions are determined by using the Barrett-Joyner-Halenda (BJH) method. Desorption data given by BJH provide a relationship between volume of adsorbed nitrogen and the monolayer coverage of adsorbed volume at a given partial pressure. Meanwhile, the Kelvin equation can be used to determine the pore size distribution in terms of the capillary condensation phenomena happened in the pores of porous material during the desorption isotherm process. (Webb and Orr, 1997)

3.4.2. Scanning Electron Microscope

Scanning Electron Microscope (SEM, shown in Figure 15), as an electron microscope, is usually applied to study the morphology and topology of the sample by obtaining an image of the objective. The high-resolution nanoscale images are achieved by scanning the sample with a high-energy beam of electrons. As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by one or more detectors to form images which are then displayed on the computer screen. When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Many signals, like secondary electrons and X-rays, are produced as a result of this interaction inside the sample. (instruments, 2021)
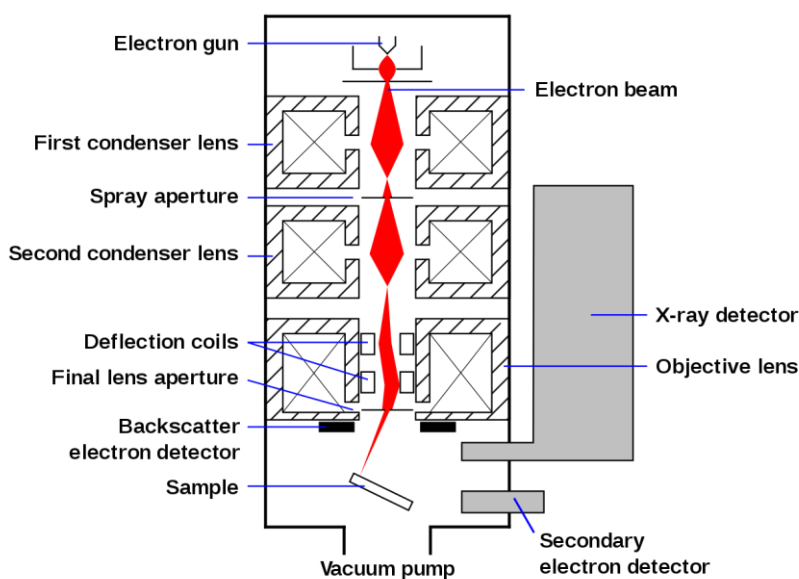
Figure 15: Schematic of an SEM

3.4.3. Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) is commonly used to characterize the CO_2 adsorption capacities and thermal stability of solid adsorbents by measuring sample weight change with temperature variation. Therefore, mass spectrometer is usually combined with TGA. Figure 16 indicates a typical configuration of TGA. CO_2 partial pressure of inlet gas could be adjusted by the mixing percentage of CO_2 and N_2 for investigating different adsorption capacities of solid

adsorbent, meanwhile pure N_2 is used for regeneration purpose in this thesis research. (Zhao et al., 2018, Zhang et al., 2014)
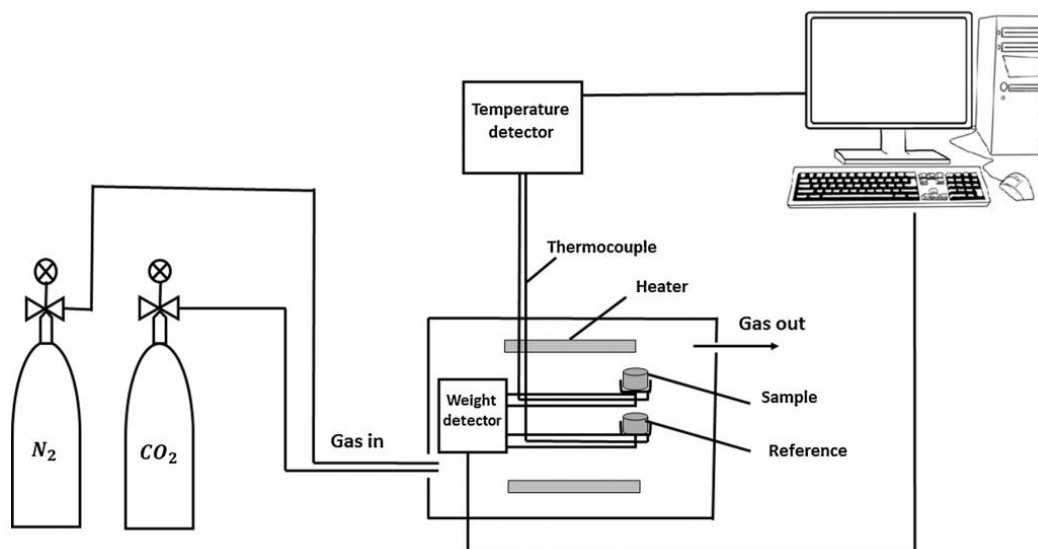
Figure 16: Schematic diagram of the TGA set-up

4.   EXPERIMENTS

4.1. Synthesis of mesoporous silica nanoparticles

Synthesis of mesoporous silica materials were carried out according to two-step protocol, as previously reported (Ma et al., 2003) by using chemicals from Sigma-Aldrich which are tetraethyl orthosilicate (TEOS, 98%) as the silica source, poly(ethylene oxide)–block–poly(propylene oxide)–block–poly(ethylene oxide) (P123, Mw=2900) as the template, cetyltrimethylammonium bromide (CTAB, 99%) as the cosurfactant, and ethanol (EtOH, 96%) as the cosolvent.

A molar ratio of TEOS: 1, P123: 0.044, CTAB: 0.122, HCl: 2.67, EtOH: 9.5 and H_2O: 116 was used in the synthesis. Thus, 1.7 g of triblock copolymer P123 and 0.6 g of CTAB were dissolved in a solution formed by mixing 3 ml of HCl (37%), 26 ml H_2O and 7.5 ml EtOH to obtain a homogeneous solution. 3 ml of TEOS was added in the aqueous solution at room temperature under magnetic stirring of 30 min. In the second step, the solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 80 °C for 5 h, and then kept at a higher temperature at 130 °C for 12 h. The product was cooled down to room temperature and then filtered and washed with ethanol several times and dried in oven at 90 °C for 24 h. The white powder was finally obtained after calcination in air at 550 °C for 5 h for template removal.

4.2. Amine-impregnation of synthesized mesoporous silica samples

Amino functionalisation of mesoporous silica samples was carried out by a typical wetness impregnation method described in previous chapter. Polyethylenimine (PEI, branched, Mw=600, Sigma-Aldrich) was used. The amine source was mixed with methanol and stirred during 30 min. Then, mesoporous silica samples were added to the solution with variable weight ratio of Amine/Mesoporous silica samples (30 ~ 60 wt.%) and stirred at 40 °C in a rate of 700

rpm for 2 h. The obtained amino-functionalised mesoporous silica samples were sealed and stored at room temperature for subsequent characterization.

4.3. Characterization

4.3.1. Nitrogen adsorption and desorption

Nitrogen isotherms were carried out using an automated gas adsorption analyser Tristar 3000 (Micromeritics, Instrument Co) at 77 K. Prior to the analysis, the Mesoporous silica samples and PEI-modified Mesoporous silica samples were degassed in VACPREP 061 unit at 200 °C and 60 °C overnight respectively. BET surface area was obtained from the adsorption branch in the relative pressure range between 0.05 and 0.3. Pore size distribution was calculated by BJH method.

4.3.2. Scanning electron microscope

The morphology and topology are studied using the Hitachi S-5500 in lens cold field emission scanning transmission electron microscope (S(T)EM), with a secondary electron (SE) detector. The acceleration voltage was set from 7 kv to 30 kv and beam current was set from 7 μA to 20 μA for different samples. All the samples were dispersed in deionized water and then dropped on a silicon wafer for test preparation.

4.3.3. Thermo gravimetric analysis

The measurements of CO_2 uptake capacity by the synthesized PEI-modified Mesoporous silica samples were carried out using the thermogravimetric analysis technique (TGA Q500 V6.7). In each run, about 10 mg of one the synthesized adsorbents were placed in an alumina oxide pan and, then, the adsorbent was degassed at 100 °C using a stream of pure N_2 gas flowing at 50 mL/min. Once the weight of the sample reached a steady value (i.e., all water is removed), the temperature was dropped to 75 °C and left to equilibrate. After the stabilization of the adsorption temperature at 75 °C after 20 min, shifted gas inlet valve to keep CO_2 partial pressure of 5 vol%, and the flow rate of CO_2 was kept constant at 50 mL/min. Then CO_2 desorption was carried out at 75 °C in pure N_2 gas flowing at 50 mL/min.

Two protocols of contact time between CO_2 and adsorbents was used in this thesis research for determine optimum and practical CO_2 uptake of synthesized adsorbents respectively. For optimum condition, the adsorption of CO_2 was monitored in time of 100 min contact until the adsorption approached equilibrium with 2 cycles. While the practical condition chosen a 10 min contact time with CO_2 but 10 cycles running to analyse the stability of adsorbents as well.

5.   RESULT AND DISCUSSION

5.1. Synthesis of mesoporous silica supports

To ensure that the adsorbent could be modified or improved without damaging its original structure, the targeted adsorbent would like to be synthesized in this thesis study should be mesoporous silica supports with high surface area, high pore volume with narrow distribution as well as with rigid morphology structure. The synthesis methods chosen was conventional sol-gel process. To achieve better overall performance on CO_2 capture performance after amine impregnation, composition of solution and operation condition of synthesis was tuned to realize targeted adsorbents that could facilitate more adsorption sites for CO_2 component.

According to different composition of solutions and/or operation condition, synthesized materials list in Table 4 were denoted as naming rule shown in Figure 17.

Table 4: Experimental parameters of mesoporous silica samples for pore regulation

	TESOS (mL)	P123 (g)	CTAB (g)	EtOH (mL)	HCl (mL)	H_2O (mL)	TEOS : P123 (Molar ratio)	CTAB : P123 (Mass ratio)
40°C_SiO$_2$_1''P123_1/6CTAB	3	0.86	0.15	7.5	3	26	1:0.022	1:6
40°C_SiO$_2$_1''P123_1/3CTAB	3	0.86	0.3	7.5	3	26	1:0.022	1:3
80°C_SiO$_2$_1''P123_1/6CTAB	3	0.86	0.15	7.5	3	26	1:0.022	1:6
80°C_SiO$_2$_1''P123_1/3CTAB	3	0.86	0.3	7.5	3	26	1:0.022	1:3
80°C_SiO$_2$_2''P123_1/3CTAB	3	1.72	0.6	7.5	3	26	1:0.044	1:3
80°C_SiO$_2$_3''P123_1/3CTAB	3	2.58	0.9	7.5	3	26	1:0.066	1:3
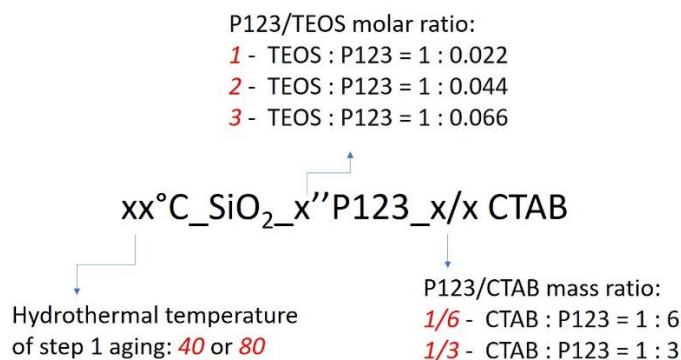
Figure 17: Sample naming rule

5.1.1. Tuning procedure for targeted adsorbent synthesis

Experiments were carried out with two heating steps: 1) 40 °C during 5 hours; 2) 130 °C during 12 hours. Total aging time was during 17 h using P123/TEOS molar ratios and P123/CTAB mass ratio of 0.022 and 6 respectively. According literature researches that the reaction mechanism firstly consists in the quick formation of ordered CTAB micelles, next P123 molecules envelop the pre-formed nucleus to form compound micelles and finally the TEOS is hydrolysed and condensed to form mesoporous silica as illustrated in Figure 18 (Liu et al., 2009). Therefore, it is necessity to add P123 to certain contents which can envelop the CTAB micelles and to carry out the co-assembly with the silicate species for the formation of silica adsorbents.
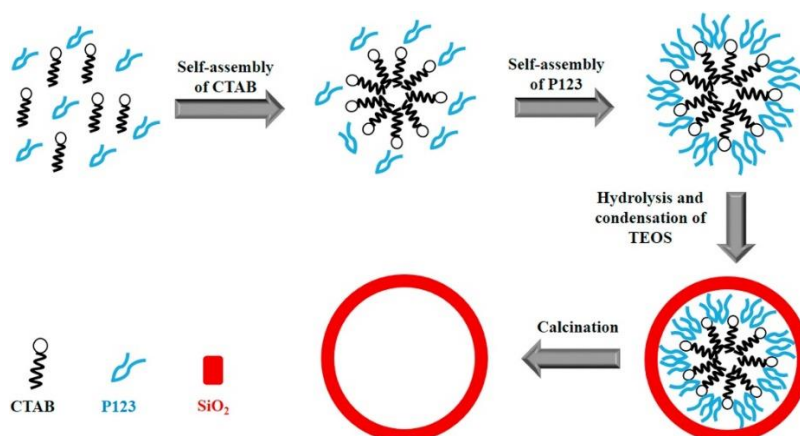
Figure 18: Mechanism for the synthesis of mesoporous silica using P123 and CTAB as template and co-template, respectively.

By identical double the amounts of CTAB while keep same operation condition, two adsorbents 40°C_SiO$_2$_1"P123_1/6CTAB and 40°C_SiO$_2$_1"P123_1/3CTAB was synthesized and characterized their physical properties. BET shown that double CTAB provided an enhancement of surface but no obvious improvement on pore volume at same time.

Mesoporous silica materials normally presented less structural order at low aging temperature because of P123 is a temperature-dependent surfactant and therefore the properties of the mesoporous silica can be tuned by adjusting the operation temperature (Galarneau et al., 2001). The hydrothermal temperature also demonstrated a positive impact on the morphology structure of mesoporous silica adsorbent as previous studies reported (Meléndez-Ortiz et al., 2016).

Thus, two new adsorbents were produced by different protocol, one was kept low P123/CTAB mass ratio of 1/6 as the initial solution composition but increase the first step heating temperature from 40 to 80 °C, whereas another was tuned both on double CTAB amounts together with temperature increasement. Samples obtained from them were named 80°C_ SiO$_2$_1"P123_1/6CTAB and 80°C_SiO$_2$_1"P123_1/3CTAB, respectively. BET results of those two new silica samples shown a fairly improvement on pore volume while maintain a high surface area as well, which proved that high aging temperature has a contribution on improving porosity.

The last step of the mesoporous silica synthesis was templates removal by calcination, i.e. remove P123 (main templates) and CTAB (co-templates). In order to enhance the porosity of finally silica support, a tuning on P123/TEOS molar ratio was carried out based on the synthesis composition and condition for 80°C_SiO$_2$_1"P123_1/3CTAB by double and tribble the amount of P123, respectively. Samples synthesized finally was named 80°C_SiO$_2$_2"P123_1/3CTAB and 80°C_SiO$_2$_3"P123_1/3CTAB. Physical properties of those two samples shown completely opposite results. The surface area, pore volume and pore size were greatly improved by double P123 composition, in contrary, with a tribble P123 input, pore volume and pore size dropped dramatically to a relevant low level. The possible explanation of this phenomenon was that excessive P123 not only did not form more micelles as expected but hindered the subsequent hydrolysis and condensation of TEOS to form mesoporous silica.

Physical properties of each silica samples were summarized in

Table **5**. Figure 19 shown the N$_2$ adsorption–desorption isotherm and pore size distribution curve demonstrated that all silica samples synthesized for structure tuning were mesoporous with a narrow pore distribution.

Table 5: Physical properties of synthesized mesoporous silica samples

	Surface arer $_{BET}$ (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
40°C_SiO$_2$_1''P123_1/6CTAB	668	1.03	5.5
40°C_SiO$_2$_1''P123_1/3CTAB	690	1.09	5.1
80°C_SiO$_2$_1''P123_1/6CTAB	674	1.18	5.5
80°C_SiO$_2$_1''P123_1/3CTAB	672	1.24	5.8
80°C_SiO$_2$_2''P123_1/3CTAB	707	1.47	6.6
80°C_SiO$_2$_3''P123_1/3CTAB	703	1.02	4.7
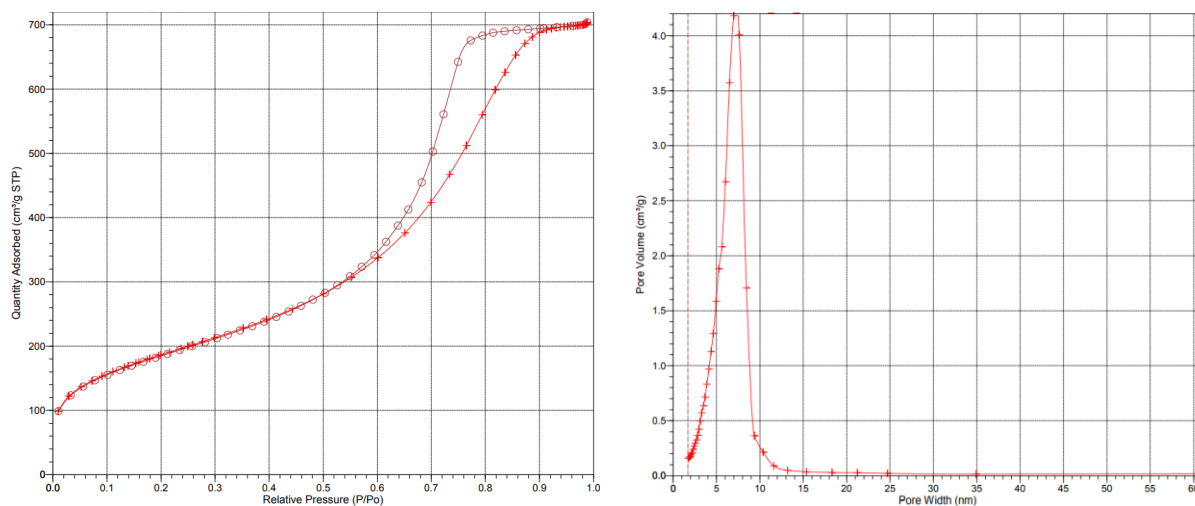
(a) 40°C_Mesoporous silica samples_1"P123_1/6CTAB
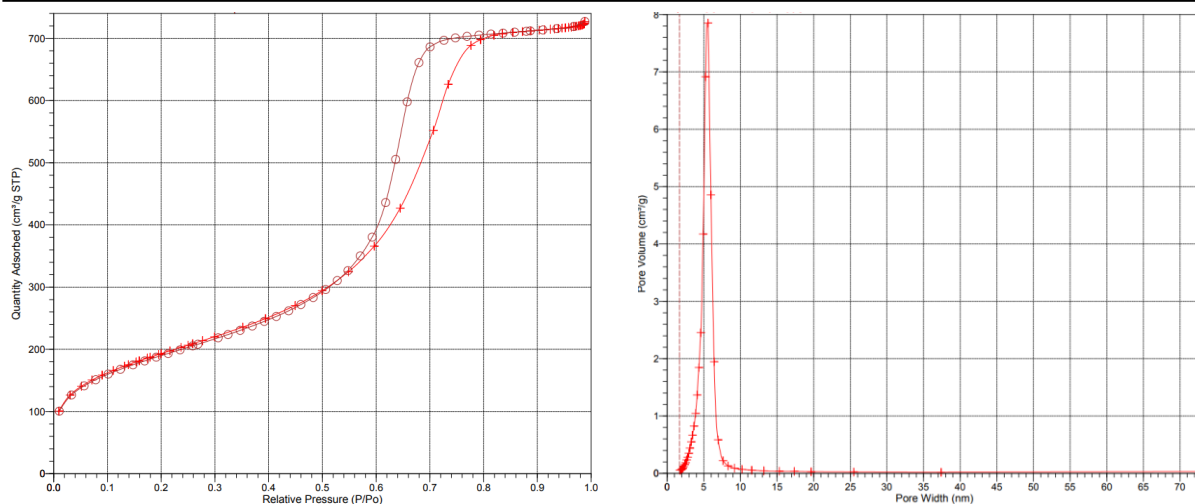
(b) 40°C_Mesoporous silica samples_1"P123_1/3CTAB
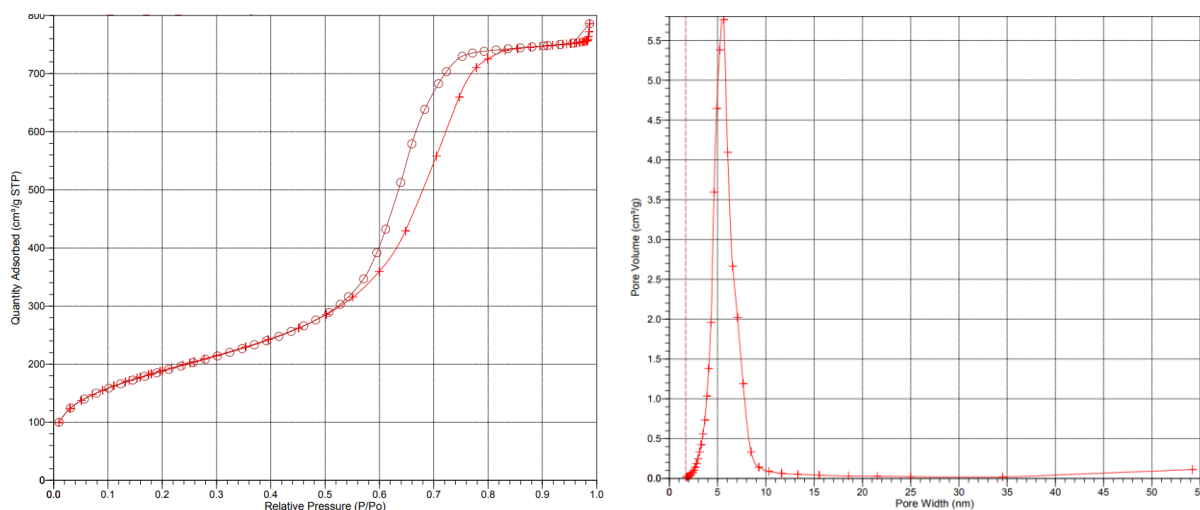
(c) 80°C_Mesoporous silica samples_1"P123_1/6CTAB
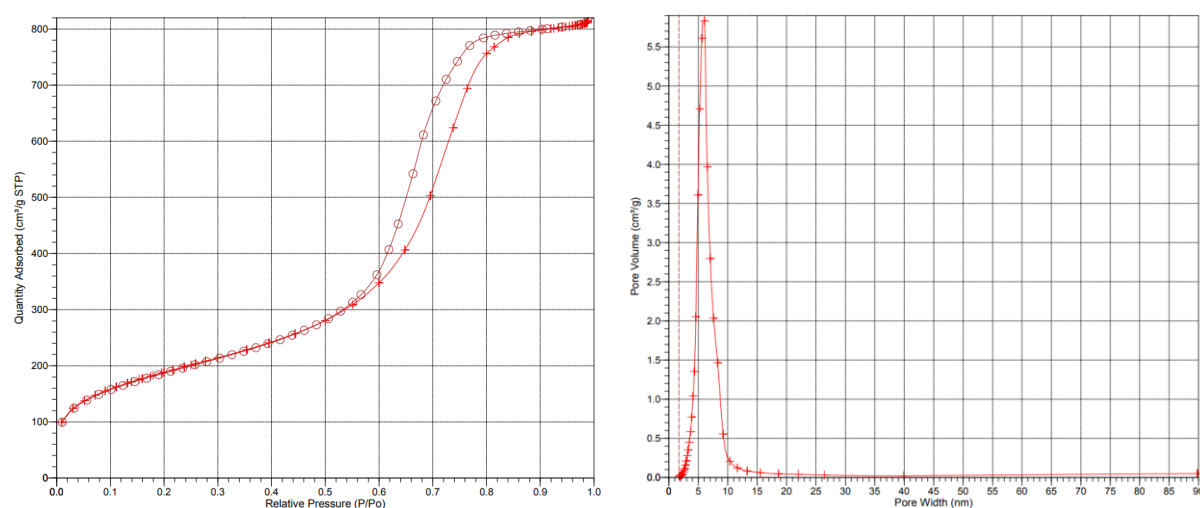
(d) 80°C_Mesoporous silica samples_1"P123_1/3CTAB
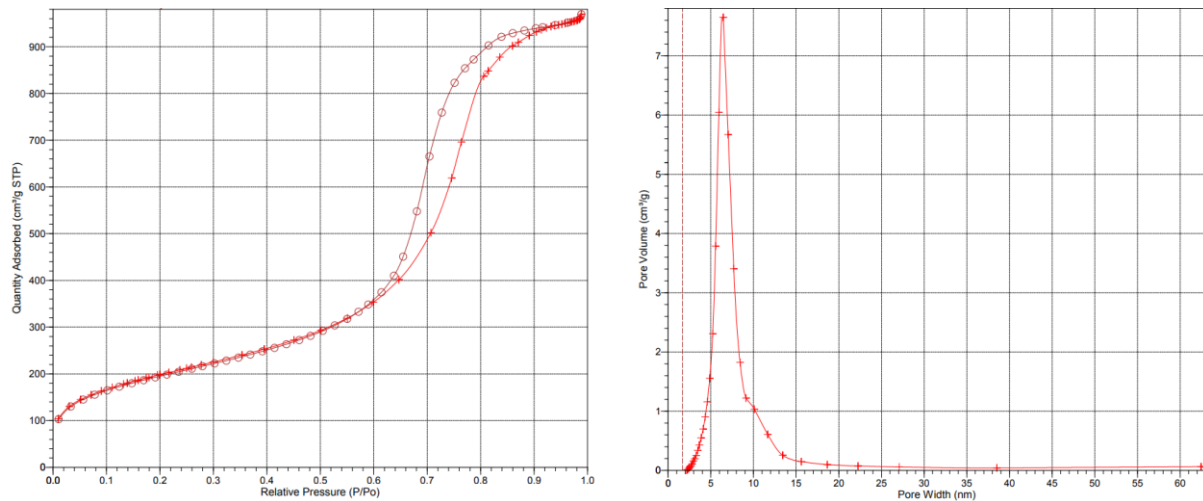
(e) 80°C_Mesoporous silica samples_2"P123_1/3CTAB
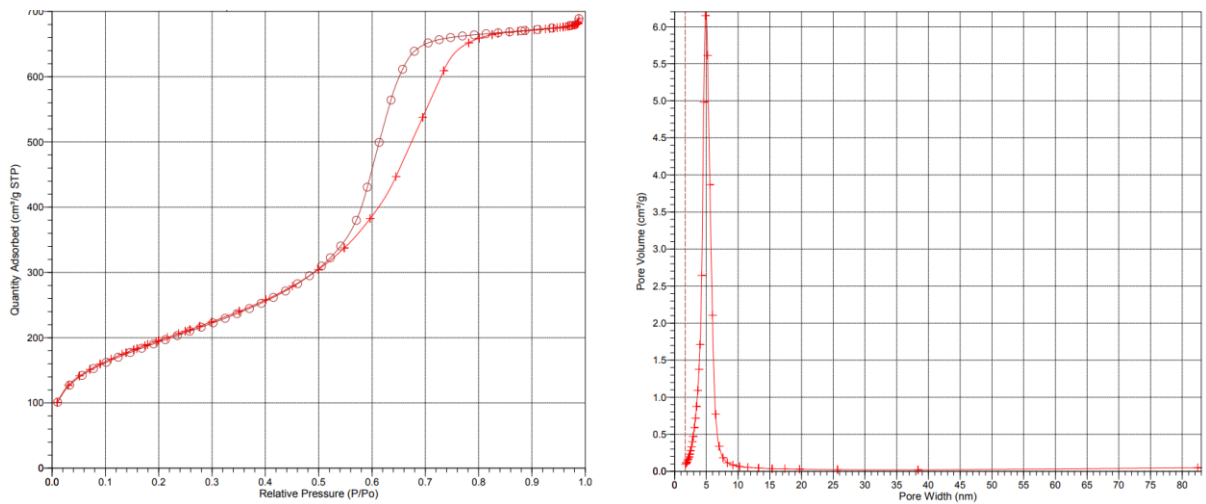
(f) 80°C_Mesoporous silica samples_3"P123_1/3CTAB

Figure 19: Isotherm Linear Plot and BJH Desorption dV/dlog(w) Pore Volume of silica samples synthesized with different solutions and temperature

5.1.2. Morphology studies

Scanning electron microscopy (SEM) images of silica samples are shown in Figure 20. It can be seen that silica adsorbents presented a non-monodispersed spherical morphology with sizes from 4 to 10 µm. Aggregation exited with all samples, but it is not much critical for the synthesis of this thesis studies, as a follow-up work of this research is a pilot test run with pellets in much large sizes.
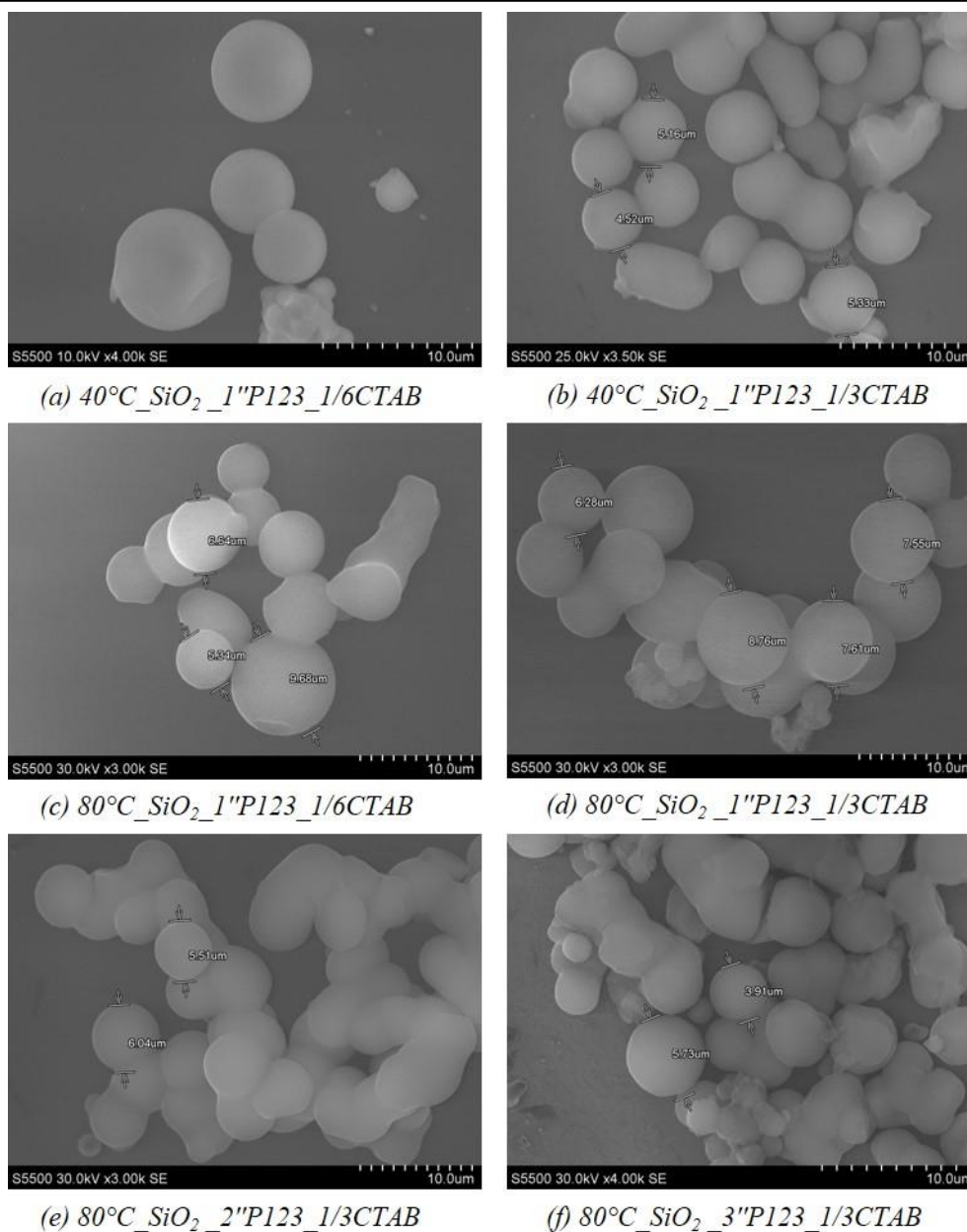
Figure 20: SEM images of silica samples synthesized with different solutions and temperature

5.1.3. Targeted samples chosen for CO_2 adsorption performance tests

As the mesoporous silica of high pore volume with narrow distribution was expected as the targeted samples chosen for followed CO_2 adsorption performance in this study, two samples chosen finally were $80°C\_SiO_2\_1"P123\_1/3CTAB$ and $80°C\_SiO_2\_2"P123\_1/3CTAB$. Yield of those two mesoporous silicas was calculated as per the mass change ratio before and after calcination, which were approximately 55 % and 62%, respectively. The silica samples were denoted as $PEI\_SiO_2\_Vp1.2$ and $PEI\_SiO_2\_Vp1.5$ according to the porosity.

5.2. CO$_2$ adsorption performance of PEI-modified mesoporous silica samples

Once the target samples were determined, the selected mesoporous silica support materials was impregnated by PEI to preferred concentration. According to the pore volume of target support samples at 1.2 and 1.5 cm3/g, the amine weight percentage chosen for loading was set up in a range of 30 to 60 wt.% (the maximum amine contents can be added in synthesized silica support for this thesis studies).

CO$_2$ adsorption performance of PEI-modified SiO$_2$ samples were analysed by using TGA as methods described in Chapter 4.3.3. To comprehensively investigate on their CO$_2$ capture capability, this study adopted two different CO$_2$ adsorption / desorption operating conditions, namely 'Mild conditions' and 'Harsh conditions'. Table 6 listed relevant parameters of the two operating conditions, respectively.

Table 6: CO$_2$ adsorption / desorption conditions test via TGA

	Adsorption			Desorption			Ads./ Des.
	CO$_2$ (vol. %)	Temp. (°C)	Durition (min)	N$_2$ (vol. %)	Temp. (°C)	Durition (min)	Cycles
Mild conditions	5	75	100	100	75	100	2
	5	75	10	100	75	10	20
Harsh conditions	5	75	100	100	120	100	10

5.2.1. CO$_2$ uptake and stability of PEI_Vp1.2 silica samples

The experimental curves presented in regard to the weight change with time of the PEI_Vp1.2 silica samples under mild conditions is shown in Figure 21. Experiments were carried out during 20 h in a combination of two protocols differentiated by contact time between adsorption / desorption gas and solid sorbents. Four different PEI_Vp1.2 samples modified were tested. The number given before PEI is donated as the weight percentages of PEI impregnated to silica supports, for instance 30PEI means that the amine contents in total solid sorbents is 30 wt.%.
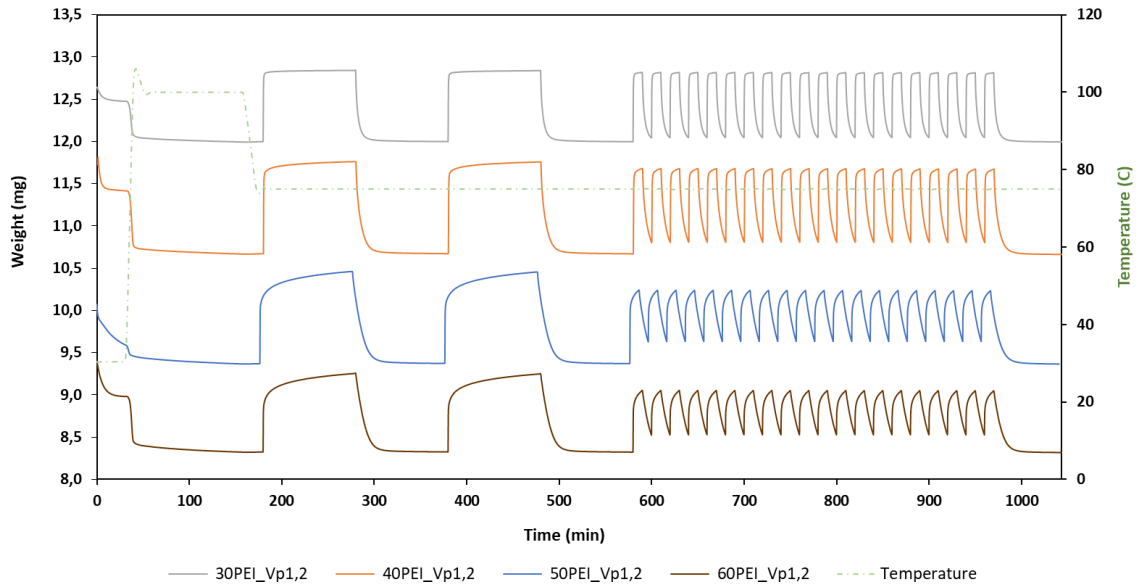
Figure 21: CO$_2$ capture performance analysis of PEI_SiO$_2$_Vp1.2 under mild conditions

The CO$_2$ adsorption capacities of each cycle related to varied PEI_Vp1.2 were calculated as per gram sorbent and per gram PEI, as referred to determine the optimum and practical CO$_2$ uptake of each PEI-modified mesoporous silica material, respectively. For details, please refer to below Table 7, Table 8, Table 9 and Table 10, Stability of each sample with 19 cycles adsorption / desorption was listed as well.

Table 7: CO_2 uptake and stability of 30PEI_Vp1.2 in mild adsorption / desorption condition

Samples: 30 wt.% PEI-modified mesoporous silica with pore volume at 1.2 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1	100 / 100	75 / 75	1.597	5.324	-
2			**1.588**	**5.294**	-
1			1.550	5.167	-
2			**1.460**	**4.866**	**100.00**
3			1.455	4.850	99.66
4			1.453	4.843	99.53
5			1.452	4.839	99.44
6			1.450	4.833	99.33
7			1.450	4.834	99.34
8			1.450	4.833	99.33
9			1.449	4.829	99.23
10	10 / 10	75 / 75	1.448	4.827	99.20
11			1.448	4.828	99.21
12			1.448	4.826	99.17
13			1.448	4.825	99.16
14			1.448	4.825	99.16
15			1.446	4.821	99.08
16			1.446	4.821	99.08
17			1.446	4.821	99.08
18			1.446	4.820	99.05
19			1.446	4.819	99.04
20			1.444	4.814	98.94

Table 8: CO$_2$ uptake and stability of 40PEI_Vp1.2 in mild adsorption / desorption condition

Samples: 40 wt.% PEI-modified mesoporous silica with pore volume at 1.2 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity mmol/g Sorbents	mmol/g PEI	Stability (%)
1	100 / 100	75 / 75	2.317	5.793	-
2			**2.307**	**5.768**	-
1			2.147	5.367	-
2			**1.849**	**4.623**	**100.00**
3			1.844	4.611	99.74
4			1.842	4.604	99.59
5			1.840	4.601	99.52
6			1.939	4.599	99.47
7			1.839	4.596	99.42
8			1.838	4.594	99.38
9			1.837	4.593	99.34
10	10 / 10	75 / 75	1.837	4.593	99.34
11			1.836	4.591	99.31
12			1.836	4.589	99.26
13			1.834	4.585	99.18
14			1.835	4.587	99.22
15			1.834	4.586	99.19
16			1.834	4.584	99.16
17			1.833	4.583	99.14
18			1.833	4.584	99.15
19			1.833	4.583	99.14
20			1.832	4.581	99.09

Table 9: CO_2 uptake and stability of 50PEI_Vp1.2 in mild adsorption / desorption condition

Samples: 50 wt.% PEI-modified mesoporous silica with pore volume at 1.2 cm^3/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO_2 adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1	100 / 100	75 / 75	2.541	5.083	-
2			**2.520**	**5.039**	-
1			2.022	4.045	-
2			**1.399**	**2.799**	**100.00**
3			1.393	2.786	99.53
4			1.389	2.779	99.29
5			1.387	2.774	99.12
6			1.386	2.771	99.02
7			1.384	2.769	98.94
8			1.383	2.766	98.85
9			1.383	2.766	98.84
10	10 / 10	75 / 75	1.382	2.765	98.79
11			1.381	2.763	98.72
12			1.380	2.761	98.65
13			1.380	2.760	98.64
14			1.380	2.760	98.62
15			1.379	2.759	98.59
16			1.378	2.757	98.50
17			1.378	2.756	98.49
18			1.378	2.755	98.45
19			1.377	2.754	98.42
20			1.377	2.753	98.39

Table 10: CO$_2$ uptake and stability of 60PEI_Vp1.2 in mild adsorption / desorption condition

Samples: 60 wt.% PEI-modified mesoporous silica with pore volume at 1.2 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1	100 / 100	75 / 75	2.193	3.655	-
2			**2.176**	**3.622**	-
1			1.710	2.850	-
2			**1.215**	**2.026**	**100.00**
3			1.209	2.016	99.49
4			1.207	2.011	99.28
5			1.206	2.010	99.24
6			1.204	2.007	99.05
7			1.204	2.007	99.07
8			1.203	2.005	98.99
9			1.203	2.005	98.95
10	10 / 10	75 / 75	1.202	2.004	98.91
11			1.202	2.003	98.85
12			1.201	2.002	98.83
13			1.201	2.001	98.80
14			1.201	2.002	98.83
15			1.201	2.001	98.78
16			1.201	2.001	98.78
17			1.199	1.999	98.66
18			1.199	1.999	98.68
19			1.200	1.999	98.70
20			1.198	1.997	98.60

As mentioned above, under mild adsorption / desorption conditions the operation is combined by two different protocol differentiated by contact time between gas and sorbents. In principle, this was a '2 + 20 cycles' CO_2 capture mode. The first two cycles operated during 100 minutes in both adsorption and desorption step. CO_2 adsorption obtained by those two cycles were used to determine the equilibrium CO_2 uptake of such PEI_SiO$_2$ sorbents, i.e. hereinafter referred to as 'Optimum Capacity'.

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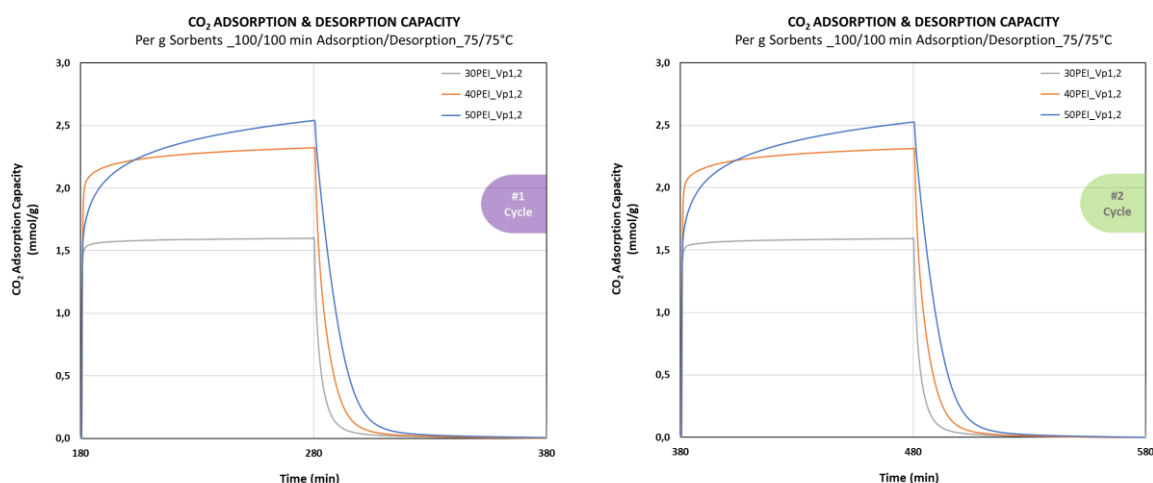
Figure 22: CO_2 uptake of the first (left) and second (right) cycle during 100 min contact time of PEI_SiO$_2$_Vp1.2

CO_2 adsorption and desorption uptake shown in Figure 22 demonstrated that different PEI_SiO$_2$_Vp1.2 samples have reached or closed to their equilibrium CO_2 adsorption capacity, meanwhile after 100 minutes desorption, samples achieved a fully regeneration that made the sorbents were free to next round CO_2 capture as shown as the second cycle above. Consideration of time-consumption to stable the machine, usually the final optimum CO_2 capacity determined for each sample was taken the value from #2 adsorption/desorption run, i.e. data in red shown in above datasheets.

Whatever in pilot instruments or actual industrial application, the contact time between gases and catalysts is too short to allow the sorbents to obtain its optimum adsorption capacity. Therefore, to get a more reliable CO_2 capacity in regard to true application environments, another 20 cycles adsorption / desorption operation was setup after then. The adsorption and desorption time were both changed from 100 minutes to 10 minutes. Figure 23 presents the first and second cycle of CO_2 adsorption / desorption for 10 minutes contact time.

CO₂ ADSORPTION & DESORPTION CAPACITY
Per g Sorbents _10/10 min Adsorption/Desorption_75/75°C

CO₂ ADSORPTION & DESORPTION CAPACITY
Per g Sorbents _10/10 min Adsorption/Desorption_75/75°C
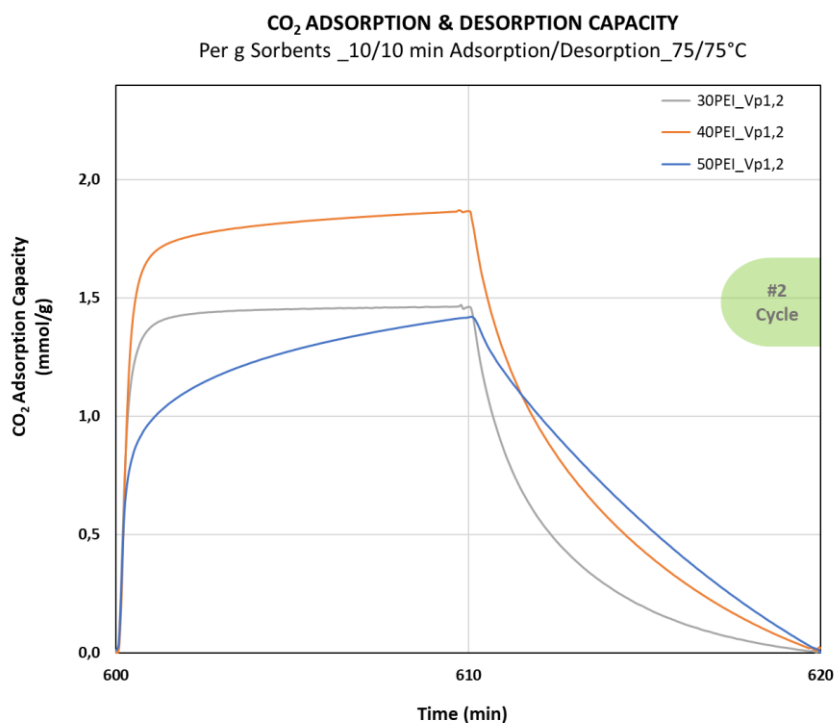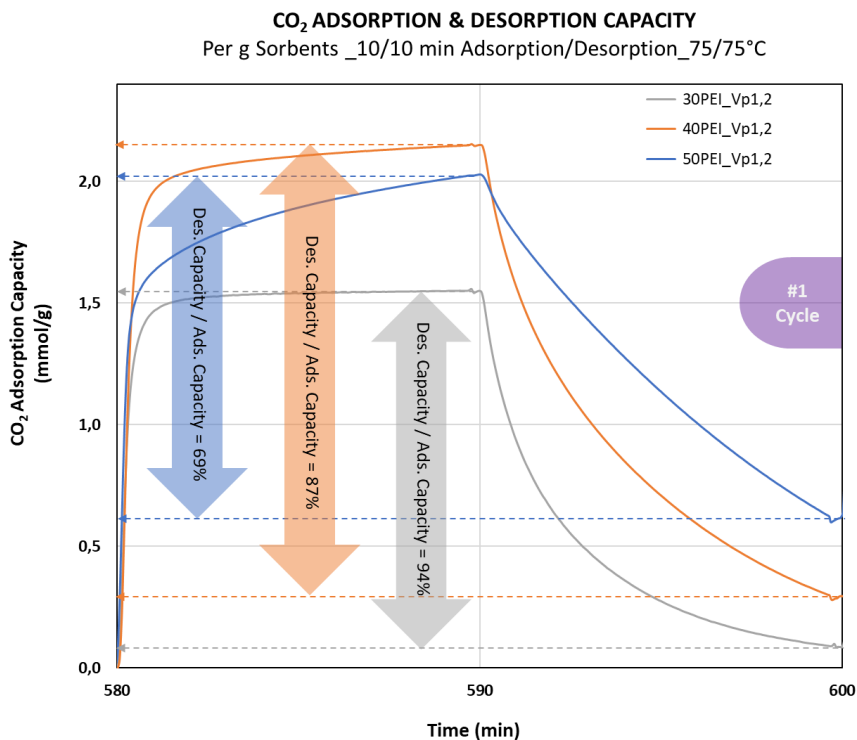
Figure 23: CO₂ uptake of the first (top) and second (bottom) cycle during 10 min contact time of PEI_SiO₂_Vp1.2

Different from the CO₂ capture performed with longer contact time, it is clear that all samples can not be regenerated completely in 10 minutes after CO₂ adsorption, as shown the #1 cycle

curve in Figure 23. The desorption capacity could reach at 94%, 87% and 69% of the adsorption capacity to samples of 30PEI_SiO$_2$_Vp1.2, 40PEI_SiO$_2$_Vp1.2, and 50PEI_SiO$_2$_Vp1.2, respectively. In other words, not all loaded PEI could react with CO$_2$ in a short time and be functionalized as it supposed to be. Since the second cycle, the balance was occurred between adsorption and desorption same as long contact time, because it only needed 10 minutes for regenerating the actual occupied active sites of the sorbents. Therefore, the CO$_2$ capacity obtained from the #2 cycle provided the 'Practical Capacity' of each sorbent.

Obviously, the SiO$_2$ impregnated with different PEI amounts have significant differences in terms of both CO$_2$ optimal and actual absorption capacity. Figure 24 shows the CO$_2$ adsorption capacities of the first two cycles with different duration. PEI loading in a range of 30 to 60 wt.% in PEI_SiO$_2$_Vp1.2 samples.
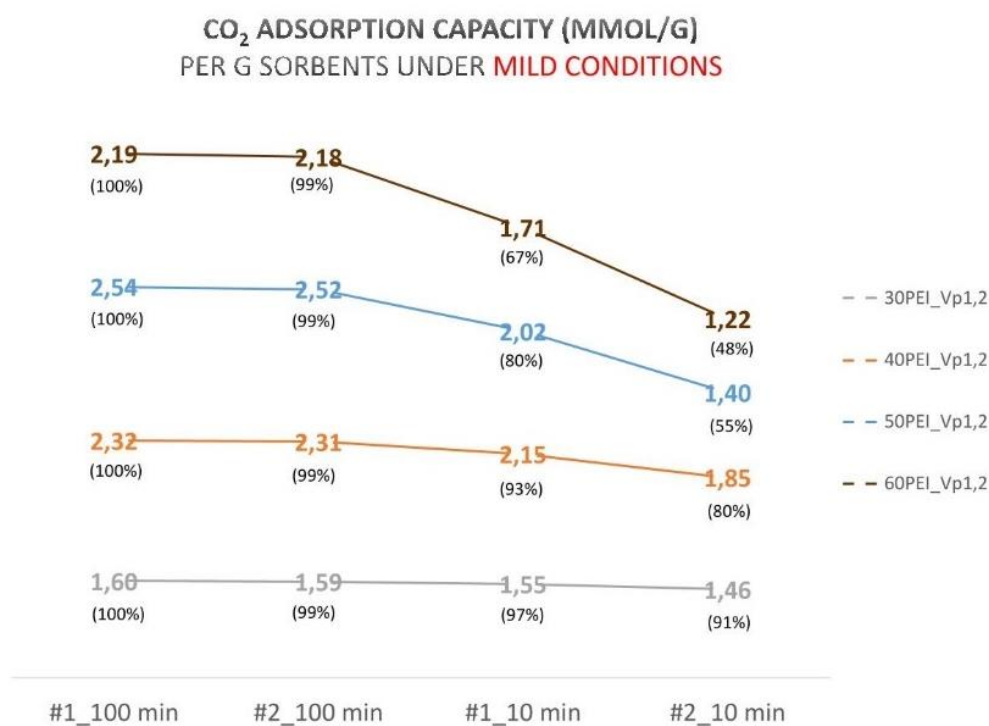
Figure 24: CO_2 uptake per gram sorbents (top) and per gram PEI (bottom) from first two cycles in different contact time of $PEI\_SiO_2\_Vp1.2$

From Figure 24 it is found that the CO_2 adsorption optimum capacity of $PEI\_SiO_2\_Vp1.2$ increases from 1.59 to 2.54 mmol/g sorbents as PEI loading increases from 30 to 50 wt.%, but there is a sharp capacity reduction on $60PEI\_SiO_2\_Vp1.2$ to 2.19 mmol/g sorbents which was less than $40PEI\_SiO_2\_Vp1.2$ with 2.32 mmol/g sorbents. Same trend was shown on the CO_2 adsorption practical capacities but $40PEI\_SiO_2\_Vp1.2$ had the best CO_2 uptake of 1.85 mmol/g.

The CO_2 adsorption optimum and practical capacity calculated as per unit PEI mass gave a similar trend on change with amine mass ratio of adsorbents, except that the $40PEI\_SiO_2\_Vp1.2$ performed best among all adsorbents at 5.77 mmol/g PEI of the optimum CO_2 capacity, whereas $30PEI\_SiO_2\_Vp1.2$ contributed the highest practical CO_2 capacity at 4.87 mmol/g PEI. As calculation, the practical capacity was 91%, 80%, 55% and 48% of the optimum capacity, respectively, for adsorbent impregnated to 30, 40, 50 and 60 wt.% PEI amounts.

Figure 25: Adsorption performance of PEI_SiO$_2$_Vp1.2 with optimum and practical CO$_2$ capacities per gram sorbents (top) and per gram PEI (bottom)

Figure 25 explicitly shows the change in CO$_2$ uptake of different PEI_SiO$_2$_Vp1.2 adsorbents over time in a given contact duration. Combined with the physical properties studies of PEI impregnated sorbents (see Table 19), the larger leftover pore volume of sorbents, the better practical CO$_2$ capacity per PEI it has due to a fast-kinetic reaction between amine and CO$_2$ as well as good gas distribution in the pore of adsorbents. A summary of CO$_2$ adsorption capacities and stability of PEI_SiO$_2$_Vp1.2 is given in Figure 26 and Figure 27, respectively.
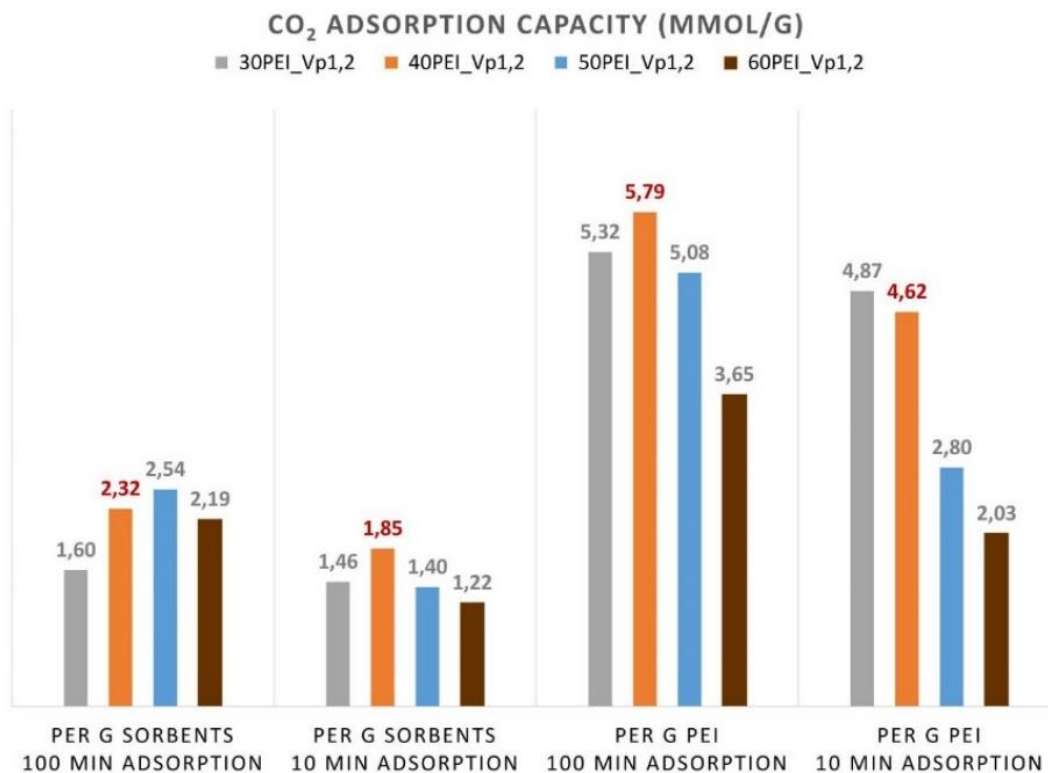
Figure 26: Comparison of the CO_2 adsorption capacity of different PEI_SiO$_2$_Vp1.2 samples under mild operation conditions

Figure 27: Comparison of the stability of different PEI_SiO$_2$_Vp1.2 samples under mild operation conditions

5.2.2. CO$_2$ uptake and stability of PEI_Vp1.5 silica samples

For a comparison purpose on the studies of CO$_2$ capture performances with different pore volume, same PEI loading was impregnated into PEI_SiO$_2$_Vp1.5 samples which varied from 30 to 50 wt.%. Based on the TGA results of PEI_SiO$_2$_Vp1.2, 60PEI_SiO$_2$ was excluded due to its poor CO$_2$ capture performance both on CO$_2$ optimum and practical capacity as well as the stability results. Figure 28 shows the experimental curves presented in regard to the weight change with time of the PEI_Vp1.5 silica samples under mild conditions.
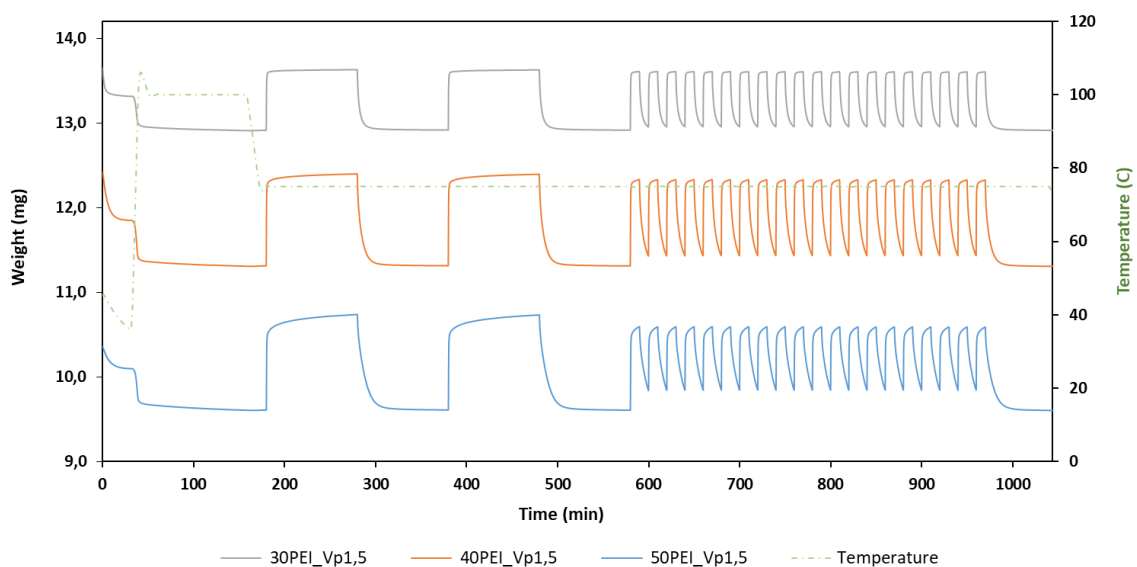
Figure 28: CO$_2$ capture performance analysis of PEI_SiO$_2$_Vp1.5 under mild conditions

Operation condition of the CO$_2$ capture performance analysis on PEI_SiO$_2$_Vp1.5 were exactly same as which implemented with PEI_SiO$_2$_Vp1.2 sorbents. Here below Table 11, Table 12 and Table 13 shown detailed CO$_2$ uptake and stability change in such '2 + 20' cycles of adsorption / desorption.

Table 11: CO$_2$ uptake and stability of 30PEI_Vp1.5 in mild adsorption / desorption condition

Samples: 30 wt.% PEI-modified mesoporous silica with pore volume at 1.5 cm^3/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	*mmol/g PEI*	
1	100 / 100	75 / 75	1.484	4.948	-
2			**1.474**	**4.913**	-
1			1.436	4.786	-
2			**1.351**	**4.504**	**100.00**
3			1.347	4.490	99.68
4			1.345	4.483	99.54
5			1.344	4.480	99.46
6			1.343	4.477	99.40
7			1.342	4.473	99.31
8			1.342	4.473	99.31
9			1.341	4.472	99.28
10	10 / 10	75 / 75	1.341	4.470	99.23
11			1.340	4.468	99.20
12			1.340	4.467	99.18
13			1.340	4.465	99.14
14			1.340	4.466	99.15
15			1.339	4.464	99.11
16			1.338	4.461	99.04
17			1.338	4.461	99.04
18			1.338	4.460	99.03
19			1.338	4.460	99.01
20			1.337	4.457	98.95

Table 12: CO$_2$ uptake and stability of 40PEI_Vp1.5 in mild adsorption / desorption condition

Samples: 40 wt.% PEI-modified mesoporous silica with pore volume at 1.5 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1	100 / 100	75 / 75	2.182	5.454	-
2			**2.169**	**5,424**	-
1			2.047	5.118	-
2			**1.799**	**4.497**	**100.00**
3			1.794	4.485	99.73
4			1.792	4.479	99.60
5			1.790	4.475	99.51
6			1.789	4.473	99.45
7			1.789	4.471	99.42
8			1.788	4.469	99.36
9			1.787	4.468	99.34
10	10 / 10	75 / 75	1.787	4.466	99.31
11			1.786	4.465	99.27
12			1.786	4.465	99.29
13			1.785	4.463	99.24
14			1.785	4.462	99.21
15			1.785	4.462	99.22
16			1.785	4.462	99.21
17			1.785	4.462	99.21
18			1.784	4.460	99.16
19			1.784	4.459	99.14
20			1.783	4.457	99.10

Table 13: CO$_2$ uptake and stability of 50PEI_Vp1.5 in mild adsorption / desorption condition

Samples: 50 wt.% PEI-modified mesoporous silica with pore volume at 1.5 cm³/g

| Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1	100 / 100	75 / 75	2.310	4.619	-
2			**2.296**	**4.593**	-
1			2.017	4.035	-
2			**1.524**	**3.048**	**100.00**
3			1.519	3.039	99.70
4			1.518	3.035	99.58
5			1.516	3.032	99.46
6			1.515	3.031	99.44
7			1.515	3.030	99.41
8			1.514	3.028	99.34
9			1.514	3.027	99.32
10	10 / 10	75 / 75	1.513	3.027	99.30
11			1.512	3.025	99.23
12			1.512	3.024	99.22
13			1.512	3.024	99.22
14			1.511	3.023	99.18
15			1.511	3.022	99.15
16			1.511	3.021	99.13
17			1.511	3.021	99.13
18			1.510	3.020	99.09
19			1.510	3.019	99.06
20			1.510	3.019	99.06
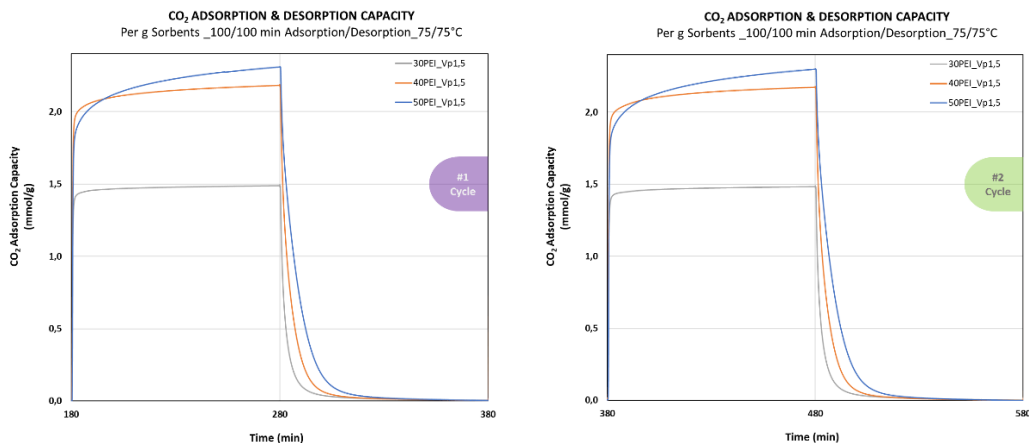
Figure 29: CO_2 uptake of the first (left) and second (right) cycle during 100 min contact time of PEI_SiO2_Vp1.5

CO_2 adsorption and desorption uptake shown in Figure 29 also demonstrated an equilibrium CO_2 adsorption of different PEI_SiO2_Vp1.5 samples and a fully regeneration after 100 minutes desorption. Same principle used for PEI_SiO2_Vp1.2, the final optimum CO_2 capacity was determined for each sample by #2 adsorption/desorption run in 100 minutes, i.e. data in red shown in above datasheets.
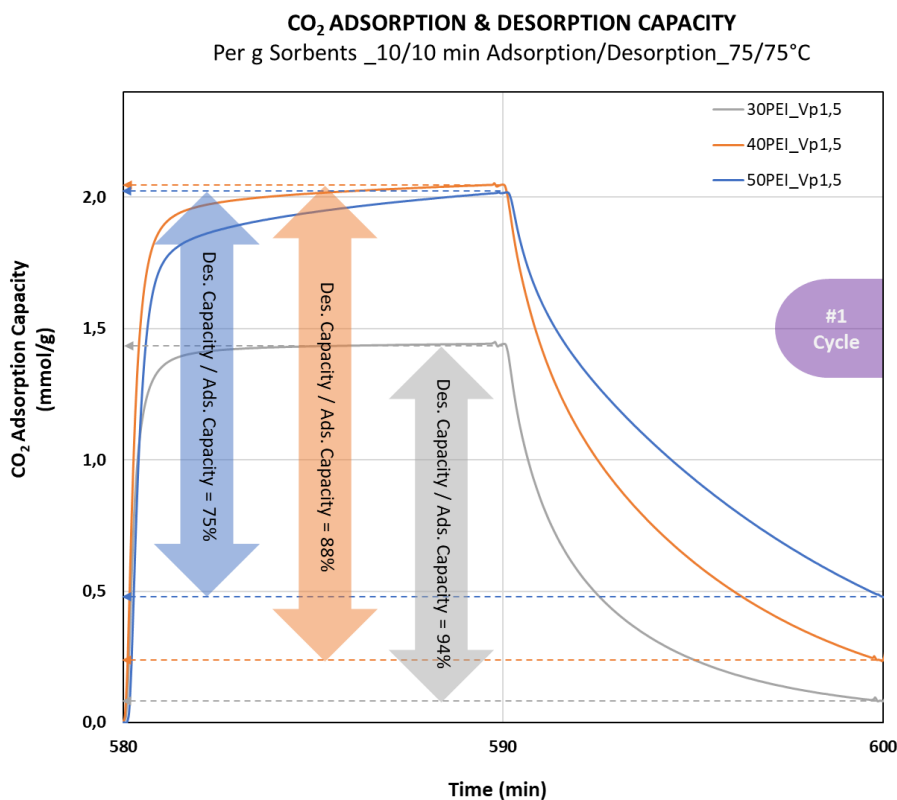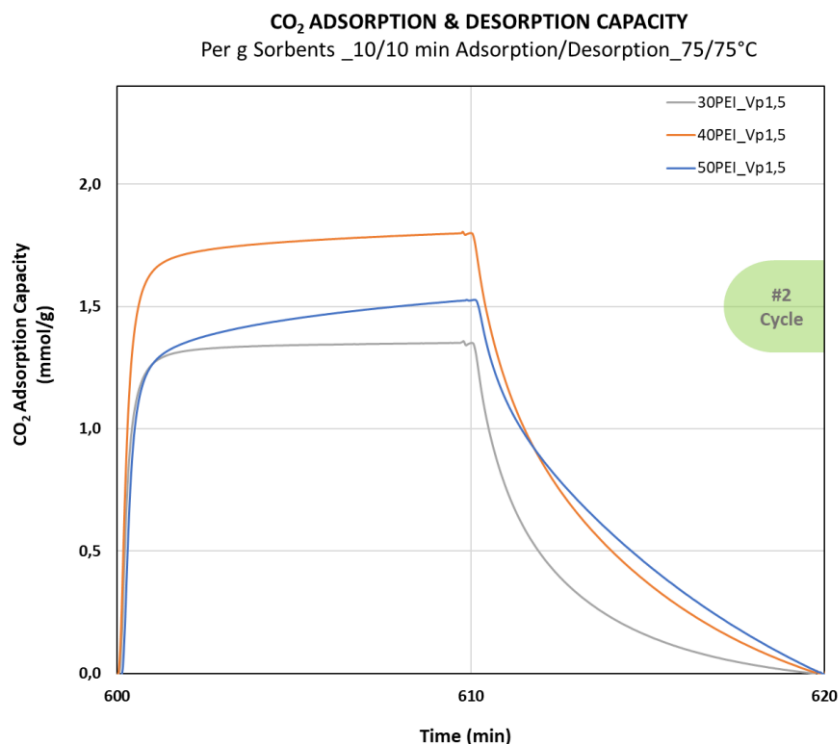
Figure 30: CO_2 uptake of the first (top) and second (bottom) cycle during 10 min contact time of PEI_SiO$_2$_Vp1.5

The first cycle of 20 cycles operating during 10 minutes per each adsorption / desorption shown an incomplete desorption phenomenon (see Figure 30) as same as PEI_SiO$_2$_Vp1.2 samples. The desorption capacity could reach at 94%, 88% and 75% of the adsorption capacity to samples of 30PEI_SiO$_2$_Vp1.5, 40PEI_SiO$_2$_Vp1.5, and 50PEI_SiO$_2$_Vp1.5, respectively. Compared the ratio to corresponding PEI_SiO$_2$_Vp1.2, there was no obvious differences on 30PEI_SiO$_2$and 40PEI_SiO$_2$, but a 6% increasing on 50PEI_SiO$_2$ in regard to the regeneration degree. Due to a larger pore volume of silica supports, more pore volume available after PEI impregnation in turn to a better gas distribution during adsorption and desorption process which further leaded to a faster kinetics on 50PEI_SiO$_2$ with a better regeneration performance.

Figure 31 shows the CO_2 adsorption capacities of the first two cycles with different duration. PEI loading in a range of 30 to 50 wt.% in PEI_SiO$_2$_Vp1.5 samples. The CO_2 adsorption optimum capacity of PEI_SiO$_2$_Vp1.5 increases from 1.47 to 2.30 mmol/g sorbents as PEI loading increases from 30 to 50 wt.%. Regarding to the CO_2 adsorption practical capacities, 40PEI_SiO$_2$_Vp1.5 presented the best CO_2 uptake of 1.80 mmol/g sorbents.

Regarding the CO_2 adsorption optimum and practical capacity calculated as per unit PEI, the 40PEI_SiO$_2$_Vp1.5 was outstanding with 5.42 mmol/g PEI of the optimum CO_2 capacity, whereas shown a practical CO_2 capacity at 4.50 mmol/g PEI same as the 30PEI_SiO$_2$_Vp1.5. As calculation, the practical capacity was 91%, 82% and 66% of the optimum capacity, respectively, for adsorbent impregnated to 30, 40 and 50 wt.% PEI amounts.
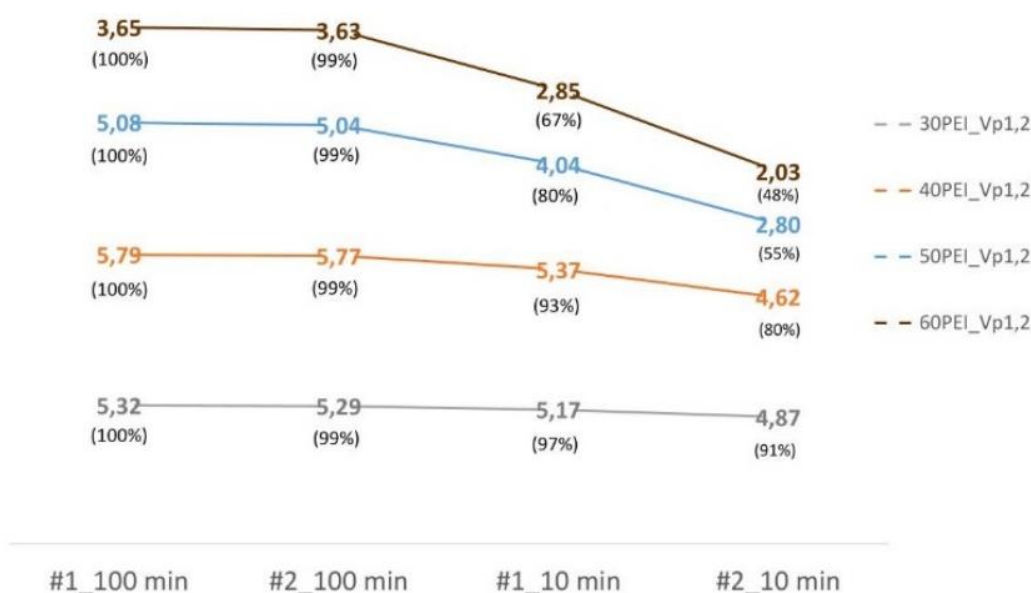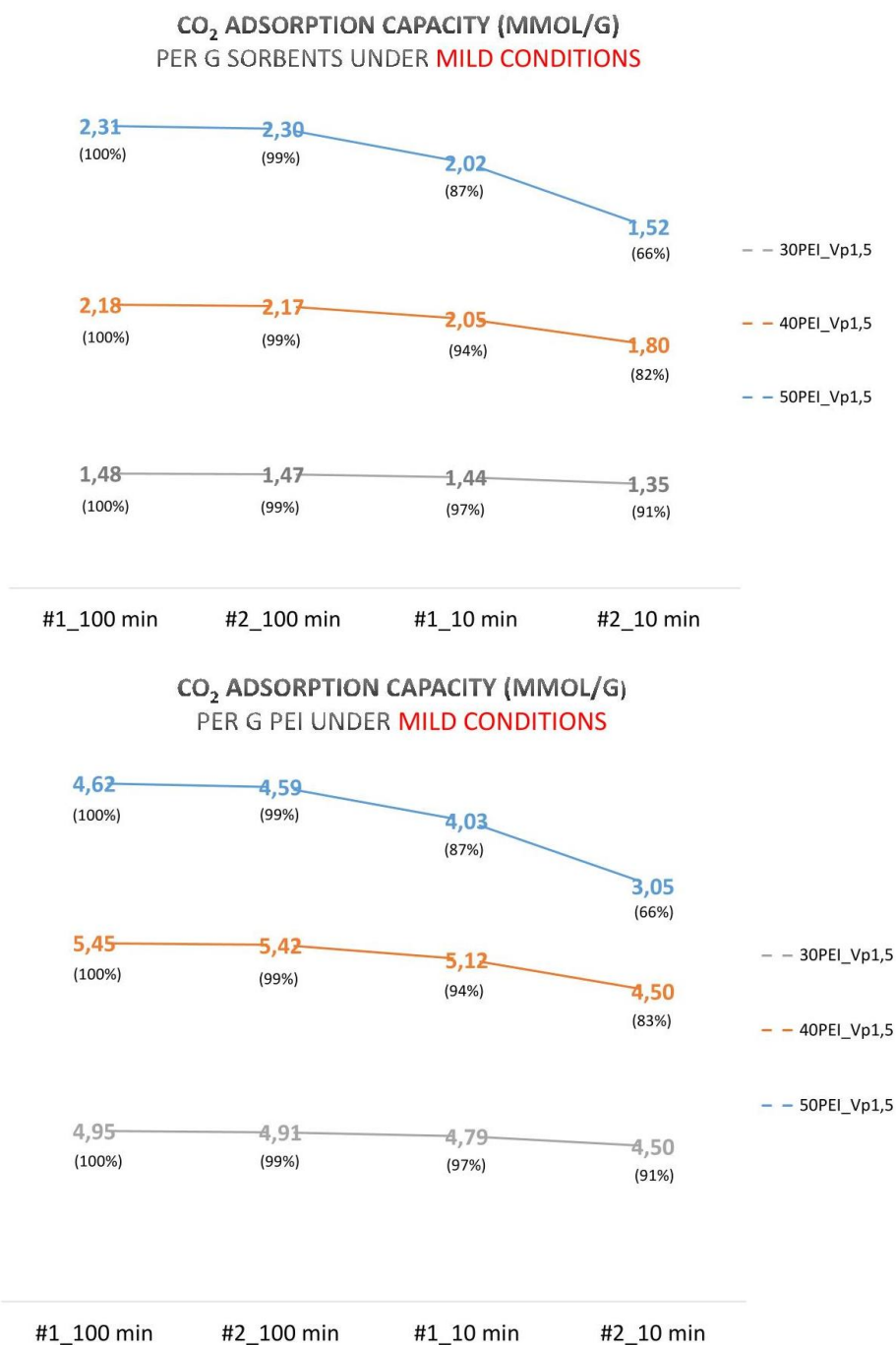

Figure 31: CO_2 uptake per gram sorbents (top) and per gram PEI (bottom) from first two cycles in different contact time of PEI_SiO$_2$_Vp1.2
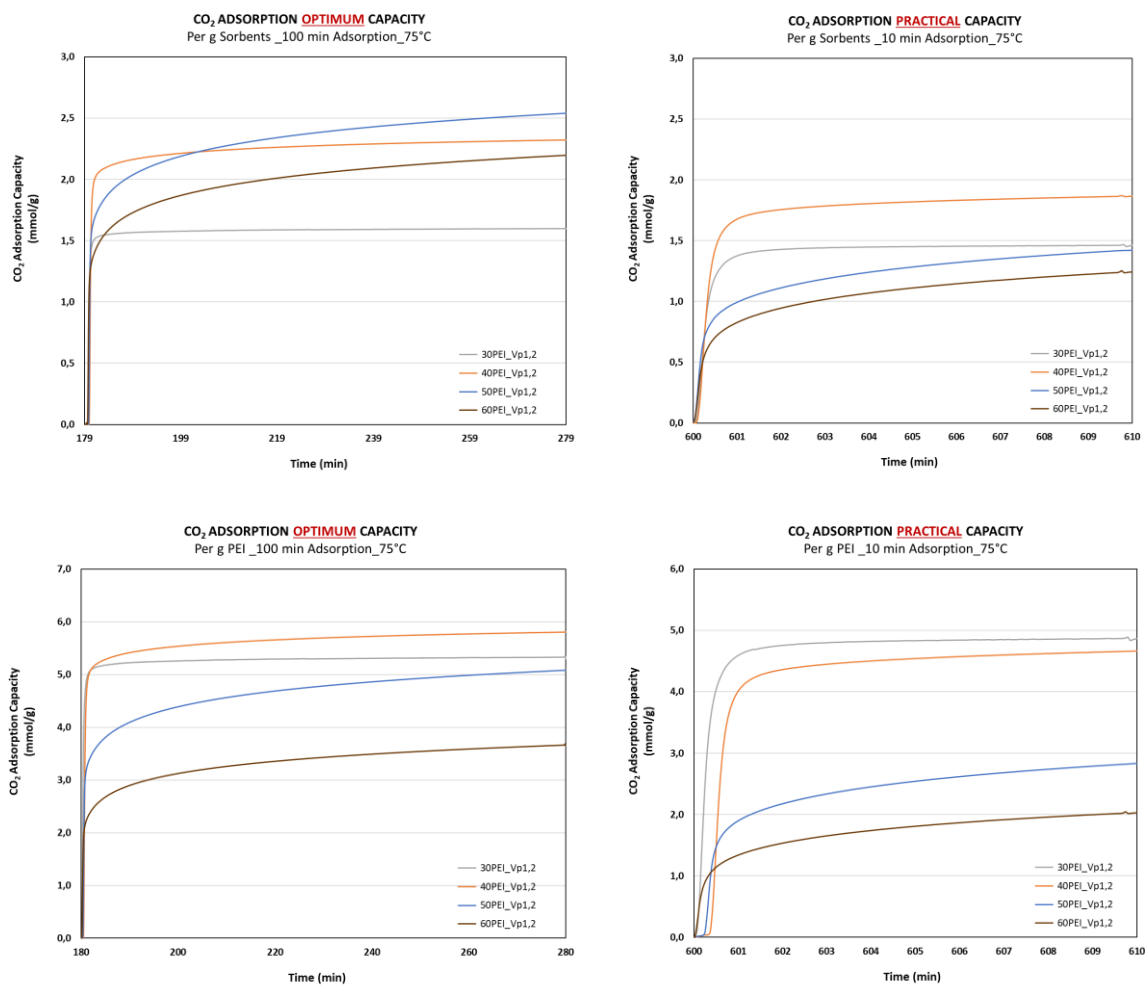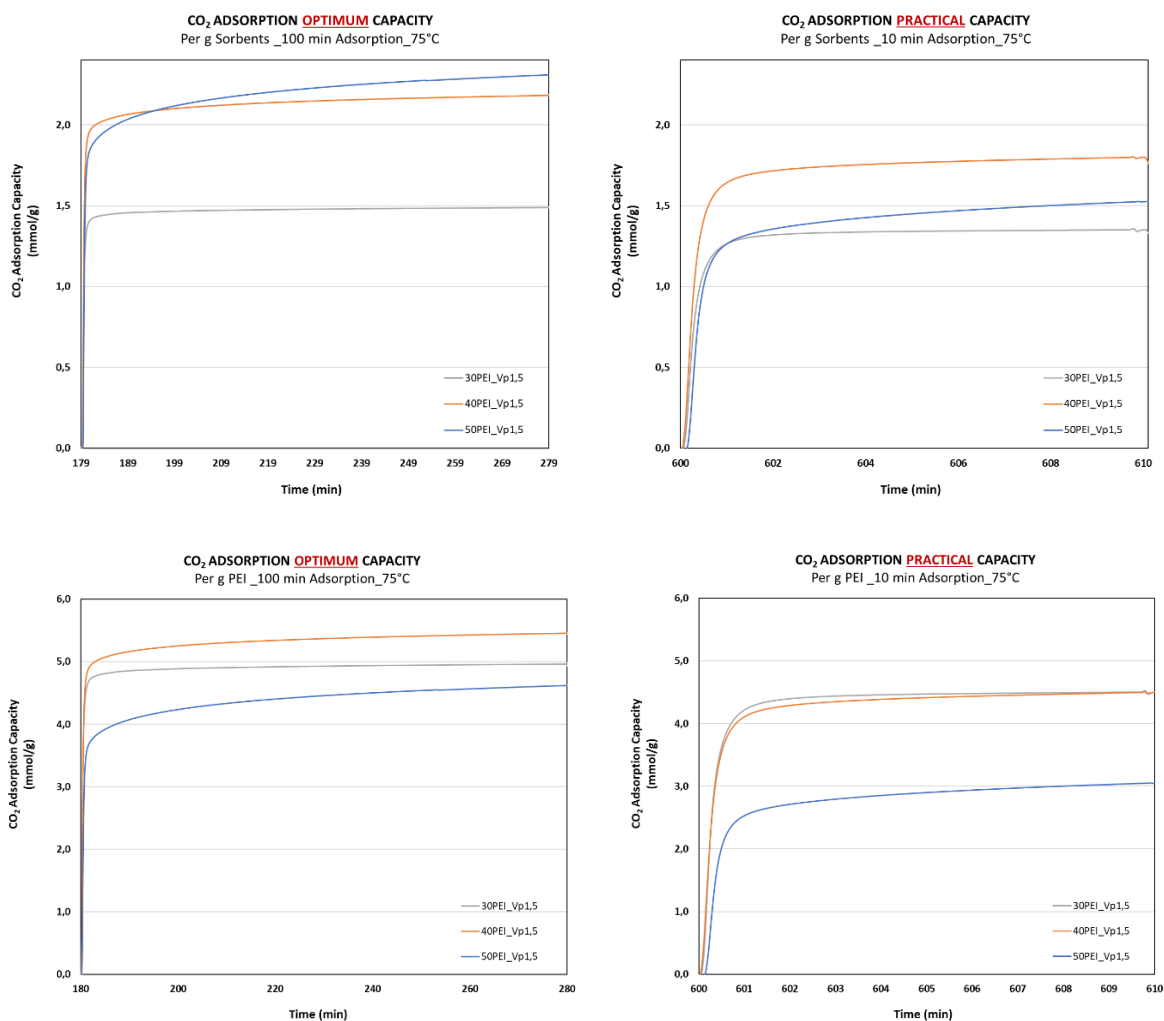
Figure 32: Adsorption performance of PEI_SiO$_2$_Vp1.5 with optimum and practical CO$_2$ capacities per gram sorbents (top) and per gram PEI (bottom)

Figure 32 explicitly shows the change in CO$_2$ uptake of different PEI_SiO$_2$_Vp1.5 adsorbents over time in a given contact duration. To be noticed that the CO$_2$ practical capacity on 50PEI_SiO$_2$_Vp1.5 was increased due to a better regeneration as discussed above. Meanwhile, 40PEI cached up to the same level as 30PEI with large pore volume supports, where it was slightly lower than 30PEI with small pore volume supports. That was contributed by more leftover space in the pore which helped on fast-kinetics reaction. A summary of CO$_2$ adsorption capacities and stability of PEI_SiO$_2$_Vp1.2 is given in Figure 33 and Figure 34, respectively.

CO$_2$ ADSORPTION CAPACITY (MMOL/G)

■ 30PEI_Vp1,5   ■ 40PEI_Vp1,5   ■ 50PEI_Vp1,5
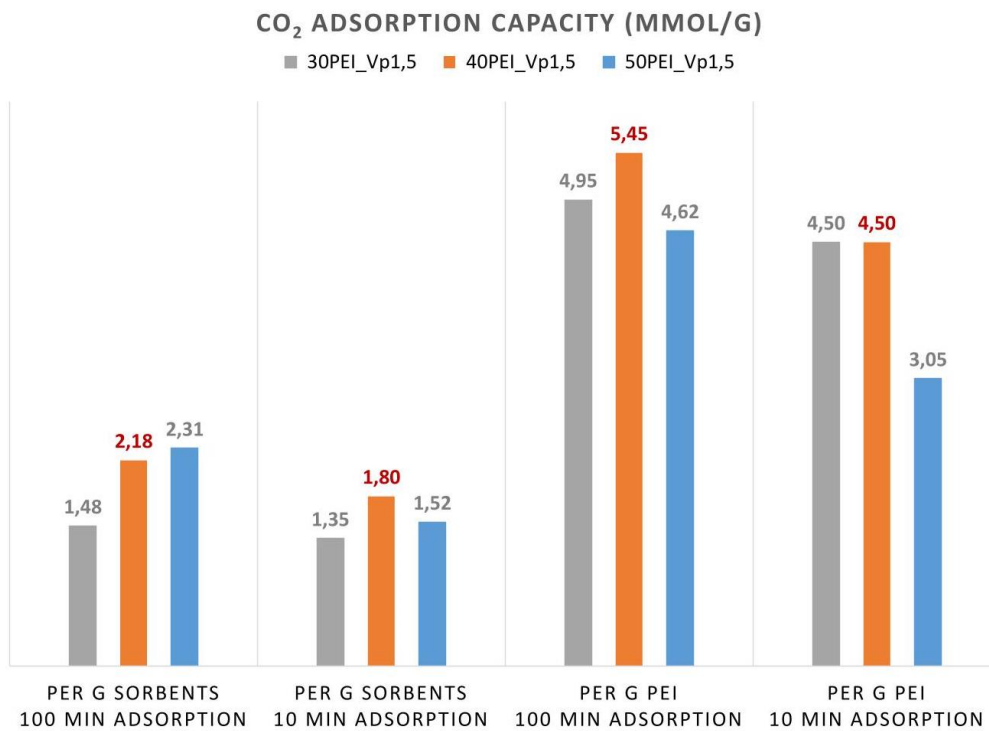
Figure 33: Comparison of the CO$_2$ adsorption capacity of different PEI_SiO$_2$_Vp1.5 samples under mild operation conditions

CO$_2$ ADSORPTION STABILITY in Mild Condition

10/10 min_Adsorption / Desorption_75/75°C

30PEI_Vp1,5   98.95 %
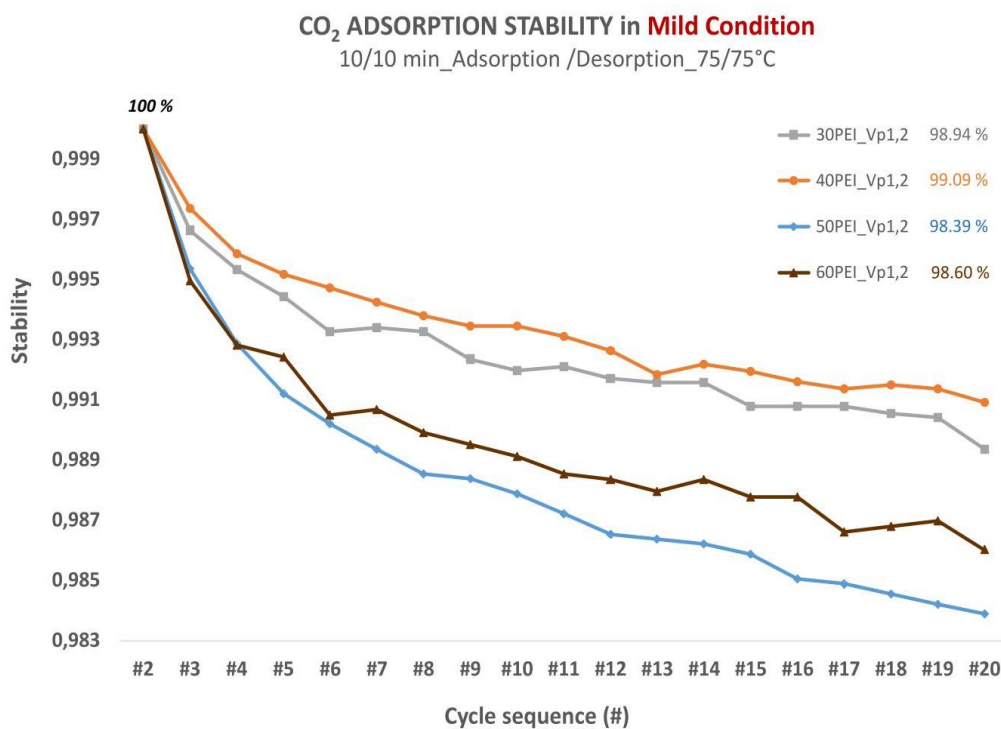40PEI_Vp1,5   99.10 %
50PEI_Vp1,5   99.06 %
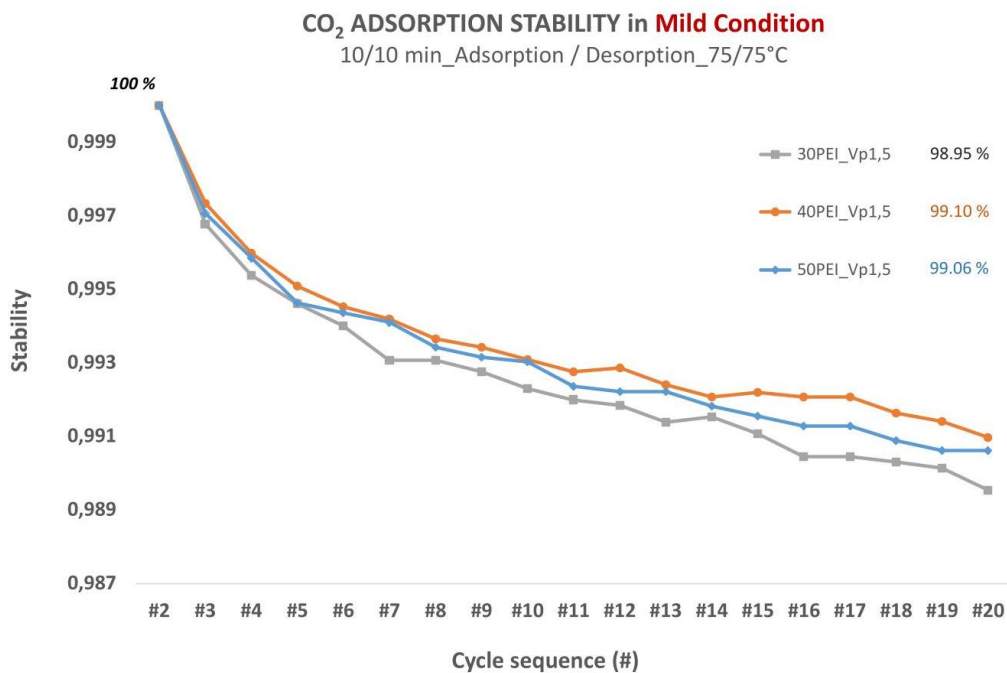
Figure 34: Comparison of the stability of different PEI_SiO$_2$_Vp1.5 samples under mild operation conditions

5.2.3. CO₂ uptake and stability of PEI_Vp1.5 silica samples in harsh condition

Low energy consumption is a vital target in CO_2 capture process, in a short, the adsorbed CO_2 should be desorbed easily, meanwhile the a fairly cyclic stability of the adsorbents used for the CO_2 adsorption / desorption technology is very important from practical application considerations. Normally, a loss of CO_2 capture capacity to different extents in the cyclic CO_2 adsorption / desorption runs is inevitably, one of reasons is the amine degradation closely related to the operation temperature and gas atmosphere. For this thesis study, two different operation conditions were chosen as described in Table 6. As shown in Table 14, PEI_SiO₂ sorbents synthesized in this study demonstrated a high CO_2 practical capture and high stability in 19 cycle runs under mild conditions. To further investigate their stability, PEI_SiO2_Vp1.5 sorbents were tested again under harsh condition, i.e., high desorption temperature at 120 °C during longer gas residence time, see Figure 35. CO_2 capture performance were given with cycles in below Table 15, Table 16 and Table 17.

Table 14: Summary of the CO_2 caputure practical performance with different PEI_SiO₂ sorbents under mild operation conditions in this thesis studies

	Ads./Des. Time (min)	Ads./Des. Temp. (°C)	Stability after 19 cycles (%)	CO₂ adsorption practical capacity (mmol/g)	
				Per sorbents	Per PEI
30PEI_Vp1.2	10/10	75/75	98.94	1.46	4.86
40PEI_Vp1.2	10/10	75/75	99.09	1.85	5.37
50PEI_Vp1.2	10/10	75/75	98.39	1.40	4.48
30PEI_Vp1.5	10/10	75/75	98.95	4.87	4.50
40PEI_Vp1.5	10/10	75/75	99.10	4.62	4.50
50PEI_Vp1.5	10/10	75/75	99.06	2.80	3.05
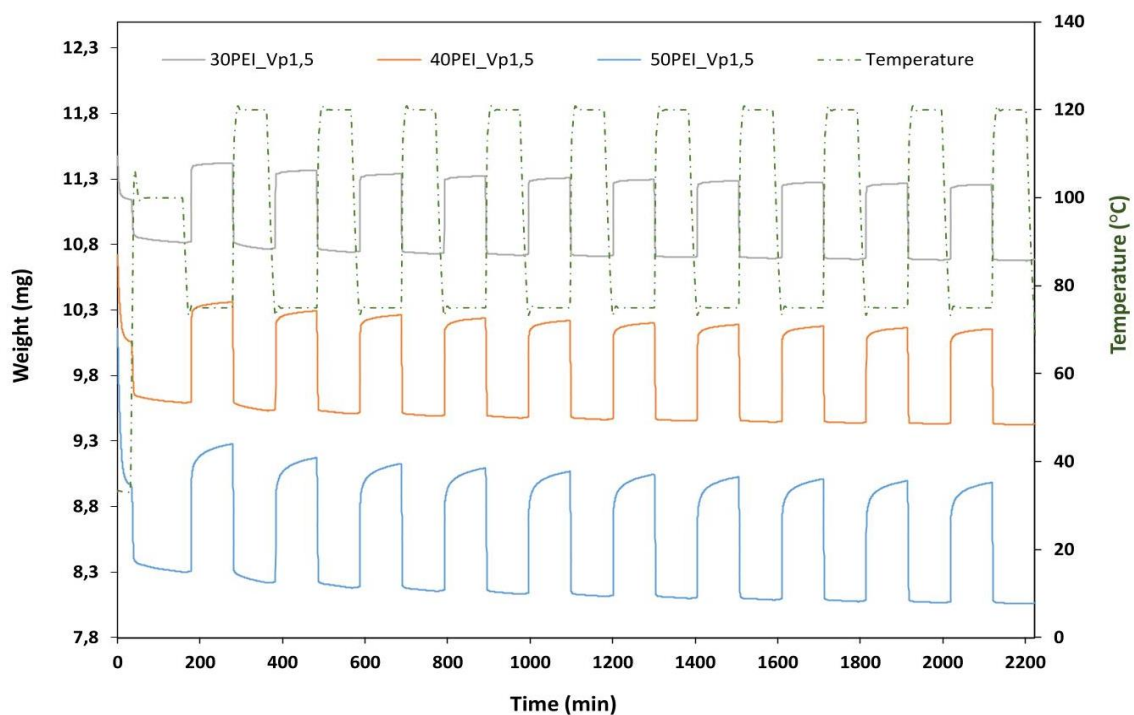
Figure 35: CO$_2$ capture performance analysis of PEI_SiO$_2$_Vp1.5 under harsh conditions

Table 15: CO$_2$ uptake and stability of 30PEI_Vp1.5 in hash adsorption / desorption condition

Samples: 30 wt.% PEI-modified mesoporous silica with pore volume at 1.5 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	*mmol/g PEI*	
1			1.484	4.948	-
2			**1.459**	**4.864**	**100.00**
3			1.450	4.833	99.35
4			1.442	4.807	98.82
5			1.431	4.869	98.04
6	100 / 100	75 / 120	1.426	4.752	97.70
7			1.414	4.714	96.91
8			1.411	4.704	96.70
9			1.407	4.689	96.39
10			1.398	4.659	95.78

Table 16: CO_2 uptake and stability of 40PEI_Vp1.5 in hash adsorption / desorption condition

Samples: 40 wt.% PEI-modified mesoporous silica with pore volume at 1.5 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO_2 adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1			2.182	5.454	-
2			**2.148**	**5.370**	**100.00**
3			2.129	5.323	99.12
4			2.112	5.279	98.31
5	100 / 100	75 / 120	2.100	5.251	97.79
6			2.084	5.209	97.00
7			2.077	5.193	96.71
8			2.067	5.168	96.25
9			2.055	5.137	95.67
10			2.049	5.123	95.41

Table 17: CO_2 uptake and stability of 50PEI_Vp1.5 in hash adsorption / desorption condition

Samples: 50 wt.% PEI-modified mesoporous silica with pore volume at 1.5 cm³/g

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO_2 adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1			2.310	4.619	-
2			**2.237**	**4.475**	**100.00**
3			2.198	4.397	98.26
4			2.184	4.368	97.63
5	100 / 100	75 / 120	2.168	4.336	96.91
6			2.162	4.324	96.64
7			2.148	4.296	96.00
8			3.143	4.285	95.78
9			2.138	4.276	95.56
10			2.120	4.260	95.21

Same as stability study operated under mild operation conditions and experiences from experimental operation, the first cycle was usually not included in the stability study with consideration of machine interference on data reliability. Table 18 gives the summary of optimum capacity and stability after 9 cycles CO_2 adsorption / desorption operation achieved by different PEI_SiO$_2$ sorbents.

Table 18: Summary of the CO_2 caputure optimum performance with different PEI_SiO$_2$ sorbents under harsh operation conditions in this thesis studies

	Ads./Des. Time (min)	Ads./Des. Temp. (°C)	Stability after 9 cycles (%)	CO_2 adsorption capacity (mmol/g)	
				Per sorbents	Per PEI
30PEI_Vp1.5	100/100	75/120	95.78	1.46	4.86
40PEI_Vp1.5	100/100	75/120	95.41	2.15	5.37
50PEI_Vp1.5	100/100	75/120	95.21	2.24	4.48

Figure 36 shows the trends of stability reduction with cycle. Both 30PEI and 40PEI silica adsorbents appeared approximately a linear decrease and reached 95.78 % and 95.41 respectively. Although the CO_2 uptake of 50PEI silica adsorbents was less competitive than other two sorbents, its stability after 9 cycle runs under hash operation conditions resulted at 95.21%, which was almost identical to the other two sorbents. In general, cycle stability is decreased with high desorption temperature from 99% to 95% compared with value gotten under mild conditions. It makes sense as the high temperature will accelerate the amine degradations during long-term CO_2 adsorption / desorption operations. Especially, the amines do not provide the strong interaction with the supporting surface via physical impregnation, which shall lead to poor cycling stability when PEI_SiO$_2$ exposed under high temperature.
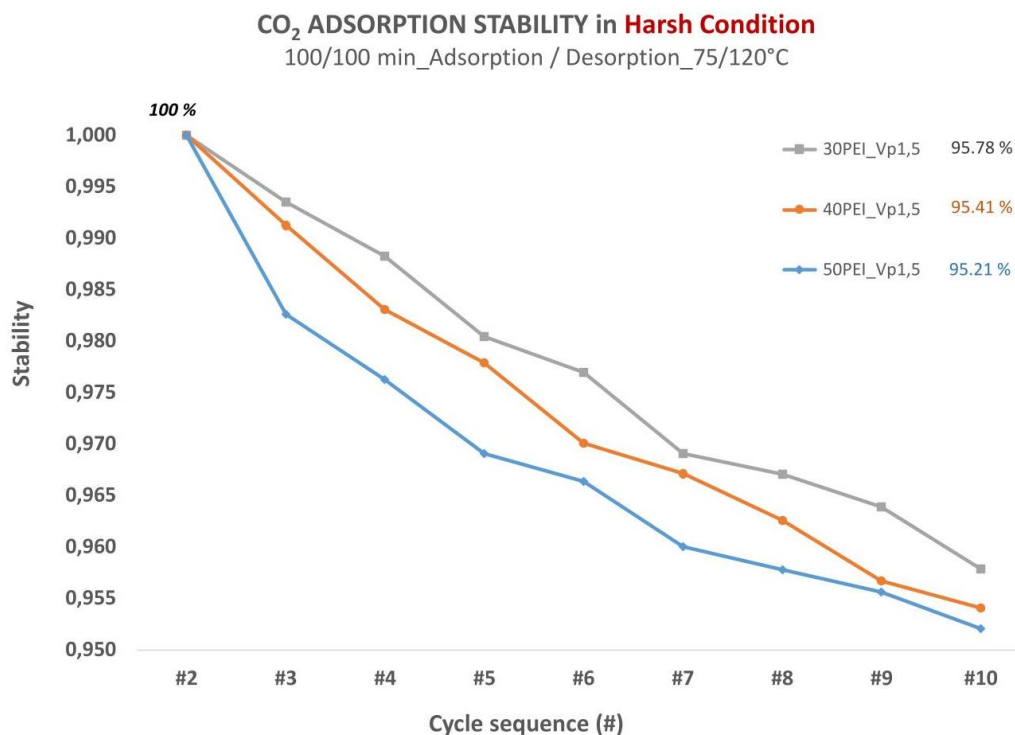
Figure 36: Comparison of the stability of different PEI_SiO$_2$_Vp1.5 samples under harsh operation conditions

5.3. CO$_2$ uptake correction as per actual PEI loading

According to the TGA test results, the CO$_2$ adsorption performances showed a good performance and increasing trend as amine concentration increased as per unit gram of sorbents. However, the data shown based on unit gram PEI provides an interesting and more reliable reference to evaluate the CO$_2$ capture performance of solid sorbents from economical perspective. Therefore, an accuracy on amine loading amounts is need.

5.3.1. Physical properties and Morphology of PEI-modified mesoporous silica

Table **19** provides the physical properties including the surface area, pore volume and pore size of silica samples after impregnated by PEI to target amine concentration. Both surface area and pore volume of PEI-modified SiO$_2$ shows a reduction trend as amine weight percentage increases, meanwhile the pore size of samples increased due to a pore expansion slightly with amine loading into the support sorbents. In theory, PEI (branched, Mw=600) used for wet impregnation has a density of 1,05 g/ml at 25 °C, which allowed a maximum PEI weight

percentage of 56% and 60% to SiO_2 _Vp1.2 and SiO_2 _Vp1.5, respectively. therefore, it is not surprising that 60PEI_SiO_2 _Vp1.2 showed a nearly zero leftover pore volume and larger pore size than non-modified support materials as probably a pore broken happened because of an exceeded mass impregnation,

Table 19: Physical properties of PEI-modified mesoporous silica samples

	Surface arer $_{BET}$ (m²/g)	Pore volume (cm³/g)	Pore size (nm)
SiO_2_Vp1.2	672	1.24	5.8
30wt.%PEI_SiO_2_Vp1.2	274	0.51	4.6
40wt.%PEI_SiO_2_Vp1.2	146	0.29	4.7
50wt.%PEI_SiO_2_Vp1.2	109	0.22	5.0
60wt.%PEI_SiO_2_Vp1.2	13	0.04	7.2
SiO_2_Vp1.5	707	1.47	6.6
30wt.%PEI_SiO_2_Vp1.5	285	0.62	5.3
40wt.%PEI_SiO_2_Vp1.5	157	0.36	5.5
50wt.%PEI_SiO_2_Vp1.5	100	0.24	5.9

Besides the physical properties check, morphology studies of PEI-modified silica samples were also implemented to assist evaluation the amine loading accuracy conducted by SEM. Figure 37 shows the morphology of the silica samples with pore volume of 1.5 cm³/g in each stages: (i) after templates removal, (ii) after PEI impregnation and (iii) after CO_2 adsorption / desorption experiments. There is almost no obvious morphological change from the images, in other words, it is difficult to evaluate the mass change of samples quantitively from the shape modification.
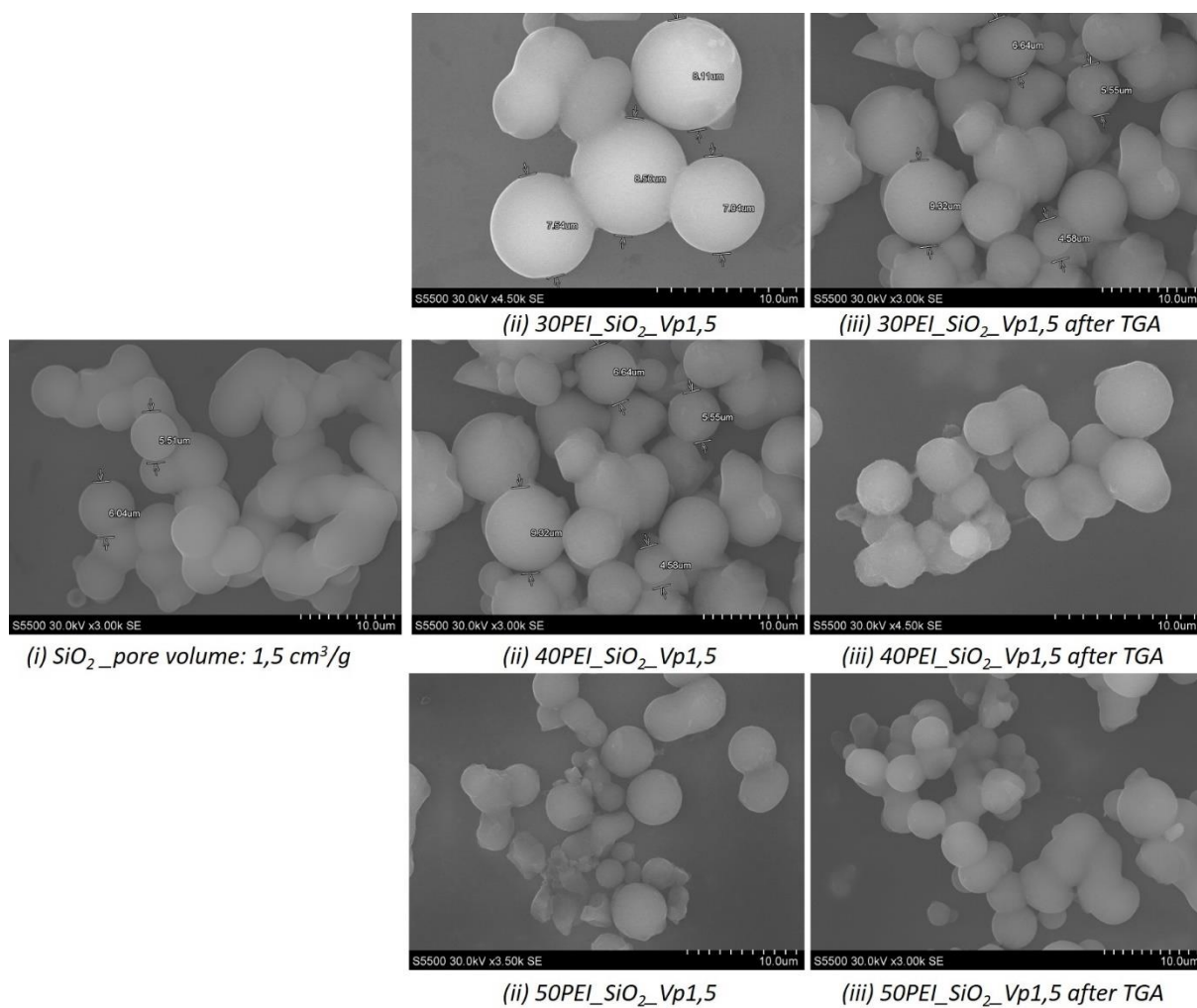
Figure 37: An example of SEM images of silica sorbents in different stage

5.3.2. Amine decomposition and remove at high temperature

As reported the amine can be decomposed and removed as volatiles at high temperatures (Xu et al., 2003), so in addition to CO_2 adsorption performance analysis, the amine loading was measured by the weight loss in the process of heating the composite to 600 °C after adsorption / desorption procedure by TGA in this thesis research as shown in Figure 38.
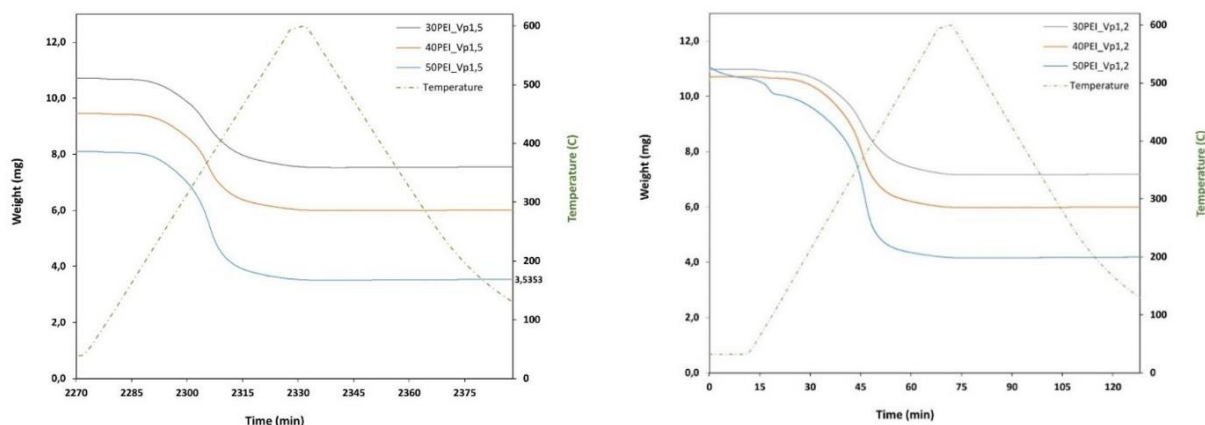
Figure 38: PEI decomposition experiments carried on different PEI-modified SIO$_2$ samples

According to the mass change of each sample, the actual PEI loading concentration has been calculated and summarized in Table 20. Based on actual amine weight percentages, relevant CO$_2$ capacity as per unit PEI was obtained as well. Table 21 and Table 22 summarized the updated optimum and practical CO$_2$ capacity of different amine functionalized mesoporous silica materials. Observations of the difference between theoretical and investigated PEI weight contents indicated that the physical impregnation of PEI procedure could be influenced by several infects for example the operation temperature, stirring ratio, mixing time, drying process, human error and etc. Although all negative effects can be avoided through experimental optimization, the procedure of PEI contents check enhanced the reliability of experimental results both on the determination of the actual amine load and subsequent CO$_2$ capture performance research of amine functionalized silica materials.

Table 20: Summary of amine loading correction to PEI-modified SiO$_2$ samples

PEI-modified mesoporous silica samples	Initial sample weight (g)	Final sample weight (g)	Δ mass = Init. − Final weight (g)	PEI loading = Δ mass / Int. weight (wt. %)
30PEI_Vp1.2	10.9710	7.1863	3.7847	34
40PEI_Vp1.2	10.5657	6.0000	4.5657	43
50PEI_Vp1.2	11.0510	4.1848	6.8662	62
30PEI_Vp1.5	10.7140	7.5476	3.1664	30
40PEI_Vp1.5	9.4584	6.0110	3.4474	36
50PEI_Vp1.5	8.1010	3.5355	4.5655	56

Table 21: Updated CO_2 optimum capacities of PEI-modified SiO_2 samples

PEI-modified mesoporous silica samples	Theoratical PEI loading (wt.%)	Investigated PEI loading (wt.%)	CO_2 adsorption OPTIMUM capacity (mmol/g PEI)	
			TGA	Correction
30PEI_Vp1.2_75°C	30	34	5.29	4.67
40PEI_Vp1.2_75°C	40	43	5.77	5.37
50PEI_Vp1.2_75°C	50	62	5.04	4.06
30PEI_Vp1.5_75°C	30	30	4.91	4.91
40PEI_Vp1.5_75°C	40	36	5.42	6.02
50PEI_Vp1.5_75°C	50	56	4.59	4.10
30PEI_Vp1.5_120°C	30	30	4.86	4.86
40PEI_Vp1.5_120°C	40	36	5.37	5.97
50PEI_Vp1.5_120°C	50	56	4.48	4.00

Table 22: Updated CO_2 practical capacities of PEI-modified SiO_2 samples

PEI-modified mesoporous silica samples	Theoratical PEI loading (wt.%)	Investigated PEI loading (wt.%)	CO_2 adsorption PRACTICAL capacity (mmol/g PEI)	
			TGA	Correction
30PEI_Vp1.2	30	34	4.87	4.30
40PEI_Vp1.2	40	43	4.62	4.30
50PEI_Vp1.2	50	62	2.80	2.26
30PEI_Vp1.5	30	30	4.50	4.91
40PEI_Vp1.5	40	36	4.50	5.00
50PEI_Vp1.5	50	56	3.05	2.72

5.4. CO_2 capture performances comparison between different samples

5.4.1. CO_2 adsorption performance of PEI_SiO₂ samples with different mesoporous structure

Figure 39 shows the CO_2 adsorption optimum capacity as per unit amine of different PEI_SiO₂ samples and desorption temperature. It is found that the PEI_SiO₂ with 40 wt.% amine loading

presented the highest CO_2 capacity in both large and small pore volume of support mesoprouse silica supports. The CO_2 adsorption optimum capacity of 40PEI_SiO2_Vp1.2 and 40PEI_SiO$_2$_Vp1.5 was 5.37 and 6.02 mmol/g PEI, repectively. With the change of porosity from 1.2 to 1.5 cm^3/g of mesoporous silica sorbents, the CO_2 optimum capacity increases by 12%. Even if it was operated for a long-term in a harsh condition with high desorption temperature, the optimum capacity was maintained with slight change within an acceptable range compared with its performance under the mild opeating conditions.
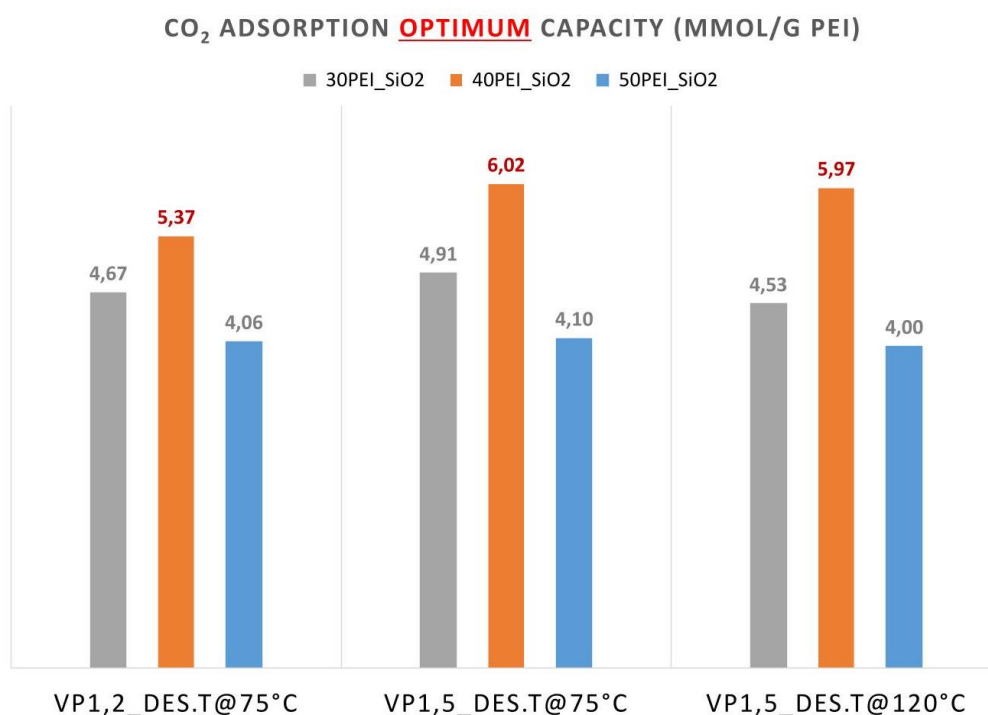
Figure 39: CO_2 optimum adsorption capacity of PEI_SiO$_2$ samples under different operating conditions

Refer to Figure 40, the practical CO_2 capacity and stability was illustrated, PEI_SiO$_2$ with 30 wt.% amine loading demostrated a strong competive performance nearly same as the 40 wt.% PEI_SiO$_2$ both within small and large porosity of silica supports. Same as the optimal capacity, With the change of porosity from 1.2 to 1.5 cm^3/g of mesoporous silica sorbents, the CO_2 practical capacity increases by 14% and 16% for 30PEI_SiO$_2$ and 40PEI_SiO$_2$, respectively.

The stability study was carried out both under mild and harsh conditions with different contact time and desorption temperature. It is found that the PEI_SiO$_2$ with different porosity and amine loading contents all have a very high stability around 99% and 95% after adsorption / desorption

cycle operation under mild conditions and harsh conditions, respectively. There are no significant differences among them, even if the PEI_SiO$_2$ with 40 wt.% amine loading shown a slight advantage than others.
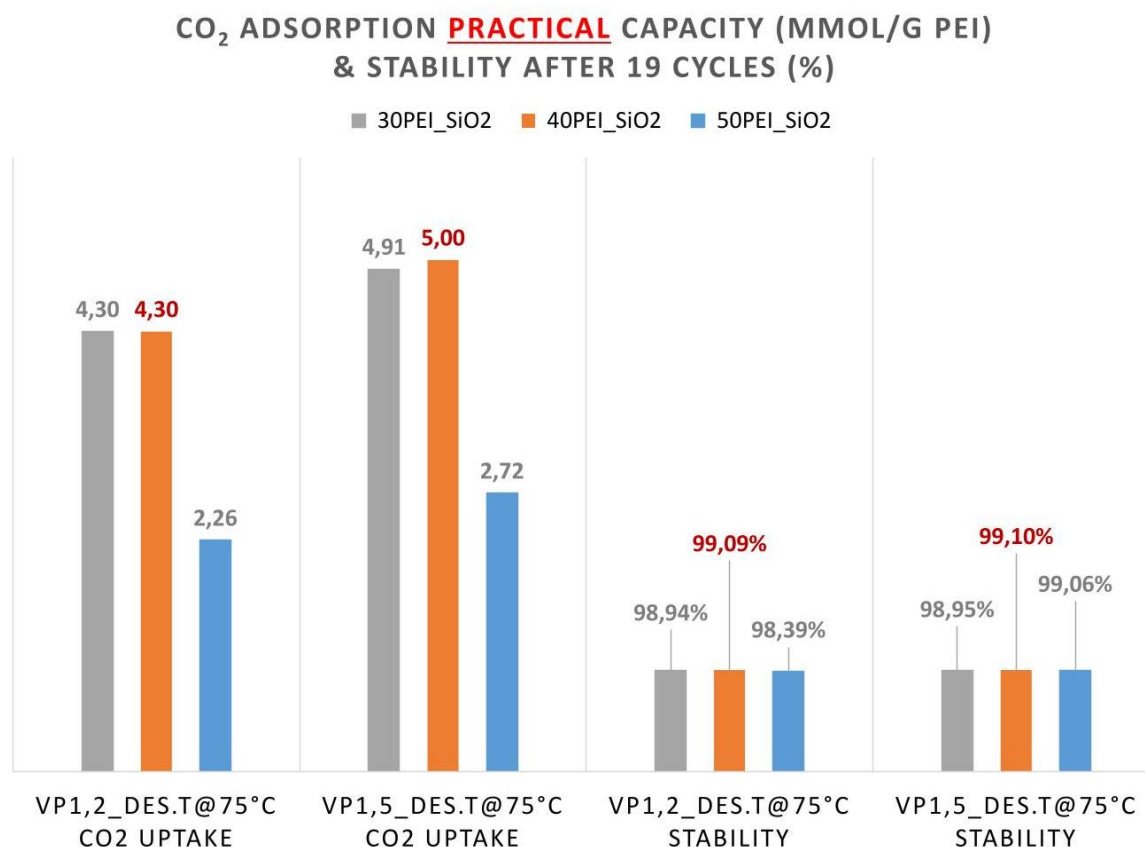
Figure 40: CO$_2$ practical adsorption capacity and cycle stability of PEI_SiO$_2$ samples with different porosity under mild conditions

5.4.2. CO$_2$ adsorption performance of 40PEI_SiO$_2$ samples compared with previous master study work

A comparison analysis on cycle stability was carried out between mesoporous silica synthesized in this thesis study and other mesoporous amine modified silica chosen from precious thesis study implemented by Siyu Wang in 2019 (Wang, 2019). As given in Table 23, the CO$_2$ adsorption and desorption operating conditions (including adsorption/desorption gas composition, adsorption temperature and cycle duration) were setup same, except the desorption temperature: 120 °C for this thesis study and 100 °C using in her research.

Table 23: CO_2 capture performance compared with other study for 40PEI_SiO$_2$ adsorbents

Samples (a): 40 wt.% PEI-modified mesoporous SiO$_2$_Vp1,5 (corrected with PEI loading check)

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI	
1			2.182	6.060	-
2			**2.148**	**5.967**	**100.00**
3			2.129	5.914	99.12
4			2.112	5.866	98.31
5	100 / 100	75 / 120	2.100	5.834	97.79
6			2.084	5.788	97.00
7			2.077	5.770	96.71
8			2.067	5.742	96.25
9			2.055	5.708	95.67
10			2.049	5.692	95.41

Samples (b): 40 wt.% PEI-modified mesoporous silica from previous thesis studies in 2019
Notes:
1. *Data was unavailable from original source. For comparison purpose with this thesis study, it was calculated from CO$_2$ uptake per g sorbents devided by PEI weight percentage.*
2. *Data were unavailabe from original source.*

Cycle sequence (#)	Ads./Des. Time (min)	Ads./Des. Temperature (°C)	CO$_2$ adsorption capacity		Stability (%)
			mmol/g Sorbents	mmol/g PEI [1]	
1			n/a [2]	n/a [2]	-
2			**1.770**	**4.425**	**100.00**
3			1.718	4.288	96.89
4			1.650	4.125	93.22
5	100 / 100	75 / 100	1.630	4.075	92.09
6			1.603	4.008	90.56
7			1.576	3.940	89.04
8			1.567	3.918	88.53
9			1.533	3.833	86.61
10			1.512	3.780	85.42

Table 24: Summary of the CO_2 caputure optimum performance between 40PEI_SiO$_2$ sorbents from this thesis studies and previous master study

	Ads./Des. Time	Ads./Des. Temp.	Stability after 9 cycles	CO$_2$ adsorption capacity (mmol/g)	
	(min)	(°C)	(%)	Per sorbents	Per PEI
40PEI_Vp1.5	100/100	75/120	95.41	2.15	5.97
40PEI/20-25 Si (750 °C)	100/100	75/100	85.42	1.77	4.43

Table 24 gives the comparison of optimum capacity and stability after 9 cycles CO_2 adsorption / desorption operation achieved by different 40PEI_SiO$_2$ sorbents. Figure 41 shows the trends of their stability reduction with cycle. Obviously, the samples synthesized in this thesis study have much better CO_2 adsorption capacity and cycle stability, compared with previous student's work. The main reason could be due to a poor structure of solid sorbents, as shown in Table 25, which leaded to a serious amine loss by both leaching during impregnation and degradation in adsorption and desorption cycle runs.
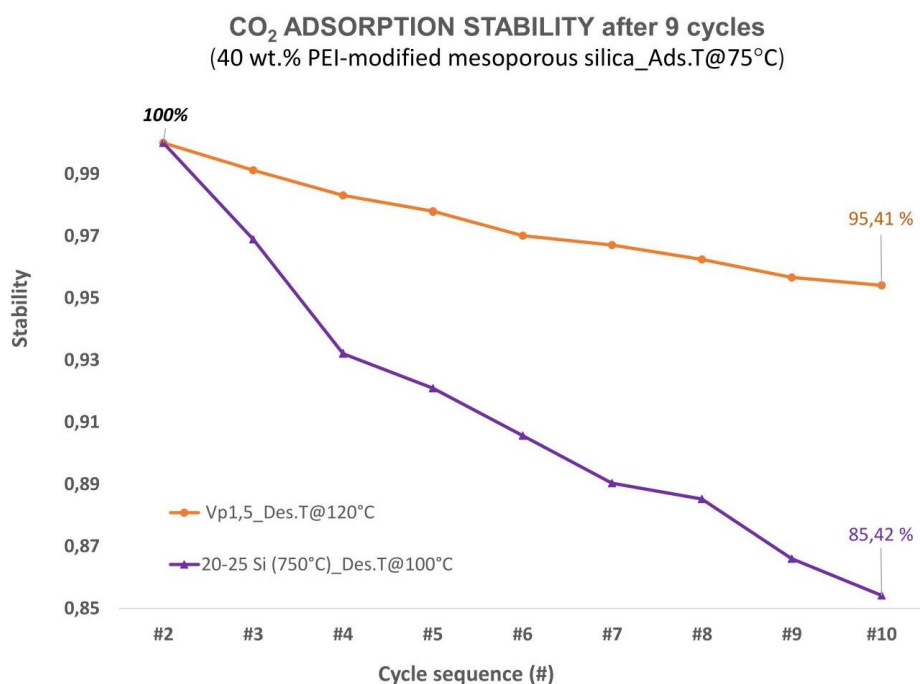
Figure 41: Comparison of the stability of 40PEI_SiO$_2$ samples with previous thesis study

Table 25: Physical properties of two 40 wt.% loaded silica materials

	Surface arer $_{BET}$ (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
40PEI_Vp1.5	707	1.47	6.6
40PEI/20-25 Si (750 °C)	137	0.51	13.7

6. CONCLUSION

Mesoporous silica sorbents were prepared at different synthesis conditions and studied by nitrogen adsorption / desorption and SEM techniques. The expected mesoporous silica materials of high surface area and large pore volume with narrow distribution were obtained by tuning the initial gel composition and operation condition. The optimal composition of solution was setup with a molar ratio of TEOS: 1, P123: 0.044, CTAB: 0.122, HCl: 2.67, EtOH: 9.5 and H_2O: 116, in two step aging procedure at 80 °C during 5 hours and 130 °C during 12 hours. According to characterization results, the surface area, pore volume, pore size of optimal silica sorbents synthesized in this study were 700 m^2/g, 1.5 cm^3/g and 7 nm. These mesoporous silica particles presented a rigid spherical morphology with sizes from 4 to 10 µm. Two mesoporous silica particles with pore volume of 1.2 and 1.5 cm^3/g were chosen as the support material for amine functionalization and further utilized as adsorbent in the CO_2 capture process application.

By physical impregnation, the mesoporous silica samples with different porosity were functionalized by PEI, and the loading amount of amine varied from 30 to 60 wt.% of total sorbents. Through customized TGA procedure, the '2 + 20 cycle' mode was used for the first time to test the CO_2 optimum and practical adsorption capacity as well as the cycle stability of PEI modified mesoporous silica materials under mild conditions, which was applied in a dry adsorption gas within 5 vol.% CO_2 and sorbents' regeneration in pure N_2.

The silica sorbents with 40 wt.% PEI loading presented the highest CO_2 capacity among different PEI modified silica materials, and high porosity of silica support sorbents provided a positive impact on increasing the CO_2 uptake as well as better cycle stability. The best performance shown in this thesis study of PEI-modified mesoporous silica was 6.02 mmol/g PEI as optimum capacity and 5 mmol/g PEI as practical capacity, while the cycle stability was 99.1 % and 95.4 % under mild and harsh condition, respectively. Study taken on the comparison

with previous thesis work results shown a huge improvement of CO_2 capacity and cycle stability obtained by adsorbents synthesized in this thesis research.

A PEI loading check program was added after CO_2 adsorption / desorption runs to determine actual amine impregnation amount in the tested adsorbents, which was helpful on the correction of CO_2 capacity and in turns to a reliable database for further economic research on amine-modified silica sorbents in the application of CO_2 capture process.

7. FUTURE WORK

Due to COVID-19 pandemic, the parallel loading capacity of the laboratory has dropped a lot compared to usual, so many expected experiments and research works cannot be implemented in this thesis study with such time limitation. By combining the previous theoretical research and experiments results from this thesis study, research on the application of amine modified mesoporous silica sorbents in CO_2 capture process could have the following directions for the future work:

- Using pure CO_2 instead of pure N_2 as the stripping gas for a thorough regeneration to solving the potential problems both on N_2 availability and contaminant of final CO_2 products by a mixture of N_2.

- Testing with an inlet gas mixture closed to real industrial conditions. The inlet gas condition chosen for most of solid sorbents in the application of CO_2 capture was a dry mixture of CO_2 and N_2 as a simulation of flue gas from post-combustion process. The effect of other gas components and water contents in the actual flue gas on the solid sorbents shall be conducted in the further laboratory research for a comprehensive study on amine-modified silica sorbents as well.

- Optimizing amine functionality and modification methods on solid support sorbents. The type of amine chosen for silica sorbents functionalization and how to impregnate it with those solid sorbents is a vital effects on CO_2 adsorption / desorption performance for the CO_2 capture process by solid sorbents, especially on the balance between energy consumption and CO_2 capacity accepted by industrial application in a feasible and economic way.

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APPENDIX

HSE RISK ASSESSMENT

			Status	**Date**
ID	33436		Created	12.06.2019
Risk Area	Risikovurdering: Helse, miljø og sikkerhet (HMS)		Assessment started	03.07.2019
Created by	Yun Liu		Measures decided	
Responsible	Yun Liu		Closed	

Risk Assessment:

CAT_Master student_2019_Yun Liu

Valid from-to date:

6/12/2019 - 6/12/2022

Location:

K5-321, K5-441, K5-425, K5-447, chemical hall D

Goal / purpose

Synthesis, characterization and test of solid sorbents for low temperature CO2 capture

Background

The synthesis, characterization and test of N doped silica spheres integrated with PEI.
The polymer spheres will be synthesis by polymerization with inverse emulsion technology. The polymerization and carbonation conditions, hard templates and reactant precursors, PEI molecular loading will be studied with aiming of controlling the size and shape of spheres, porosity, pore size distribution, integration of PEI and silica surfaces. The capacity, kinetics, stability of solid will be studied at both dry and wet conditions.

Description and limitations

Silica spheres are fabricated by using resorcinol and formaldehyde as carbon precursors, colloidal nano-particle as silica source. Other chemicals used also includes span80, paraffin oil.
Formaldehyde is toxic chemical. But it will be only used inside of the fume cabinet.
Temperature is around 80 □ at atmosphere pressure.
Synthesis procedures are done at Lab-321.
Acetone for cleaning.

Calcination of silica spheres is done at Chemical hall D
Temperature is 500-700□ using air as inlet gas.

Impregnation is done at Lab-321 under ventilation.
PEI is used to impregnate into silica spheres.
Methanol is used in the impregnation process.
Temperature is 35 □ under atmospheric pressure.

TGA is done at Lab-441 and BET is done at Lab-425.
S(T)EM is done at Nano lab.

April-Mai 2020 - preventive measures towards Covid-situation:
1) Switch off procedure for MY SET-UP (No fixed setup for my lab work, but heating plates with magnetic mixer will be used during synthesis)
- Synthesis will be executed in lab K5-321
- Switch off the power of apparatus
- Leave the chemicals in the fume hood

2) Risk related to shortage of personnel in the labs:
- No special risks

3) Safety measures related to spread of covid-19 infection
- Avoid touching the face
- Disinfection before and after with ethanol on all surfaces I will in contact with (door knob – card reader with code panel – common equipment (BET 3000 and TGA-TA) keyboard – mouse – screen – desk)
- Keep 2m distance from colleagues
- Use nitrile gloves when touching shared lab set-ups and equipment
- Wash hands as often as possible

Prerequesites, assumptions and simplifications

For the synthesis of silica spheres, the stirring reactor is placed in the fume hood. The SDS of the chemicals involved in the project are presented in Attachments.
New SDS will be uploaded if using new chemicals

Attachments

SDS Formaldehyde Solution-2019.pdf
SDS Polyethylenimine-2019.pdf
SDS Resorcinol-CASNO-108-46-3.pdf
SDS Acetone.pdf
SDS Colloidal silica.pdf
SDS Span_80.pdf
SDS Methanol.pdf
SDS Paraffin_oil.pdf
SDS TEOS.pdf

References

[Ingen registreringer]

Summary, result and final evaluation

The summary presents an overview of hazards and incidents, in addtition to risk result for each consequence area.

Hazard:	**Hazardous chemicals used for adsorbent's synthesis and implegnation**

Incident:	**Spillage of formaldehyde**

Consequence area:	Helse	Risk before measures:	🟡 Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢 Risiko after measures:	⚪

Incident:	**Spillage of resorcinol**

Consequence area:	Helse	Risk before measures:	🟡 Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢 Risiko after measures:	⚪

Incident:	**Spillage of PEI**

Consequence area:	Helse	Risk before measures:	🟡 Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢 Risiko after measures:	⚪

Incident:	**Spillage of methanol**

Consequence area:	Helse	Risk before measures:	🟡 Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢 Risiko after measures:	⚪

Incident:	**Spillage of TEOS**

Consequence area:	Helse	Risk before measures:	🟡 Risiko after measures:	⚪
	Ytre miljø	Risk before measures:	🟢 Risiko after measures:	⚪

Hazard:	**Cleaning and waste handling**				

Incident:	**Inhale or spill acetone on skin**				

Consequence area:	Helse	Risk before measures:	🟢	Risiko after measures:	⚪

Hazard:	**Instruments (apparatus, reactors) manipulation**				

Incident:	**Skin burns when operating calcination oven**				

Consequence area:	Helse	Risk before measures:	🟢	Risiko after measures:	⚪

Incident:	**Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen**				

Consequence area:	Helse	Risk before measures:	🟡	Risiko after measures:	⚪

Hazard:	**Pressurized gas manipulation**				

Incident:	**Large leak of CO2, O2 or N2**				

Consequence area:	Helse	Risk before measures:	🟢	Risiko after measures:	⚪

Hazard:	**Working in the lab under covid-situation**				

Incident:	**Personnel infection caused by covid-19**				

Consequence area:	Helse	Risk before measures:	🟡	Risiko after measures:	⚪

Final evaluation

Organizational units and people involved

A risk assessment may apply to one or more organizational units, and involve several people. These are lsited below.

Organizational units which this risk assessment applies to

 - Institutt for kjemisk prosessteknologi

Participants

De Chen

Estelle Marie M. Vanhaecke

Ainara Moral Larrasoana

Anne Hoff

Kumar Ranjan Rout

Readers

[Ingen registreringer]

Others involved/stakeholders

[Ingen registreringer]

The following accept criteria have been decided for the risk area Risikovurdering: Helse, miljø og sikkerhet (HMS):

Helse	**Materielle verdier**	**Omdømme**	**Ytre miljø**

Overview of existing relevant measures which have been taken into account

The table below presents existing measures which have been take into account when assessing the likelihood and consequence of relevant incidents.

Hazard	Incident	Measures taken into account
Hazardous chemicals used for adsorbent's synthesis and implegnation	Spillage of formaldehyde	SDS
	Spillage of formaldehyde	Local exhaust
	Spillage of formaldehyde	Fume hood
	Spillage of formaldehyde	Personal measures
	Spillage of formaldehyde	Personal measures
	Spillage of formaldehyde	Fume hood
	Spillage of formaldehyde	Local exhaust
	Spillage of formaldehyde	SDS
	Spillage of resorcinol	Personal measures
	Spillage of resorcinol	Fume hood
	Spillage of resorcinol	Local exhaust
	Spillage of resorcinol	SDS
	Spillage of PEI	Personal measures
	Spillage of PEI	Fume hood
	Spillage of PEI	Local exhaust
	Spillage of PEI	SDS
	Spillage of methanol	Personal measures
	Spillage of methanol	Fume hood
	Spillage of methanol	Local exhaust
	Spillage of methanol	SDS
	Spillage of TEOS	Personal measures
	Spillage of TEOS	Fume hood
	Spillage of TEOS	Local exhaust
	Spillage of TEOS	SDS
Cleaning and waste handling	Inhale or spill acetone on skin	Personal measures
	Inhale or spill acetone on skin	Personal measures
Instruments (apparatus, reactors) manipulation	Skin burns when operating calcination oven	Personal measures
	Skin burns when operating calcination oven	Procedures
	Skin burns when operating calcination oven	Previous risk assessment for instruments/methods
	Skin burns when operating calcination oven	Apparatus card

Instruments (apparatus, reactors) manipulation	Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen	Personal measures
	Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen	Instrument/method training
	Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen	Procedures
	Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen	Previous risk assessment for instruments/methods
Pressurized gas manipulation	Large leak of CO2, O2 or N2	Personal measures
	Large leak of CO2, O2 or N2	Fume hood
	Large leak of CO2, O2 or N2	Local exhaust
	Large leak of CO2, O2 or N2	SDS
	Large leak of CO2, O2 or N2	Instrument/method training
	Large leak of CO2, O2 or N2	Gas detection
	Large leak of CO2, O2 or N2	Procedures
Working in the lab under covid-situation	Personnel infection caused by covid-19	Personal measures
	Personnel infection caused by covid-19	Nitrile gloves
	Personnel infection caused by covid-19	NTNU guidelines for laboratory work
	Personnel infection caused by covid-19	NTNU guidelines for laboratory work

Existing relevant measures with descriptions:

Personal measures
Safety goggles
Lab coat
Safety goggles
Gas mask (6075)

Fume hood
[Ingen registreringer]

Local exhaust
[Ingen registreringer]

SDS
[Ingen registreringer]

Instrument/method training
[Ingen registreringer]

Gas detection
Where it is installed

Procedures
Operation procedure
Instrument manual

Ergonomic measures

[Ingen registreringer]

Previous risk assessment for instruments/methods

[Ingen registreringer]

Apparatus card

[Ingen registreringer]

Gas trolley

[Ingen registreringer]

Nitrile gloves

[Ingen registreringer]

NTNU guidelines for laboratory work

[Ingen registreringer]

Risk analysis with evaluation of likelihood and consequence

This part of the report presents detailed documentation of hazards, incidents and causes which have been evaluated. A summary of hazards and associated incidents is listed at the beginning.

The following hazards and incidents has been evaluated in this risk assessment:

- **Hazardous chemicals used for adsorbent's synthesis and implegnation**
    - Spillage of formaldehyde
    - Spillage of resorcinol
    - Spillage of PEI
    - Spillage of methanol
    - Spillage of TEOS
- **Cleaning and waste handling**
    - Inhale or spill acetone on skin
- **Instruments (apparatus, reactors) manipulation**
    - Skin burns when operating calcination oven
    - Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen
- **Pressurized gas manipulation**
    - Large leak of CO2, O2 or N2
- **Working in the lab under covid-situation**
    - Personnel infection caused by covid-19

Detailed view of hazards and incidents:

Hazard: Hazardous chemicals used for adsorbent's synthesis and implegnation

Hazardous chemicals involved in synthesis: formaldehyde, resorcinol;
Hazardous chemicals involved in Impregnation: PEI, methanol.

Incident: Spillage of formaldehyde

Solution spill or beaker broken

Likelihood of the incident (common to all consequence areas):   **Less likely (2)**

> *Kommentar:*
> Use of gloves, labcoat and fume hood

Consequence area: Helse   *Risk:*

> *Assessed consequence:* **Large (3)**
>
> *Comment:* Formaldehyde:
>
> > H226 Flammable liquid and vapour.
> > H301 + H311 + H331 Toxic if swallowed, in contact with skin or if inhaled.
> > H314 Causes severe skin burns and eye damage.
> > H317 May cause an allergic skin reaction.
> > H335 May cause respiratory irritation.
> > H341 Suspected of causing genetic defects.
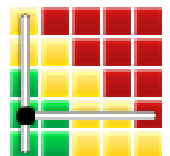> > H350 May cause cancer.
> > H370 Causes damage to organs

Consequence area: Ytre miljø   *Risk:*

> *Assessed consequence:* **Small (1)**
>
> *Comment:* [Ingen registreringer]

Incident: Spillage of resorcinol
- -

Solution spill or beaker broken

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

      Kommentar:

      Use of gloves, labcoat and fume hood

Consequence area: Helse

    Assessed consequence: **Large (3)**

        Comment: H302 Harmful if swallowed.
                   H315 Causes skin irritation.
                   H317 May cause an allergic skin reaction.
                   H319 Causes serious eye irritation.
                   H370 Causes damage to organs (Central nervous system, Blood, Respiratory
                   system) if swallowed.
                   H410 Very toxic to aquatic life with long lasting effects.

Risk:

Consequence area: Ytre miljø

    Assessed consequence: **Small (1)**

        Comment: [Ingen registreringer]

Risk:

Incident: Spillage of PEI
- -

Solution spill or beaker broken

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

      Kommentar:

      Use of gloves, labcoat and fume hood

Consequence area: Helse

    Assessed consequence: **Large (3)**

        Comment: Hazard statement(s)
                   H302 Harmful if swallowed.
                   H317 May cause an allergic skin reaction.
                   H319 Causes serious eye irritation.
                   H411 Toxic to aquatic life with long lasting effects.
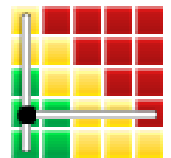
Risk:

Consequence area: Ytre miljø

Risk:

Assessed consequence: **Small (1)**

Comment: [Ingen registreringer]

Incident: Spillage of methanol
- -

Solution spill or beaker broken

Likelihood of the incident (common to all consequence areas): **Less likely (2)**

Kommentar:

Use of gloves, labcoat and fume hood

Consequence area: Helse

Risk:

Assessed consequence: **Large (3)**

Comment: Hazard statement(s)
H225 Highly flammable liquid and vapour.
H301 + H311 + H331 Toxic if swallowed, in contact with skin or if inhaled.
H370 Causes damage to organs

Consequence area: Ytre miljø

Risk:

Assessed consequence: **Small (1)**

Comment: [Ingen registreringer]

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Incident: Spillage of TEOS

- -

Solution spill or beaker broken

Likelihood of the incident (common to all consequence areas):   **Less likely (2)**

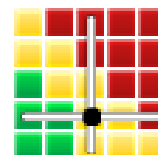> *Kommentar:*
> Use of gloves, labcoat and fume hood

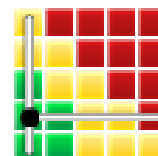**Consequence area: Helse**   *Risk:*

> *Assessed consequence:* **Large (3)**
>
>> *Comment:* H226 Flammable liquid and vapour.
>> H319 Causes serious eye irritation.
>> H332 Harmful if inhaled.
>> H335 May cause respiratory irritation

Consequence area: Ytre miljø   *Risk:*

> *Assessed consequence:* **Small (1)**
>
>> *Comment:* [Ingen registreringer]

Hazard: Cleaning and waste handling

Incident: Inhale or spill acetone on skin

- -

Likelihood of the incident (common to all consequence areas):   **Less likely (2)**

       Kommentar:

       Work in fume hood, change gloves if spillage or use Barrier gloves that are resistant to acetone

Consequence area: Helse   *Risk:*

    Assessed consequence: **Medium (2)**

          Comment: H225 Highly flammable liquid and vapour.
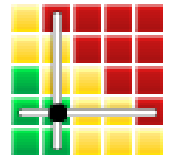   H319 Causes serious eye irritation.
                    H336 May cause drowsiness or dizziness

Hazard: Instruments (apparatus, reactors) manipulation

Incident: Skin burns when operating calcination oven

Likelihood of the incident (common to all consequence areas):   **Unlikely (1)**

Kommentar:

Heat protecting gloves
Screen for reading the temperature value
Instrument training

Consequence area: Helse   *Risk:*

Assessed consequence: **Medium (2)**

Comment: The calcination is realized at elevated temperatures and in order to avoid skin burns the temperature should be read on the screen or to use heat protecting gloves resistant to a limited temperature value

Incident: Frostbite when manipulation the liquid nitrogen during the utilization of BET instrumen

Likelihood of the incident (common to all consequence areas):   **Unlikely (1)**

Kommentar:

Personal protective equipments

Consequence area: Helse   *Risk:*

Assessed consequence: **Large (3)**

Comment: Skin burns if there is a direct contact of liquid nitrogen with the skin or the unprotected skin is near the nitrogen container

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Hazard: Pressurized gas manipulation

Incident: Large leak of CO2, O2 or N2

- -

Likelihood of the incident (common to all consequence areas):   **Less likely (2)**

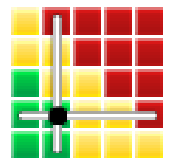   *Kommentar:*

        Personal protective equipments, gas detector, fume hood

Consequence area: Helse

    Assessed consequence: **Medium (2)**

        Comment: If a large gas leak occurs, especially in a limited room space, the person in contact can suffer a suffocation

Risk:

Hazard: Working in the lab under covid-situation

Incident: Personnel infection caused by covid-19

Likelihood of the incident (common to all consequence areas):   **Less likely (2)**

> *Kommentar:*
> Strict guidelines for lab work, personal protective equipment

Consequence area: Helse   *Risk:*

> *Assessed consequence:* **Large (3)**

> > *Comment:* covid-19 is a virus which is highly infectious and highly lethal

Overview of risk mitiating measures which have been decided:

Below is an overview of risk mitigating measures, which are intended to contribute towards minimizing the likelihood and/or consequence of incidents:

Overview of risk mitigating measures which have been decided, with description:

Detailed view of assessed risk for each hazard/incident before and after mitigating measures

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