Preparation and Evaluation of New Nanoporous Silica Materials for Molecular Filtration and for Core Materials in Vacuum Insulation Panels

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Abstract

Nanoporous materials for gas purification and thermal insulation have been studied and developed for application in many areas. It is known that a single adsorbent may not adequately control multiple contaminants. Further the utilization of nanoporous material as thermal insulator in building applications is limited due to high cost. Moreover, in view of the global environmental movement for clean air and reduction of heating energy consumption in built environment, the development of new and better nanoporous materials will not only facilitate major advances in gas adsorption and thermal insulation technology, but also meet the new challenges that cannot be met with the nanoporous materials that are currently available. This thesis presents a synthesis of new nanoporous silica based materials, and the characterization and application of these materials for molecular filtration and thermal insulation. Commercial nanoporous materials have been used for benchmarking for the pore properties, the applicability, and the performance of these new materials.

First a double metal-silica adsorbent has been synthesized. The preparation procedure is based on the use of sodium silicate coagulated with various ratios of magnesium and calcium salts which yields micro-meso porous structures in the resulting material. The results show that molar ratios of Mg/Ca influence the pore parameters as well as the structure and morphology. The bimodal pore size can be tailored by controlling the Mg/Ca ratio.

In the second synthesis, pure mesoporous silica, SNP has been prepared using glycerol as pore forming agent and monovalent salts as coagulant. This leads to material with large surface area and uniformed pore size centred at 43 or 47 nm. The materials further exhibits a low bulk density in the range of 0.077 to 0.122 g/ml and possess a high porosity in the range of 95-97%. The influence of acid type (organic or inorganic) on the pore parameters and on the tapped density has also been investigated.

A synthesis method has also been developed for the preparation of carbon-silica composites. The method involves a number of routes, which can be summarised as addition of activated carbon particles to (I) the paste, (II) the salt solution, or (III) with the sodium silicate solution. In route II and III the activated carbon is present before coagulation. The routes presented here leads to carbon-silica composites possessing high micro porosity, meso porosity as well as large surface areas. The results further shows that pore size distribution may be tailored based on the route of addition of the carbon particles. Following route I and III a wide pore size (1-30 nm) was obtained whereas by route II a narrow pore size (1-4 nm) was observed.

MgCa-silica chemisorbents were also developed using either potassium hydroxide or potassium permanganate as impregnate chemicals. A direct or post-impregnation procedure was employed. The results revealed that the impregnate route and amount cause a reduction in both specific surface area and pore volume.

Finally the thermal conductivity and dynamic adsorption of H$_2$S, SO$_2$ and toluene were measured. Results show that at room temperature and atmospheric pressure, a thermal conductivity of 28.4 and 29.6 mW/m.K were obtained for the SNP mesoporous silicas. The dynamic adsorption behaviour of the chemisorbents and composites indicate their ability to absorbed H$_2$S, SO$_2$ and toluene respectively. The highest H$_2$S uptake corresponds to chemisorbents with 11.2-13.6 wt% KMnO$_4$. The effect of impregnation route, amount of KMnO$_4$ and its location in the pore system are likely the key factors in achieving a large H$_2$S uptake. For SO$_2$ adsorption, the highest uptake capacity was observed for MgCa-68/32-KOH. The results further suggest that the key to large SO$_2$ uptake is as a result of the synergetic effect between
large mesopore diameter and extensive mesopore volumes. Carbon-silica composites with carbon content 45 wt % exhibits high toluene adsorption with composite via route I having the highest toluene adsorption capacity (27.6 wt % relative to carbon content). The large uptake capacity of this composite was attributed to the presence of high microporosity volume and a wide (1-30 nm) bimodal pore system consisting of extensive mesopore channels (2-30 nm) as well as large surface area. These capacity values of carbon-silica composites are competitive to results obtained for commercial coconut based carbon (31 wt %), and better than commercial alumina-carbon composite (9.5 wt %).

**Keywords:** Adsorbents, activated carbon, MgCa-silica, carbon-silica composite, characterization, porous parameters, molecular filtration, thermal conductivity, thermal insulation
“Make all you can, save all you can, give all you can.”

-John Wesley

To My Family
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Four delightful, challenging and inspiring years journey has come to an end and I have been very blessed to have an enormous support from supervisors, colleagues, friends and family. I could not have done this without you! And will like to express my gratitude.

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# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Al-C</td>
<td>Commercial Alumina-Carbon Composite</td>
</tr>
<tr>
<td>ASAP</td>
<td>Accelerated Surface Area Porosimeter</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>CAC</td>
<td>Coconut Activated Carbon</td>
</tr>
<tr>
<td>CTC</td>
<td>Carbon Tetrachloride</td>
</tr>
<tr>
<td>d&lt;sub&gt;mes&lt;/sub&gt;</td>
<td>Maximum Mesopores Size</td>
</tr>
<tr>
<td>d&lt;sub&gt;mic&lt;/sub&gt;</td>
<td>Maximum Micropores Size</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>HK</td>
<td>Horvath-Kawazoe</td>
</tr>
<tr>
<td>IAP</td>
<td>Indoor Air Pollutants</td>
</tr>
<tr>
<td>IAQ</td>
<td>Indoor Air Quality</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>NLDFT</td>
<td>Non-local Density Functional Theory</td>
</tr>
<tr>
<td>p/p&lt;sup&gt;°&lt;/sup&gt;</td>
<td>Relative Pressure</td>
</tr>
<tr>
<td>PSD</td>
<td>Pore Size Distribution</td>
</tr>
<tr>
<td>S&lt;sub&gt;BET&lt;/sub&gt;</td>
<td>Specific Surface Area Obtained via Brunauer-Emmet-Teller-equation</td>
</tr>
<tr>
<td>S&lt;sub&gt;mes&lt;/sub&gt;</td>
<td>Mesoporous Surface Area Obtained via t-plot</td>
</tr>
<tr>
<td>S&lt;sub&gt;mic&lt;/sub&gt;</td>
<td>Micropore Surface Area Obtained via t-plot</td>
</tr>
<tr>
<td>SNP</td>
<td>SilicaNanoPorous material</td>
</tr>
<tr>
<td>V&lt;sub&gt;mes&lt;/sub&gt;</td>
<td>Mesoporous Pore Volume Obtained via t-plot</td>
</tr>
<tr>
<td>V&lt;sub&gt;mic&lt;/sub&gt;</td>
<td>Microporous Pore Volume Obtained via t-plot</td>
</tr>
<tr>
<td>V&lt;sub&gt;tot&lt;/sub&gt;</td>
<td>Total Pore Volume</td>
</tr>
<tr>
<td>VOC’s</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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1. General Introduction

The emergent mechanization and industrialization of society has resulted in most people spending by far more than 90 per cent of their lives indoors (Consumer product safety commission 1994; Leech et al. 2002). Much of our time spent indoors is either at work or home and the rest being in the leisure centres, shopping centres and even a small amount inside vehicles. To ensure occupant’s health and comfort in the built environment, the indoor air quality and thermal comfort must be at acceptable targets. In agreement with this, four important features for assessment of high-quality buildings have included indoor air quality (IAQ), thermal comfort, visual and acoustic characteristics, as well as a low impact on the environment (Krzaczek and Tejchman 2012; McIntyre 1980).

Exposure to indoor air pollutants (IAP) over the past decades has been on increased. This has been brought about by a variety of factors including: construction of tightly sealed buildings, reduction of ventilation rates (for energy saving) and use of synthetic building materials and furnishings (Krzaczek and Tejchman 2012). Other sources of IAP arise from chemically formulated personal care products, pesticides and household cleaners as well as from printer machines. Finally through our activities such as cooking, laundry, entertainment, painting, hobbies, etc. we release odours into indoor air. The effect of chemical pollutants on the perceived IAQ and its health effects on the occupants have been investigated in numerous studies. The exposure to volatile organic compounds (VOCs) for instance were suspected to cause “Sick Building Syndrome”, with symptoms like eye and upper respiratory irritation, nasal congestion, headache, rash, fatigue and asthmatic symptoms (Consumer product safety commission 1994; McIntyre 1980).

Not only has air contaminates been associated with health risks and reduced work productivity (Consumer product safety commission 1994) but could also cause irreversible damage to vulnerable artefacts (Parmar and Grosjean 1991). Air pollutants such as sulphur dioxide (SO₂) and hydrogen sulphide (H₂S) damage to works of art and other cultural property has emerged as a key issue in art conservation (Parmar and Grosjean 1991). The removal of air pollutants from air streams could be achieved by adsorption onto a solid porous material, plasma-induced reaction, catalytic oxidation and absorption with liquid solution (John et al. 2000). Dynamic adsorption by porous adsorbents has by far been proven as method for the abatement of indoor air pollutants at low ppm level (John et al. 2000). Not only do the other techniques and materials operations not fit in indoor air purification but also have some major drawbacks such as cause of secondary pollution after invalidation. Molecular filtration is the term used to describe filtration (in air) of non-particle species. Molecular filter generally contains porous adsorbents and employ the principles of adsorption.

Wherever artificial climates are created for human occupation, the aim is that every individual is adapted to the thermal environment so that each will be in thermal comfort. Observed in broader perspective, it can perhaps even be maintained that man’s desire for thermal environment is the prime motivation for building houses in any way. Generating thermal comfort for building occupants is a primary reason for heating and air conditioning indoor environment, and this has a major influence on the building construction and the choice of materials (Fanger 1970). Heating indoor space is an energy driven process and with current high demand for energy savings in all sectors of the societies (EU commission 2008), there is a need to manage or prevent energy loses in the buildings. Research has shown that a major portion of supplied space heating energy is lost through poorly insulated building fabric (Annex 39 2005). Preventable heat losses
in buildings are main cause for heating related energy consumption and subsequently increased living costs. It been suggested that future demands to obtain effective insulating building fabrics may require wall thickness up to 500 mm filled with mineral wool (Annex 39 2005). Not only will this pose a challenge to both architects and engineers in terms of building aesthetic and technical constraints, but also will cause severe space limitations as well as an economic burden. An insulation material that may offer the best solution to this problem is vacuum insulation panels (VIP). VIPs are flat in general and have insulation performance of about five to eight times better than conventional insulation of the same thickness (Annex 39 2005; Simmler and Brunner 2005). They are made of an evacuated open porous material placed inside a multilayer envelope and make use of vacuum to suppress the gaseous heat transfer to zero. The porous material is the central part of a VIP and its role is to physically support the VIP envelope. Further through their small pore sizes, porous materials suppress the gaseous heat transfer even at atmospheric pressure (Annex 39 2005; Simmler and Brunner 2005; ISO/FDIS10456 2007; Baetens et al. 2010).

Hence, the performance of molecular filter devices and VIP is directly determined by the qualities of the nano-porous (adsorbents) material placed in them. Hence, major advances in gas adsorption and insulation technologies will come from the development of new and better nanoporous material. Currently the most dominating commercial nanoporous materials used as sorbents for molecular filtration and as thermal insulation media are activated carbon, activated alumina, silica gel, silica aerogel, fumed silica, precipitated silica, zeolites and related crystalline molecular sieves (Simmler and Brunner 2005; Baetens et al. 2010; Schweitzer 1979; Yang 2003). An overview of these commercial nanoporous materials are presented in section 4. Considering the global environmental movement for clean air and reduction of heating energy consumption in built environment, the development of new and better sorbents will not only facilitate major advances in gas adsorption and insulation technology, but also to meet the new challenges that cannot be met with the nanoporous materials that are currently available.
2. Scope and Objectives of the Thesis

The scope and objectives of this thesis are in two-fold. In first instance the scope and objectives (1) deals with the adsorbents for molecular filtration. In two, the focus is on nanoporous silica for thermal insulation applications.

2.1 Scope

Scope I

- To investigate the physical and adsorption properties of a newly developed class of nanoporous materials for use as molecular filter media.
- To tailor the adsorption performance, through the modification via incorporation of trapping chemicals or co-adsorbents.
- To contribute a better understanding of filtration performance in relation to the physical and adsorption properties, that are essential for the selection of nanoporous material as better adsorbents to meet the needs of commercial filter media application.

Scope II

- To develop a new nanoporous material and explore it with regard to physical and porosity properties which are essential for its applicability as a thermal insulation material.

2.2 Objectives

- **Objectives I:** To study the parameters affecting the synthesis of double metal-silica adsorbent and its effect on adsorption properties (Paper I).

- To investigate the impregnation of MgCa-silica through different preparation routes. The effects of the preparation route and the impregnate loading amount on the pore system of impregnated MgCa-silica and its relation in adsorption of chemical pollutants have further been studied (Paper II).

- To develop a synthesis route for a carbon-silica composite by investigating different routes of incorporating carbon, loading amount, different particle size grades of carbon and to identify the effects of these parameters on the porous properties (Paper III and IV).

To explore the applicability and performance of modified metal-silica as adsorbents for H₂S, SO₂ and toluene adsorption and to compare the performance with selected commercially available adsorbents materials. (Paper I, II and IV)

- **Objectives II**

  - To develop a simple preparation route for nanoporous silica material hereby investigating different parameters that affects the density and pore structure.

  - To investigate the physical and pore structure properties as well as it performance as thermal insulation material (V and VI).
2.3 List and Summary of Papers
This thesis is based on the following papers, referred to in the text by Roman numerals. Reprints were made with the permission of the corresponding publishers.

Paper I
**Preparation and Characterization of Double Metal-Silica Sorbent for Gas Filtration**
Ebenezer Twumasi Afriyie, Peter Norberg, Christer Sjöström and Mikael Forslund
*Adsorption Volume 19, Issue 1 (2013), Page 49-61*

This paper presents the factors affecting the preparation of a porous (Mg, Ca) silicate structure. The sorbents obtained have been characterized using scanning electron microscope (SEM), X-ray diffraction (XRD) and nitrogen physisorption isotherm. Further, the applicability and performance of the sorbent impregnated with potassium hydroxide for removal of sulphur dioxide (SO$_2$) is demonstrated.

Paper II
**Textural and Hydrogen Sulphide Adsorption Behaviour of Double Metal-Silica modified with Potassium Permanganate**
Ebenezer Twumasi Afriyie, Peter Norberg, Christer Sjöström and Mikael Forslund

In this paper MgCa-silica material is impregnated with KMnO$_4$ for dynamic adsorption of H$_2$S. Investigation of the effect of the impregnation preparation routes and loading amount on the pore system of impregnated MgCa-silica and the adsorption of H$_2$S is emphasised.

Paper III
**Textural and Adsorption Properties of a Carbon-Silica Composite Adsorbent for Air Filtration**
Ebenezer Twumasi, Mikael Forslund, Peter Norberg and Christer Sjöström

The paper presents different synthesis routes developed for carbon-silica composites. The paper describes how different routes of incorporating carbon into the silica structure affect the porous parameters. Additionally, the applicability and performance of the carbon-silica composites for adsorption of toluene at low level concentration is shown.

Paper IV
**Carbon-Silica Composites Prepared by the Precipitation Method. Effect of the Synthesis Parameters on Textural Characteristics and Toluene Dynamic Adsorption**
Ebenezer Twumasi, Mikael Forslund, Peter Norberg and Christer Sjöström
*J. Porous Mater.* 2012, 19, 333-343

The paper builds on the findings in paper III and develops composites with increased carbon content by employing a more finely grinded carbon phase. The effects of preparation route and of carbon content are thoroughly investigated. Using better controlled challenge testing equipment the actual availability and capabilities of the carbon phase in the composite was compared to pure activated carbon. The relationship between the porous parameters and the dynamic toluene adsorption is also treated. And finally introductory testing of the ignition temperature behaviour of the composites using TGA is reported and compared to that of pure activated carbon and commercial composite product.

Paper V
**Textural and thermal conductivity properties of a low density mesoporous silica material**
Ebenezer Twumasi Afriyie, Peyman Karami, Peter Norberg, Kjartan Gudmundsson

*To be submitted to Energy and buildings*

The paper focuses on the development of low density nanoporous material for thermal insulation application. A simply synthesis route was developed using sodium silicate and glycerol as pore forming agent to design low density mesoporous. The effects of synthesis parameters such as acid type on pore parameter, particle morphology, tapped density as well as thermal conductivity were investigated.

Paper VI
**A comparative study of methods for evaluating the thermal conductivity of nanoporous silica materials for vacuum insulation panels**
Peyman Karami, Ebenezer Twumasi Afriyie and Kjartan Gudmundsson

*To be submitted to Construction and building materials*

This paper put emphasis on comparing different laboratory methods for evaluating the thermal conductivity of nanoporous silica core materials in terms of time frame, sample size and boundary conditions while giving an account of the theoretical requirements of each method. The thermal transmissivity is studied through stationary measurements with a self-designed hot plate apparatus and with the Transient Hot Bridge (THB) method as well as a Transient Plane Source (TPS) method.

**The Work Performed and Contribution to the Papers**

In paper I-V, the materials preparation, characterization, and the interpretation of the results were performed by the author of this thesis, with exception of the execution of the dynamic adsorption and TGA measurements.

In paper VI, I prepared the two materials referred to as candidates A and B and contributed to the writing of the manuscript.
3. Indoor Air Quality and Thermal Comfort in built environment

Indoor environment covers those features of the thermal environment and air quality that influence our comfort, health and safety in the built environment. The interest in indoor environment quality standards has increased sharply in recent years. This development has come about due to a number of reasons. The advance of knowledge in epidemiological studies and global warming had alerted us to the potential dangers of global warming and its effects on our environment hereby the possible harmful effects of air pollutants on our health (Krzaczek and Tejchman 2012; McIntyre 1980). At the same time increasing evidence of the inadequate nature of our major energy resources and large costs, had stepped-up the adoption of a number of energy saving schemes, including sub-optimum temperature control and a reduction of fresh-air ventilation rates (Krzaczek and Tejchman 2012; McIntyre 1980). However, just reducing ventilation rates worsen the indoor air quality and consequently cause unwanted effects such as the respiratory illness and loss of productivity (Krzaczek and Tejchman 2012). IAQ, as the scenery of air in an indoor environment has effect on the occupant health and comfort. IAQ is ranked as one of the 5 top environmental risks to the public health according to comparative risk studies performed by United States Environmental Protection Agency (USEPA) (Krzaczek and Tejchman 2012).

Air contaminates likely to be found in indoor environment usually include the volatile and semi-volatile organic compounds, sulphur oxides, carbon monoxide, nitrogen oxides, oxidant as well as aerosols or solid particulates, Many of these pollutants exist in indoor air in the absence of outdoor source of contamination. The presence of typical environment from which many of these gas pollutants originate has been well established. Sulphur dioxide and carbon monoxide for example have indoor concentration governed by that outdoor concentration. On the other hand many contaminate are generally emitted from consumer products found in the indoor environment. The WHO air quality guidelines provided criteria for what a healthy indoor air quality should be (WHO statistics 2010).

Human health in the indoor environment is not only affected by airborne pollutants, but also by conditions of thermal comfort. The comfort that is experienced by people in indoor environment is dependent on a complex combination of physical activity, clothing, air temperature, mean radiant temperature, air velocity, and humidity (Fanger 1970). Creating thermal comfort for people is a prime purpose for heating and air conditioning indoor environment, and this has a major influence on the person performance (Fanger 1970). Thus the thermal comfort can be justified from the standpoint of human performance. The state of thermal discomfort is generally easy to identify when complaints are often directed at a specific reason such as draft, heat or cold. For favourable thermal comfort in indoors, a temperature was decided to be between 20-24°C for winter and 20-26°C for summer, 19°C for floor temperature with air velocity 0.10 m/s (Fanger 1970; Boverket 1998).

3.1 Molecular Filtration

Molecular filtration is the term used to describe filtration of chemical air pollutants having sizes at the molecular scale. Molecules are 1,000 to 10,000 times smaller than the finest particles removed by any HEPA filter. HEPA filters are successful in filtering particles down to about 0.3 micron size range and will therefore not able to remove chemical contaminants such as gases and volatile organic compounds (VOCs) whose sizes are measured in Ångstroms (1 Ångstrom is 1/10,000,000,000 of a meter).

There are more molecular contaminations in the air surrounding us than particles. The source of molecular contamination can therefore be present both inside and outside built environments. The sources of outdoor pollution include traffic fumes, aviation fuel (at airports), emissions from waste water treatment plant, combustion by-products from
manufacturing processes, waste management facilities, chemical storage areas, agricultural and animal farming. Indoor contaminants are generally emitted from consumer products, human metabolic by-products, building and construction materials, ozone from photocopiers and fugitive emissions from electronic equipment. Other sources of indoor pollution arise from our activities such as cooking, laundry, entertainment, painting, hobbies, etc. we release odours into indoor air.

These emitted gases may be classified into four groups each base on how it affects us and how each is requiring different control approach. These groups are as follows:

- **Odorous:** These are gases normally emitted from rotten food, traffic fumes, cooking smells and aviation fuel. They generally affect the olfactory senses and carry negative undertones.

- **Corrosives gases:** Include acidic gases in paper mills, museums, microelectronics production and pharmaceutical production. These gases cause irreversible damage to products or properties in indoor environment. They may also have harmful effect on human occupants.

- **Irritant:** They include gases such as ozone (from photocopiers), ammonia, from onions, HCHO and VOCs. People exposed to many of these gases experience symptoms of pain or discomfort to the eyes, skin, mucous membranes, or respiratory system.

- **Toxic:** Include molecular contaminants such as isocyanates, hydrogen cyanide, war gases, dioxins and nuclear gases. Exposure to toxic gas may cause damage to living tissue, impairment of the central nervous system and even death.

The abatement of these chemical contaminants in air could be achieved via three approaches:

- **Source control:** Removal of the gas pollutant from source.

- **Dilution:** Ventilation is used to dilute indoor air with suppose fresh air from outside.

- **Cleaning Air:** Filter is employed to clean the air in indoor environment.

Air cleaning is usually preferred to source control and ventilation. Removal of air contaminants from higher concentration sources is often neither realistic nor practical while ventilation dilution are not workable in all cases as the use of large quantities outdoor dilution air is cost intensive and has high energy demand (John et al. 2000). Moreover, allowing in extra amounts of outside air might result in swapping one group of contaminants for another hereby the outdoor contaminant source for those internally generated, especially in highly polluted cities. It will therefore be more economical and a preventive measure to clean the indoor air and recycle a certain portion of it than possible humidify or dehumidify the air from the outside (John et al. 2000).

A typical molecular filter for contaminant adsorption may consist of a bed shaped compartment made of perforated plates into which adsorbents are packed (see Fig.1). An air stream polluted with low concentrations of contaminated gas is forced through the bed via the perforated plates and the molecular pollutants are adsorbed. The performance of molecular filtration devices is directly determined by the performance of the adsorbent. The other important engineering parameters are for the given air flow during the application to keep the pressure drop as low as possible and the contact time (calculated as bed volume divided with flow rate) at a long enough time to ensure adsorption. Further, the adsorbent particle size, resistance to airflow, concentration and characteristics of the contaminant(s) in the air stream, the relative humidity and temperature of the air-stream also affect the performance of molecular filter.
3.2 Thermal Building Insulation

There is an increase in demand for energy reduction in all aspects of the societies. This is important, not only due to limitations of our major energy resources, but also due to escalating CO$_2$ and greenhouse emissions. This has accelerated the adoption of a number of energy – saving targets. EU for example has set a goal to achieve a reduction of 20% of the total energy consumption and greenhouse emissions by 2020 and with 50% reduction by 2050 compared to 1990 (EU commission 2008). Buildings account for 40% of total energy use in EU and it’s large part used for space heating in buildings and production of domestic hot water (EU directives 2010/31). Studies have shown that a large portion of supplied space heating energy is lost through poorly insulated building fabric (IEA/ECBCS Annex 39 2005). Future demands to obtain effective insulating building fabrics may require wall thickness up to 500 mm filled with mineral wool (Simmler and Brunner 2005). Not only will this pose a challenge to both architects and engineers in terms of building aesthetic and technical constraints, but also will cause severe space limitations as well as a high price of land in densely populated areas.

In order to reach consumption targets of a 20% reduction in 2020 and a 50% reduction by 2050, further decisive actions are needed. One approach to reach these targets is to improve the thermal insulation of buildings. Hereby improving both new buildings and the large-scale retrofitting of existing ones is needed. Improved insulation materials and techniques achieve significant gains concerning the energetic efficiency of building envelops. Further, not only does it increase the building energy efficiency in cold climates but also in warm and hot regions due to the reduction of need for air condition power. Below are brief descriptions of properties of a number of important thermal insulation materials are given.

- **Mineral wool**: Includes glass wool and rock wool, which are produced from borosilicate glass at 1400°C and from diabase or dolerite at 1500°C respectively. Mineral wool has
densities between 20-80 kg/m$^3$ and typical thermal conductivity values are between 30 and 40 mW/(m·K). However, their thermal conductivity may increase from 37 mW/(m·K) to 55 mW/(m·K) because of increase in temperature, moisture content and density (Jelle 2011).

- **Cellulose fibre**: This insulation material is made from recycled paper or wood fibre mass. Cellulose insulation can be produced as both a filler material or as boards. Generally thermal conductivity values for cellulose fibre insulation are in the range of 40 and 50 mW/(m·K) and varies with temperature, moisture content and density (Jelle 2011). The thermal conductivity of cellulose insulation may increase from 40 mW/(m·K) to 66 mW/(m·K) with moisture content increase (Jelle 2011).

- **Expanded (EPS) and extruded polystyrene (XPS)**: They are both made from styrene with an expansion gas. EPS contains partially open pore structure while XPS has a closed pore structure. EPS exhibits a thermal conductivity between 30 and 40 mW/(m·K). The thermal conductivity may increase from 36 mW/(m·K) to 54 mW/(m·K) upon increase in temperature, moisture content and density (ISO/FDIS10456 2007; Jelle 2011). The same scenario can be said of XPS which typical thermal conductivity between 30 and 40 mW/(m·K) may increase from 34 mW/(m·K) to 44 mW/(m·K) above 25ºC (Jelle 2011).

- **Polyurethane**: Is a product obtained from reaction between isocyanates and polyols. The material can be formed into boards with a typical thermal conductivity between 22 and 30 mW/(m·K) (ISO/FDIS10456 2007). The thermal conductivity may increase from 25 mW/(m·K) to 46 mW/(m·K) with increase in temperature, moisture content and density.

- **Vacuum insulation panels (VIP)**: Consist of an open porous material placed inside an envelope of multilayer metalized polymer laminate which is evacuated by vacuum to suppress the gaseous heat transfer to zero. VIP has the lowest thermal conductivities ranging from 3 to 4 mW/(m·K) (Jelle 2011). VIP with time increase in thermal conductivity due to water vapour and diffusion of air through the envelope. Further, in case the VIP envelop becomes punctured the thermal conductivity will increase substantially to the range of about 20 – 30 mW/m·K. The VIP that gives better thermal conductivity at both low and high pressure normally consist of porous fumed silica or aerogel as core material. The pore structure and thermal properties of these two nanoporous materials will be discussed under section 4.

### 3.2.1 Heat transfer in insulation materials

The purpose of an insulation material is to retard the rate of heat transport by solid includes the effects of conduction, gas conduction and radiation. Total thermal conductivity ($\lambda_{\text{tot}}$) can therefore be expressed as (Simmler and Brunner 2005)

$$\lambda_{\text{tot}} = \lambda_{\text{solid}} + \lambda_{\text{gas}} + \lambda_{\text{rad}} \quad \text{(mW/(m·K))}$$

where $\lambda_{\text{solid}}$, $\lambda_{\text{gas}}$, and $\lambda_{\text{rad}}$ (mW/(m·K)) are solid thermal conductivity, gas thermal conductivity and radiative thermal conductivity respectively. Fig. 2 shows the relationship between density and conductivity. Generally material with large amount of solid structure contributes primarily to largest solid conduction. Whiles on the contrary, the radiation parameter will decrease. A good insulation material is the one where the sum of the contributions from radiation and solid conduction is at a minimum. This in addition to the gas (air) conduction 26 mW/(m·K) for conventional insulation gives a total thermal conduction down to a minimum around 30 mW/(m·K). For nanoporous material such as aerogel the gas conduction may be reduced to lower values to gives a lower total thermal conduction around
14-20 mW/(m·K), even at atmospheric pressure owing to their pore diameter in nano-scale (Jelle 2011; Simmler and Brunner 2005).

- **Solid conduction**: Transport through the solid structure of porous material, whereby the heat is transferred via the physical contact of the constituent particles of the pore structure. Its magnitude depends upon material structure and density. The following relationship was suggested for the variation of solid conductivity with density of the porous material (Alam et al. 2011).

\[
\lambda = \rho^\alpha
\]

where \(\rho\) is the density (kg/m\(^3\)) and the index \(\alpha\) has a unity value for foams and ranges over 1.5-2 for nanoporous materials. This is visibly evident from eq. (2) and Fig.2 where the materials with a low density yield a smaller solid conductivity.

![Fig.2 Total thermal conductivity in porous materials comprising of solid conduction, gas conduction and radiation (Simmler et al. 2005)](image)

- **Radiation**: Radiative heat flow by the electromagnetic waves which is emitted by all surfaces. Radiation heat transfer requires no medium and the net radiation in material is the difference between the radiation from the warm surface and the radiation from the cold surface (Alam et al. 2011). Radiative heat transfer increases with temperature and can be reduced by adding opacifier (e.g. TiO\(_2\) or carbon) to the insulation material. Studies have shown that at room temperature thermal conductivity of pure silica is 0.002-0.003 W/(m·K) higher than that of silicon carbide opacified precipitated silica (Alam et al. 2011).

- **Gas conduction**: The heat transport via gas conduction is described in (Baetens el at. 2010).
4. Nanoporous Materials

Nanoporous materials have the presence of pores that render them unique chemical and physical properties that the bulk equivalent materials do not possess (Lu and Zhao 2004). They have large specific area, fluid permeability and high surface reactivity which non-porous materials are lacking. In general porous materials have porosity (ratio of pore volume to the bulk volume of the material) in the range of 20-95%. There are two types of pores: open and closed pores. Open pores are cavities or channels which connect to the surface of the material, and closed pores which are inaccessible from the outside (Lu and Zhao 2004). In this thesis, materials with open pores are of interest as it is the main requirement in filtration and in VIP applications. In accordance with International Union of Pure and Applied Chemistry (IUPAC) definition, the size of a pore is micropores when less than 2 nm in diameter, mesopores 2 to 50 nm and macropores when larger than 50 nm. Porous materials with varying structural and compositional properties have diverse pore and surface properties that may ultimately determine their potential applications. For different applications, nanoporous materials have to fulfil different performance criteria that would require different properties.

4.1.1 Performance Criteria for Adsorbent (Schweitzer 1979; Yang 2003; Lu and Zhao 2004)

1. High adsorption capacity. Fundamental properties that influence adsorption capacity are specific surface area, interfacial reactivity nature and pore size distribution. These parameters dictate the amount of adsorbates (contaminants) taken up by the adsorbent and the amount of adsorbent required.

2. High selectivity. The adsorbent selectivity nature depends on the pore size distribution, pore size, pore shape as well as the characteristic of the adsorbate components. Selectivity is highly desired for separation of multicomponent mixture.

3. Good adsorption kinetics. Adsorbate transfer kinetics is related to intraparticle mass transfer resistance. The micro-, meso and macroporosity which originate from the intraparticle of the adsorbent as well as the particle size determined the adsorption kinetics. The type of binder and amount used sometimes, would also affect the adsorption transport process kinetics. A good kinetics is achieved when the adsorption rate is fast or controllable depending on the prerequisite of a particular application.

4. Mechanically robust and stable. Adsorbents need to be mechanically strong and robust to resist attrition, erosion and crushing in adsorption columns or vessels. The adsorbent has to have high bulk density and crushing strength, and resistance to abrasion.

5. Good stability and durability in use. Generally, adsorbents are subject to harsh chemical, pressure and thermal environmental attack that could reduce the life expectancy of the adsorbent. To ensure long life or durable utilization in these environments, a good stability of the adsorbent is essential. Further the material has to be water stable, thus the sorbent should not soften, swell or disintegrate when it comes in contact with water.
4.1.2 Performance criteria for nanoporous materials as core material for vacuum insulation (Baetens et al. 2010)

1. Low gas conductivity. The parameters that affect the gas conductivity in vacuum insulation are pore size and vacuum level. The core materials pore diameter has to be very small. To obtain reduced gas conductivity in insulation materials with large pore sizes, the pressure has to be very low. This condition however is difficult to maintain by organic envelopes materials. As a result, a nano-structured core material with ideal pore size 10 nm or less in combination with a pressure in the range of 2-10 mbar (Alam et al. 2011) is preferred in VIPs. With such pore structure, the gaseous conductivity could be reduced to low values even at atmospheric conditions.

2. High Porosity. In order to be able to evacuate any gas in the core material, the pore structure needs to be 100% open. The porosity of a material is dependent on bulk density and therefore having low bulk density will be desirable.

3. Good resistance to compression. Although 100% open cell structure is required, the pore structure at the same time has to be stable enough so the pores do not collapse upon panel evacuation. The VIPs produced at present have an internal pressure in the range of 0.2-3 mbar. Thereby, the pressure load on the panel is about 1 bar or 100 kN/m². Therefore the core material has to be able to sustain at least this load.

4. Impermeable to infrared radiation. In order to reduce the radiation transfer, in the material has to be as impermeable as possible to infrared radiation. Hereby a very low conductivity value could be reached.

4.2 Overview of Nanoporous Materials

Different porous materials have diverse properties with respect to; pore size (PS), porosity, pore size distribution (PSD), composition and surface properties that determine and eventually render them their potential applications. Many types of inorganic porous materials exist, of which the most industrially used are; activated carbon, activated alumina, silica aerogel, silica gel, and zeolite. Other porous materials such as carbon-mineral composite (Leboda and Dabrowski 1996), metal oxides (Rouquerol et al. 1996; Yang 2003) and clay (Yang 2003) are also used, although to a less prominent extent.

4.2.1 Activated Carbon

Activated carbon (AC) is a porous carbonaceous material which has been subjected to reaction with gases (steam, CO₂, and air) and sometimes with addition of phosphoric acid or zinc chloride before, during or after carbonization in order to increase its adsorptive properties (Marsh 2001). The production and the use as a general-purpose industrial adsorbent date back to the 19th century (Yang 2003). Its usefulness derives from its large adsorption capacity which originates mainly from its large micropore and mesopore volumes and the resulting high BET-surface area (500 to 2000 m²g⁻¹) (Marsh 2001; Yang 2003). Its pore widths can range from <1.0 nm to 50 nm with surface compositions varying from clean graphitic to oxygenated surfaces exhibiting significant polarity (Marsh 2001). Fig.3 shows Pore Size Distribution (PSD) of a typical activated carbon compared with several other sorbents. Activated carbon materials are less polar than other adsorbent but not completely non-polar due to the presence of surface oxides (Schweitzer 1979; Yang 2003). Activated carbons are widely used for the removal of very low concentrations (sub ppm) of harmful volatile organic
compounds (VOCs) from process and indoor air streams due to its developed microporosity which ensures good adsorption capacity (Fletcher et al. 2002). This thesis is directed towards the use of coconut based activated carbon (CAC) with a Carbon Tetrachloride (CTC) value of 50 and 55 for synthesis of carbon-silica composite adsorbent for removal of VOC of very low concentrations (sub ppm).

4.2.2 Activated Alumina

Activated alumina is a porous form of aluminium oxide prepared by the heat treatment of some form of hydrated alumina (Rouquerol et al. 1996). The BET-surface area is in the range 200 to 500 m²/g with total pore volumes near 0.5 cm³/g (Yang 2003). These materials contain some micropores and considerable mesopores with sizes greater than 5nm (Yang 2003). Oxygen vacancies are easily formed on its surfaces, thus alumina has both Lewis and Brønsted acid sites. The surface chemistry, as well as the pore structure can be modified for specific application. As a result, activated alumina is more versatile and has been applied as a sorbent (Yang 2003). Generally activated alumina is widely used as a desiccant because of the large capacity for water and the ease of regeneration (~175°C, compared with 350°C for regenerating zeolites) (Schweitzer 1979; Yang 2003). Moreover alumina tailored via either activation process or chemical dopants are employed in removal of acidic gases (COS, CO₂, H₂S, CS₂), polar organic compounds, oxygenates and Lewis bases as well as HCl and HF (Rouquerol et al. 1996; Yang 2003).

4.2.3 Zeolites and Molecular Sieves

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements (Yang 2003). Molecular sieves generally belong to the zeolite class of minerals which have three-dimensional interconnecting pore network structure of silica and alumina tetrahedral (Schweitzer 1979; Kohl and Nielsen 1997). The pores are of molecular dimensions and are the basis for the sieving action of these materials (Kohl and Nielsen 1997). Although about 40 different zeolite structures have been discovered, only three dominant synthetic types; A, X and Y zeolites and molecular sieves are widely used commercially for adsorption and ion exchange application (Yang 2003; Kohl and Nielsen 1997). The unique surface chemistries and crystalline pore structures of zeolites give them special adsorption properties. A large portion of commercial zeolites are employed in the field of ion exchange and catalyst application (Yang 2003). They are also used in other ranges of applications such as desiccants for dehydrating gas (Kohl and Nielsen 1997), gas separation and purification (Yang 2003). The zeolite of LTA-type and especially its modification with Ca²⁺ for H₂S removal has been reported to give good results (Bulow et al. 1999).

4.2.4 Porous Silica Materials

Synthetic amorphous silica’s are materials that have found a wide use in a diverse range of industrial applications such as in vacuum insulation panel, as desiccants etc. However the environmental application of silica sorbents for air filtration have yet not been utilised commercially. Under this section the properties and applications of silica materials as adsorbents as well as thermal insulation media will be looked at.
4.2.4.1 Aerogel

Silica aerogels is made up of a cross-linked internal structure of SiO$_2$-chains with a large number of air filled pores. These pores of aerogel are in nano-scale ranging between 5 and 100 nm depending on the synthesis method and the silica source used (Van Bommel et al. 1997; Baetens et al. 2011). These pores occupy about 85 to 99.8% of the total bulk volume. Because of the small pores and high porosity, aerogel exhibits extraordinary physical, thermal, acoustical and optical properties (Baetens et al. 2011). These pores occupy about 85 to 99.8% of the total bulk volume. Because of the small pores and high porosity, aerogel exhibits extraordinary physical, thermal, acoustical and optical properties (Baetens et al. 2011). The high porosity makes aerogels the lightest solid material known currently. They have a bulk density as low as 3 kg/m$^3$ and skeleton density of ~2200 kg/m$^3$ (Baetens et al. 2010; Baetens et al. 2011). The silica aerogels used at present for thermal insulation applications have an overall bulk density of about 70-150 kg/m$^3$ (Baetens et al. 2011).

The high porosity however results in a very low mechanical strength which makes the material very fragile (Baetens et al. 2011). This problem of low tensile strength however may be solved by incorporating the aerogel in a fibre matrix (Baetens et al. 2011). Another drawback of aerogel is its water instability; if not well hydrophobized, the aerogel structure will disintegrate when it comes in contact with water (Baetens et al. 2011). The tight envelope in the VIP does also offer protection of the core material against dampness.

An overall thermal conductivity of ~17 mW/ (m. K) at ambient pressure has been reported (Baetens et al. 2010) for aerogel and even lower value of 4 mW/mK can be reached by applying a pressure of about 50 mbar or less making it suitable for VIP application (Baetens et al. 2010). Another benefit of silica aerogel is that it is nonflammable. However, it has not been widely used in VIPs for building applications due to its high cost (Baetens et al. 2010).

4.2.4.2 Fumed Silica

Fumed silica is made up of submicron-sized spheres, which are somehow fused into short chains, very highly branched and about 0.1-0.2 microns long. For a given grade, they possess uniform spheres but have relatively variable chain length. This branched nature of fumed silica renders it porosity greater than 90% and a bulk density in the range of 60-220 kg/m$^3$. The material also has a specific surface area in the range of 100-400 m$^2$/g which varies with the particle size. Thus the smaller the particles size the larger the estimated surface area (Gun’ko et al. 2005; Quenard and Sallee 2005). Another beneficial feature of fumed silica is its pore size distribution and the maximum pore diameter. These identify the range of vacuum required for the transition to low thermal conductivity. Fumed silica has a maximum pore diameter of 300 nm, which is in the same order of scale as the mean free path (70 nm) of air molecules at standard temperature and pressure. As a consequence of their pore size distribution and porosity, they have a thermal conductivity of about 20 mW(mK)$^{-1}$ even at atmospheric pressure. The pore properties makes it possible for the material to further yield a low thermal conductivity of 0.003-0.006 W m$^{-1}$K$^{-1}$ whilst requiring a pressure of about 2-10 mbar (Alam et al. 2011). The same advantages of nonreactive and nonflammable of silica aerogel could be said of fumed silica.

One drawback of the fumed silica encounters as core material is its high market price (IEA/ECBCS Annex 39 2005; Alam et al. 2011).

4.2.4.3 Silica gel and Precipitated Silica

Silica gel is most widely used as desiccant because of its large capacity for water uptake (~40% by weight) and ease in regeneration (~150°C, compared with 350°C for regenerating zeolites) (Yang 2003). Precipitated silicas on the other hand are commercially important in the manufacture of paper, paints and rubber (Iler 1979; Othmer 1997; Rouquerol et al. 1996).
Although there is close relation between silica gel and precipitated silica as both are prepared from aqueous sodium silicate solutions, silica gel is formed in acidic solution in which silicic acid polymerizes to extremely small particles, which chain together to form a network of gel throughout the water. Precipitated silica on the other hand is formed under alkaline conditions, and the particles are brought together into aggregates by forces of coagulation (Iler 1979; Papirer 2000). The two silicas also differ from each other in terms of different properties (e.g. specific surface area, pore volume and pore size distribution) which are important in describing the sorption characteristics of the nanoporous silica (Iler 1979; Bergna and Roberts 2006). In this thesis the precipitation synthesis route has been used in preparing new MgCa-silica sorbents to be used as gas filter media.

4.2.4.4 Ordered Mesoporous Silica’s

A new family of ordered mesoporous silicas have recently been developed using surfactant micelles or folic acid as templates. This has led to a breakthrough of production of various mesoporous molecular sieves such as MCM-41(2d hexagonal, $P_6m$), MCM-48 (cubic, $Ia3d$) (Beck et al. 1992), SBA-1 (cubic Pm3n), SBA-2 (3d hexagonal $P6/mmc$), and SBA-3 (hexagonal $P6m$) (Huo et al. 1994; Huo et al. 1996), NFM-1(2d hexagonal, $P6m$) (Aturi et al. 2009), KIT-1 (disordered network) (Ryoo et al. 1996). These mesoporous silicas exhibit high surface area and narrow pore size distribution in meso-scale. These properties offer promises for potential applications in fields such as molecular sieving, catalysis, selective adsorption of pollutant gases, and so on (Zheng et al. 2007). However, industrial applications of the mesoporous materials have been inhibited by toxicity of the surfactants and high cost (Lu 2004), low hydrothermal stability for example in boiling water, low mechanical stability (Ryoo et al. 1996; Bonneviot et al. 1998) and other issues which still needs to be investigated (Antonietti and Ozin 2004). The frameworks of MCM-41 and MCM-48 were for example reported to collapse during the attempt to pelletize with compression above 1000 kg cm$^{-1}$ (Bonneviot et al. 1998). The disintegration of MCM-41 and MCM-48 during impregnation in aqueous solutions has also been reported (Bonneviot et al. 1998) and it provokes a doubt about its durability in practical application.

In other words, to obtain useful adsorption performance of porous silica materials, there is a need to modify either the surface chemistry or the pore structure. One principle advantage of porous silica is the abundance of surface hydroxyl groups (Yang 2003), and its amenability to surface functionalisation with different chemical moieties via a number of direct and indirect methods (Zheng et al. 2007). Different silica sorbents have been successfully modified with functional organics (amines, thiol etc.,) and are used for removal of acidic gas contaminants such as CO$_2$, NO$_2$, SO$_2$ and H$_2$S and VOC (Zheng et al. 2007; Kosuge et al. 2007; Hernández and Velasco 2004).

4.2.5 Carbon-Mineral Composites

Carbon–mineral composites represent sorbents consisting of two components; carbon and some inorganic sorbent. The composites may be prepared by mixing carbon and inorganic sorbents in some way, or the carbon substance may be a stable deposition on the surface of the inorganic sorbent. The properties depend on the amount of carbon deposited on the inorganic sorbent (Leboda 1992). Comprehensive studies on preparation of carbon-mineral composites by different methods have been reported by several groups and summarized by Leboda (Leboda 1992). In different adsorption processes; the composite sorbents utilize the advantages of either carbon or inorganic components or both. Most of the composite materials are characterized by micropores and high ignition temperature coupled with heterogeneous surfaces which are good incentives for its application as sorbent for purification of a wide
range of contaminated gases (Leboda and Dabrowski 1996; Glover et al. 2008; Leboda 1993; Osborne 1989). Today alumina-carbon (Al-C) composites are commercially used for removal of H$_2$S, SO$_2$ and VOCs contaminants (www.purafil.com/products/media/puracarb accessed 2013). However, the investigation of the adsorptive properties and development of applications of carbon-silica composites are still on-going (Leboda and Dabrowski 1996; Glover et al. 2008). In this thesis, carbon-silica composites were developed and their porous properties as well as VOC adsorption capacities were investigated (see Section 6.3.1).

Fig.3 Pore size distributions for activated carbon, activated alumina, molecular-sieve carbons (MSC), silica gel and zeolite 5A ref. (Yang 2003) included by permission
5. Experimental Section

5.1 Materials for Synthesis

For the synthesis of double metal silica sorbents, water glass (SiO$_2$:Na$_2$O = 3.35) as silica source and calcium chloride (CaCl$_2$·2H$_2$O) and/or magnesium chloride (MgCl$_2$·6H$_2$O) salts as coagulants agents were used. Glycerol (CH$_2$OHCHOHCH$_2$OH) employed as template in pure mesoporous silica. Sodium bicarbonate (NaHCO$_3$), potassium permanganate (KMnO$_4$) and potassium hydroxide (KOH) were used as impregnate chemicals. Other chemicals such as sulphuric acid (H$_2$SO$_4$) and Oxalic acid (HO$_2$CCO$_2$H) were also used. A coconut based activated carbon (CAC) with a CTC value 50 and 55 were obtained from Jacobi carbons AB, Sweden. Carbon of particles <150 micron and 3mm were obtained. The water glass was purchased from Askania, Göteborg, Sweden, and the salts originated from retailers of agricultural chemicals. The chemical impregnates were purchased from VWR, Sweden.

5.1.1 Synthesis of Double Metal-Silica Sorbents

A series of silica sorbents containing various amount of Ca and Mg were prepared by varying Mg/Ca molar ratio while maintaining sodium silicate solution at 1.5 M (with respect to SiO$_2$). A 500 ml salt solution of either pure 0.43 mol CaCl$_2$·2H$_2$O or pure 0.43 mol MgCl$_2$·6H$_2$O was prepared or mixtures of said solutions in ratios indicated in Table 1. The synthesis was done by pouring 500 ml salt solution into a 1.5 M (with respect to SiO$_2$) sodium silicate solution (500 ml), which was being agitated in an ordinary food mixer at room temperature.

Table 1 Chemical composition of sorbent in relation to sodium silicate (1.5M SiO$_2$) molar ratio 3.35 precipitated with various Mg- and /or Ca- molar ratios

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pre-mixing condition</th>
<th>Chemical composition of sorbent</th>
<th>Mean Si/(Mg+Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg$^{2+}$ mol%</td>
<td>Ca$^{2+}$ mol%</td>
<td>Si atom%</td>
</tr>
<tr>
<td>PSS-MgCa-0/100</td>
<td>0</td>
<td>100</td>
<td>26.4</td>
</tr>
<tr>
<td>PSS-MgCa-50/50</td>
<td>50</td>
<td>50</td>
<td>27.2</td>
</tr>
<tr>
<td>PSS-MgCa-68/32</td>
<td>68</td>
<td>32</td>
<td>27.8</td>
</tr>
<tr>
<td>PSS-MgCa-75/25</td>
<td>75</td>
<td>25</td>
<td>27.6</td>
</tr>
<tr>
<td>PSS-MgCa-100/0</td>
<td>100</td>
<td>0</td>
<td>25.2</td>
</tr>
</tbody>
</table>

The resulting solution immediately began to coagulate. The reaction is assumed to occur according to the following reaction formula:

$$\text{Na}_2\text{O} \cdot \text{nSiO}_2 \ (l) + \frac{1}{2}\text{MgCl}_2 \ (l) + \frac{1}{2}\text{CaCl}_2 \ (l) \rightarrow (\frac{1}{2}\text{Mg}, \frac{1}{2}\text{Ca}) \ \text{O} \ \text{nSiO}_2 \ (s) + 2\text{NaCl} \quad (3)$$

The reaction yielded a white coagulum and was allowed to settle for up to one hour and the clear liquid above the precipitated coagulum was removed by decanting. Then, the coagulum was mixed with a defined amount of water followed by stirring and the coagulum allowed to settle before decanting the clear liquid. This step was repeated a number of times until the decanted liquid was virtually free from sodium chloride as detected by adding a few drops of
dilute AgNO₃ reagent. The coagulum obtained after the final washing was vacuum filtered through a filter paper until a paste holding as much as 85% of water was obtained. The paste was then made into pellets and subsequently dried overnight in a stationary dryer at 105 °C. The precipitated Silica Sorbent obtained were designated by an abbreviation; e.g. a sorbent made by 100 mol % Mg will be called PSS-MgCa-100/0, 75 mol % Mg and 25 mol % Ca will be PSS-MgCa-75/25, 68 mol % Mg and 32 mol % Ca will be PSS-MgCa-68/32, 50 mol % Mg and 50 mol % Ca will be called PSS-MgCa-50/50, and 100 mol % Ca will be called PSS-MgCa-0/100.

5.1.2 Synthesis of Mesoporous Silica, SNP

In preparation of mesopores silica in this work, glycerol (CH₂OHCHOHCH₂OH) has been employed as templating agent (Rao and Kulkarni 2002; Kim et al. 2009; Uchida et al. 1994). We rely on its ability to form extended hydrogen –bond network on the silica cluster and provide a steric shielding around the colloidal particles. A possible reaction mechanism adopted from (Kim et al. 2009) is shown in eq.4.

A fast and environmental route is then followed to control the particle size, pore size and bulk density. The synthesis is performed at room temperature and does not require any organic solvents. The Silica NanoPorous (SNP) powders obtained were designated by abbreviations indicating the acids, sulphuric acid (SA) and oxalic acid (OA), such as SNP-SA and SNP-OA.

5.1.3 Synthesis of Carbon-Silica Composites

In the preparation of a carbon-silica composite, coconut based activated carbon with a CTC value of 50 was grinded and sieved to a size less than 500 microns. In addition CAC with a CTC value of 56 powder of particle size less than 150 microns was used in the synthesis. Three probable routes denoted I-III were employed to incorporate CAC into silica sorbents containing 68 mol % Mg and 32 mol % Ca as shown in Fig.4. The composite formation was performed as follows: (I) Activated carbon was added to step 5 and vigorously mixed for 30 minutes. At that time the carbon appeared to be fully dispersed. Activated carbon was mixed with (II) the salt solution or (III) with the water glass solution in step 1. In route II and III the carbon is present even before coagulation. The Precipitated Silica Carbon composites obtained were designated by an abbreviation; e.g. a composite made by method I containing 8 wt % CAC1 of particles size < 500 micron will be called PSC(I)-8 whiles sorbent made with 8 wt % CAC2 of particles sieved to size <150 micron will be called PSC(I)-8F.
5.1.4 Synthesis of Impregnated MgCa-Silica

Two routes (I-II) have been employed to impregnate MgCa-silica with either KOH or KMnO₄ and NaHCO₃.

Route I. Measured amounts of impregnate chemicals, KOH or KMnO₄ and NaHCO₃ in the form of powder were added to step 5 (coagulum) Fig.4 and stirred for 30 min. At that time the impregnate the chemicals were subsequently dissolved in the remaining (85%) water phase of the coagulum. The mass percentages of impregnate chemical were calculated based on the dry content of the coagulum and ranged from 8 to 13 wt%. The resultant slurry is formed into pellets and dried. Pellets obtained from KOH impregnated were dried at 105°C while pellets impregnated with KMnO₄ and NaHCO₃ were dried in a constant humidity cabinet at 60°C at 50% RH for 4 h. For comparison of textural properties, MgCa-silica sample that was not impregnated was also dried using the same drying scheme as KMnO₄ and NaHCO₃ impregnate samples. This sample is referred to as PSS 60.

Route II. An impregnate solution was prepared by dissolving a known amount of KMnO₄ with addition of an equal amount of NaHCO₃ in 250 ml deionized water and stirred at room temperature; 105g of PSS pellets pre-dried at 105°C were then added to the solution and was allowed to soak. After soaking the PSS for 30 min, the excess solution was drained and the PSS was dried in a constant humidity cabinet at 60°C at 50% RH for 4 h. The concentration of the impregnating solution was varied from 8 to 13 wt% of impregnate chemicals while keeping water at 250 mL. The mass percentage was based on the mass of pellets used.

When dry NaHCO₃ comes into contact with moisture it will absorb water leading to hydrolysis and further decomposition depending on the relative humidity and the temperature (Kuu et al.1998). Further, the degree of NaHCO₃ decomposition is high at humidity and temperature in the range 76% RH at 25°C to 48% RH at 40°C (Kuu et al.1998). This suggest that heating the impregnated samples at 60°C at 50% RH will results in the decomposition of NaHCO₃ to Na₂CO₃ and CO₂.

The samples obtained were designated by an abbreviation; e.g. sample made by method I with starting 8 wt% KMnO₄ and 8 wt% NaHCO₃ is called PSS (I)-8. For method II, with starting 8 wt% impregnates in solution is denoted PSS (II)-8. The uniform distribution of impregnates throughout the KMnO₄ chemisorbents prepared are clearly shown by the representative microphotographs (Fig.5) of cross section of impregnated samples.
5.2 Characterization Techniques

5.2.1 Measurement of potassium permanganate content

The KMnO$_4$ loading on the MgCa-silica was measured using a Milton Roy Spectronic 401 spectrophotometer. In doing the analysis, 200 ml of 10% (v/v) phosphoric acid was added to 0.5 g of the various media to extract the KMnO$_4$ from the MgCa-silica substrates. The pellets were ground before the extraction. The permanganate absorption band at 525 nm was measured and the KMnO$_4$ content was subsequently determined from an established calibration curve.

5.2.2 Powder X-Ray Diffraction Analysis (XRD)

The powder X-ray diffraction technique is fundamentally used to determine crystallographic and textural properties of materials. When an incident X-ray radiation of wavelength $\lambda$ interacts with a target sample of regular pattern, a number of lattice planes separated by interplanar distance $d$ will reflect the incident beam and consequently producing constructive interference known as diffraction. The distance between two waves undergoing constructive interference is known as the path difference and can be written as $2d\sin\theta$, where $\theta$ is the diffraction angle. The intensity of the diffracting beam as a function of diffraction angle gives a diffraction pattern. From the angles and relative intensities of these diffraction patterns, a particular crystal structure can be identified. Although mesoporous materials are amorphous materials on a short range scale, the long range order of ordered mesophases produces distinct diffraction patterns at angles in the range of $0^\circ < 2\theta < 5$. However this is not the case.
in disordered mesophases of short range scale and therefore additional methods such as electron microscopy and nitrogen physiosorption studies are necessary for identification of textural properties.

The X-ray diffraction (XRD) patterns of all the samples presented in this thesis were performed on a Bruker AXS D8 Advance diffractometer equipped with a secondary monochromator and automatic divergence slits filtered Cu-Kα radiation (λ= 1.54056 Å) at 40 kV and 40 mA. The diffraction patterns were recorded between 5°-70° 2θ using a step size of 0.01° and count time per step of 1s.

5.2.3 Scanning Electron Microscopy (SEM)

The surface morphologies of the samples presented in this thesis were observed by SEM. A beam of electrons emitted by a filament is scanned across the surface of the sample. The electrons interact with the atoms that build up the sample. This produced signals including secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, etc. which contain information about the sample’s surface topography, composition etc. The detectors collect the required signals and convert them to a signal that is sent to a viewing screen. This method can be combined with energy dispersive X-ray microanalysis (EDX) to analyse the secondary and back-scattered electrons to obtained information about the elemental composition of the sample. MgCa-silica SEM images were obtained using a Hitachi S-3000N SEM (Hitachi, Japan) at an acceleration voltage of 4 kV and at magnifications of about 3,000x whereas images of SNP were taken by Carl Zeiss SEM. The image was recorded on samples with no sputtered coating. The elemental analysis was done with EDX equipped in the SEM.

5.2.4 Nitrogen adsorption/desorption isotherms

Gas adsorption is a widely used method for characterization of porous materials. Information concerning the surface area and pore architecture (pore size, pores size distribution, pore volume) can be extracted from the adsorption isotherm which represents the amount of gases (adsorbate) adsorbed in a porous solid (adsorbent) as a function of the partial pressure of the gas-phase at a constant temperature (Sing et al. 1985). Adsorption is brought about by the interactions between the porous solid and the molecules in the fluid phase. The strength between the porous solid and the molecules give rise to either physical adsorption (physiosorption) or chemisorption. Chemisorption interactions are characterized by strong interaction between adsorbent-adsorbate which is essentially responsible for the formation of chemical compounds. The physical adsorption on the other hand is due to mainly dispersion forces, i.e. weak intermolecular forces between non-polar molecules. The latter is more preferential for porosity measurements because of its non-destructive nature and the ease of quantification of the adsorbate. Nitrogen is generally considered to be the standard adsorptive for micro and mesopore size analysis. Its usefulness derives from the fact that nitrogen has a permanent quadrupole moment which is responsible for the formation of a well-defined monolayer on most surfaces (Rouquerol et al. 1996). At the same time, the level of specificity is not high enough to give strong localization on most surfaces as it possesses a sufficiently small heat of adsorption in the first adsorbed layer (Rouquerol et al. 1996).

Physiosorption adsorption on porous solids is generally achieved by volumetric technique (point-by-point procedure). During the analysis nitrogen is introduced in successive amounts to known amount of sample in a sample tube that is immersed in liquid nitrogen. The process proceeds until any micropores in the surface are initially filled, then the free surface becomes completely covered, and finally large pores are filled. At each stage the measurement is made only when adsorption equilibrium is attained. As the bulk condensation point of nitrogen is
reached at higher relative pressure, desorption process may begin in which pressure steadily is reduced resulting in liberation of the adsorbed nitrogen. In this way two sets of data are obtained; the adsorption and desorption isotherms as each point of adsorbed and desorbed amount are plotted against successive points of pressure. From the isotherm, information about the internal surface area, pore volume and pore size can be derived.

The isotherms (see Fig.6) may be grouped into six types according to IUPAC classification (Sing et al. 1985). The Type I isotherm represents microporous materials where pore filling may take place either in pores of molecular dimensions at very low relative pressure or in wider micropores over a range of higher relative pressure. The Type II isotherm is normally related with infinite monolayer-multilayer adsorption on non-porous, macroporous or even, to limited extent, micropores. This shape of isotherm is termed Type IIa (Rouquerol et al. 1996). In Type IIb, adsorption-desorption isotherms exhibits Type H3 hysteresis with no plateau at high relative pressure. This kind of Type IIb isotherm is obtained from aggregates of plate-like particles, which therefore possess non-rigid slit-shaped pores (Rouquerol et al. 1996). Type III and Type V isotherms are limited to a few systems in which adsorbate-adsorbent interactions are weak. The Type III isotherms are associated with some non-porous and microporous adsorbents whereas Type V isotherms relates to some microporous or mesoporous materials. Type IV isotherm is a variation of Type II, but with limiting uptake over a range of high relative pressures corresponding to complete capillary condensation filling in mesopores. In some cases the Type IV isotherm exhibits two characteristic types of hysteresis loop. In the first case (a Type H1 loop) a relatively narrow loop with almost vertical and nearly parallel adsorption and desorption branches; whereas in the second case (a Type H2 loop), the loop is broad, the desorption branch being much steeper than the adsorption branch. Hysteresis loop occurs when the amount adsorbed is not brought to the same level by desorption after adsorption at a given equilibrium pressure or bulk concentration. The reasons for the different hysteresis loops are still an on-going discussion.

One practical application of adsorption isotherms is their use for selection of adsorbent or even the adsorption process as a unit operation for the adsorptive separation of gases (Schweitzer 1979). For adsorption isotherm shape Type I, II, or IV, adsorption can be used to remove the adsorbate from the carrier gas. If it is Type III or V, then adsorption will probably not be economical.

![Fig.6 Types of sorption isotherms (A) and (B) types of hysteresis loops of different porous materials (Sing et al. 1985)](image)
In this work, nitrogen sorption isotherms of all the samples were obtained at liquid nitrogen temperature (77K) using a Micromeritics (Accelerated Surface Area Porosimeter) ASAP2010 and a TriStar II 3020 volumetric adsorption instrument. For samples run on ASAP2010, the pure PSS-MgCa -68/32 and impregnates samples were degassed under vacuum for 20 h at 150°C whereas composites samples were degassed under vacuum for 4hr at 250°C before measurement. On TriStar II 3020 the samples were degassed under flowing nitrogen at 250°C for 4hr. The specific surface area ($S_{\text{BET}}$) was calculated using the standard BET equation (Sing et al. 1985). This was evaluated using nitrogen adsorption isotherm data in the relative pressure ($p/p^o$) range from 0.05 to 0.3. Multipoint BET surface areas ($S_{\text{BET}}$) were obtained for all samples with a minimum of 8 points and a correlation coefficient of 0.9999. The total pore volume ($V_{\text{tot}}$) was estimated on the basis of the amount adsorbed at $p/p^o \approx 0.99$. The $t$-plot calculated via Harkins and Jura equation with thickness range of 0.4 nm to 0.5 nm has been applied to determine the area and volume of micropore and mesopore in the materials (Rouquerol et al. 1996).

The Pore Size Distributions (PSD) curves of the materials prepared were derived from the adsorption branch of the isotherms by fitting a variety of models. PSD models used in this thesis were Horvath-Kawazoe (HK) (Horvath and Kawazoe 1983) and density functional theory (DFT) models (Webb and Orr 1997). The DFT models employed in this thesis includes nonlocal density functional theory (NLDFT) for pillared clay model and N$_2$ – Cylindrical Pores-Oxide surface model. Cylindrical pore geometry was assumed for both models. Carbon Slit Pores by NLDFT model and slit pore geometry were also used. The HK method in its original form was applied to calculate the micropores in molecular sieve carbons assuming slit-shaped pores (Horvath and Kawazoe 1983). Recently the HK method has been extended to cylindrical and spherical pore shapes (Cheng and Yang 1994). The model is limited to micropore size. However, the DFT models are applied over the entire range of the adsorption branch of isotherm and are not restricted to a limited range of relative pressure or pore size. The DFT method is based on the principle that uses a molecular-based statistical thermodynamic theory that allows relating the adsorption isotherm to the fluid-fluid and fluid-solid interaction energy parameters, the pore size, the pore geometry, and the temperature. Based on the thermodynamic properties of the confined fluid in the pore, the equilibration density profile for all locations in the pore is calculated by minimizing the free energy for a pore system with a bulk gas phase (Webb and Orr 1997).

### 5.2.5 Dynamic Adsorption of $\text{H}_2\text{S}$, $\text{SO}_2$ and Toluene

The common concentration range for contaminating gasses in indoor environment is very low and by far the principle of dynamic adsorption has been employed for removal of such gases (Schweitzer 1979; Ashrae Standard I45.I 2008). Therefore, in this work, the performance of the tailored silica adsorbents for filtration of contaminating gases has been tested by dynamic adsorption at indoor conditions in other to mimic the real life scenario. However the contaminated gas concentrations are increased in order to arrive at acceptable test times.

The analysis was performed in a system similar to the setup in ASHRAE 145.1 (Ashrae Standard I45.I 2008) but with four parallel columns as shown in Fig.7. Air with controlled temperature and humidity is fed from a large supply chamber and the selected challenge gas is injected from a pressurised gas cylinder by means of a computer controlled mass flow valve. The $\text{H}_2\text{S}$ and $\text{SO}_2$ are measured by a Thermo Environmental 43 C UV fluorescence instrument with a TE 340 $\text{H}_2\text{S}$ converter. Four parallel samples of ~50 g each were loaded into the four columns forming 52 mm high beds. The flow rate was 0.9 m$^3$/h and the contact time 0.2 s and 0.4 s. The inlet air stream containing concentrations of ~12000 ppb $\text{H}_2\text{S}$, 3100 ppb $\text{SO}_2$, 4870 ppb or 80 ppm toluene at 23 °C and 50% RH were made to pass through the columns. In the
adsorption of SO$_2$, the columns were loaded with ~31g of adsorbent in order to achieve a bed height of 26 mm. The flow rate was 1.8 m$^3$/h, giving a contact time of 0.1s. The concentration of contaminating gas was measured with time up-stream of the filters and directly after each filter column with time. The removal efficiency [%] in relation to adsorbed amount in grams was also calculated.

Fig. 7 Setup of dynamic adsorption challenge test

5.2.6 Measurement of spontaneous ignition temperature

The spontaneous ignition temperature (SIT) behaviour of the composite materials was assessed using TGA. The TGA equipment Pyris 1 from Perkin Elmer was used in this study. Samples weighing between 10 - 30 mg were weighed and introduced into the sample storage carousel. The samples were then automatically in turn introduced into the balance equipped furnace and subjected to an air flow at 20 mL/min. The temperature was increased from 20 to 600 °C using the following profile for temperature increase. Between 25 and 105 °C the rate was 20ºC/min. The sample was then held at 105 °C for 30 min in order to remove any excess adsorbed moisture. After this the temperature rate was 5ºC/min between 105 and 600 °C. Due to apparently insufficient moisture removal at 105 °C the relative weight loss was calculated at 180°C giving an additional 15 min for removing moisture. The resulting weight loss (%) vs sample temperature is used for analysis of SIT. The SIT is measured as the point where the tangent to the point of inflection intersects the baseline (100% weight retained).

5.2.7 Thermal conductivity measurements

The thermal conductivity of materials made has been measured by Transient Plane Source (TPS).

- **TPS**: This method is based on the use of a transiently heated plane sensor. The details of how TPS works has already been described in (Gustavsson el at. 1994). A test setup involving a sensor holder has been developed which enables the powder to be compacted and thereby eliminating large pores between aggregates and to enhance thermal contact between the powder and the sensor (see Fig.8). So, different measurements can be made at
different densities by squeezing the powder to different volumes. In actual measurement, first a piston-shaped seal is placed at the bottom of a hollow cylinder (Part B) and is filled with known amount of powder to the top edge, then the sensor with radius 6.403 mm is placed on top of the powder and tightened to Part B holder. Second, the other part of the hollow cylinder (Part A) is placed on Part B, and is also filled with an equal amount of powder. This is followed by another piston-shaped seal placed in the hollow cylinder. The two parts A and B with a sensor in between are tightened. The initial volume on each part is measured and from that an initial density is calculated. The volume change as squeezing the powder is measured and then subsequent densities are calculated. The thermal conductivity is measured at 25ºC with an output power of 0.005 W and a measurement time of 160s. A time lapse of 20 min between each reading was employed.

![Test setup for performing the transient thermal measurement on SNPs powders](image)

**5.2.8 Density measurements**

The tapped density of the mesoporous silica powders was measured by placing a defined amount of the powder into a graduated cylinder, which was tapped 500 times using Jolting Volumeter STAV II (J. Engelsmann AG, Germany). The volume occupied by the powder was then read and the density calculated based on the mass to volume ratio. The porosity of the samples was calculated by the relation:

$$\text{Porosity (\%)} = \left[1 - \frac{\rho_b}{\rho_s}\right] \cdot 100$$

where $\rho_b$ and $\rho_s$ are the tapped and skeletal densities of the SNP, respectively. The skeletal density $\rho_s$ of pure silica 2.5 g/cm$^3$ was used.
6. Results and Discussions

6.1 Structure and Morphology

6.1.1 X-Ray Diffraction

The wide-angle powder X-ray diffraction patterns of MgCa-silica with various Mg and or Ca mol % are shown in Fig.9. All the samples exhibits broad peaks centred at 2θ value of around 20-30° which is consistent with typical amorphous nature of the silica. The small peaks observed in the PSS-MgCa-0/100 indicate the presence of small amounts of crystalline compounds but the exact compounds could not be identified. Further weak peaks were also observed in PSS-MgCa-50/50. Thus as the mol % of Ca decreases and mol % Mg increases, the characteristic peaks of crystalline compounds becomes weaker, and invisible as the Ca mol% become less than 50 and the Mg mol % more than 50, whereas instead the characteristic hump of silica becomes more marked.

![XRD patterns of sorbents prepared with various Mg and/ or Ca mol %](image)

Fig.9 XRD patterns of sorbents prepared with various Mg and/ or Ca mol %

6.1.2 Morphology

The elemental composition of the sorbents, determined by EDX in SEM is reported in Table 1. The analysis was done to see if the Mg$^{2+}$ and Ca$^{2+}$ were able to replace 2Na$^{+}$ in the (Na$_2$O nSiO$_2$) as given by the reaction (1). The sorbents prepared had mean Si/ (Mg+Ca) ratios in the range of 2.5-3.4, a range very close to the SiO$_2$/Na$_2$O molar ratio of 3.35. This is a sign
that (Mg, Ca) O might have formed and replaced the Na₂O in the (N₂O nSiO₂) in the final sorbent produced. Fig. 10 displays SEM micrographs of the MgCa-silica sorbents. The micrographs show that sorbents prepared are composed of primary particle sizes which are very small and platelike which tend to cohere to form a porous structure. Sorbents prepared with single Ca metal are observed to be composed of more compact particles whereas the corresponding sample made with 100 mol % Mg (PSS-MgCa-100/0) show plate particles that are more porous in nature. Further magnification reveals that PSS-MgCa-75/25 was made of small agglomerates of plate particles. In case of PSS-MgCa-68/32, a monolith made of particles that are smaller and homogenous in size was observed. When a monolith PSS-MgCa-68/32 was impregnated or incorporated with activated carbon, a similar particle and morphology were observed.

Fig. 10 SEM micrographs of MgCa-silica prepared with various Mg and / or Ca mol %
Fig. 11 SEM images of the SNPs made with different acids. A, C: oxalic acid and B, D: sulphuric acid.

Fig. 11 shows the SEM images of the SNPs made with different acids and have different tapped densities. The SNP-OA exhibits morphology of spherical and plate like particles whereas SNP-SA displays only particles of spherical nature. Both morphologies also confirm the porous nature of the powder with relatively uniform pores in the particles (Fig. 11c, d).

6.2 Porous Properties as determined by Nitrogen Physisorption

6.2.1 Surface area and pore volume of MgCa-silica

The adsorptive properties of all the nanoporous silica developed in this thesis have been studied by nitrogen adsorption. Nitrogen adsorption isotherms of all sorbent samples with various Mg/Ca mol% are presented in Fig. 12a and the corresponding physicochemical parameters are summarized in Table 2. All the MgCa-silica sorbents prepared yields completely reversible type IIb isotherms with a clear type-H3 hysteresis loop based on IUPAC classification (Sing et al. 1985; Rouquerol et al. 1996). Several models have suggested that the calcium silicate hydrate gel consists of very thin sheets (Jennings et al. 2008) and Magnesium silica hydrates consist of agglomerates of thin plate particles (Brew et al. 2003). Such sheets in the MgCa-silica sorbents prepared may well produce networks of plate-like or slit-shaped pores with varied size and thus contributes to the shape of type-H3 hysteresis loop. An adsorption at very low relative pressure, \( p/p^* < 0.1 \) was observed for all the samples prepared indicating the presence of some micropores in the samples. In a comparison between the sorbents made with solely Mg (PSS-MgCa-100/0) and Ca (PSS-MgCa-0/100), the later exhibits the highest uptake at low pressure range (micropore range).
indicating the presence of high micropore area. The PSS-MgCa-0/100 has the lowest uptake among all the samples. For sorbents with both Mg and Ca it was observed that the nitrogen uptake at low relative pressure begins to increase when the mol % of Mg is 50% or more. The uptake at low p/p° then increases accordingly as the Mg mol % increases. A sharp rise in nitrogen uptake at higher p/p° was also observed among the MgCa-silica sorbents. The very small hysteresis loop above p/p° ≈ 0.9 in their isotherms is a sign of condensation in intraparticle cavities of colloidal-sized silica. The nitrogen uptake at both low and high relative pressure range was found to be sensitive to changes of the Mg/Ca molar ratio. For instead PSS-MgCa-68/32 sample exhibits a distinctive future of wide Type- H3 hysteresis loop with a small sharp step in the amount desorbed at about p/p° =0.40. Sharp steps in the nitrogen adsorption isotherms of homogeneous mesoporous silica materials are usually observed around p/p° =0.3 (Kruk et al. 1997). The PSS-MgCa-68/32 material in Fig.12a however exhibits heterogeneous mesopore size distribution as evidenced by the gradual shift of p/p° value in the p/p° =0.3 region. This was further shown in the PSD (Fig.12b) where PSS-MgCa-68/32 has interconnected meso pores in a broad size range. These features were not exhibited by the rest of the MgCa-silica sorbents.

Overall, it is evident that varying the Mg/Ca ratio has influence on the particle morphology which also affects the adsorptive properties of the MgCa-silica sorbents prepared. From Table 2 it can be observed that samples made with 100 mol % Ca (PSS-MgCa-0/100) exhibits low S BET whereas the corresponding sample made with100 mol % Mg (PSS-MgCa-100/0) show a significantly higher S BET. It may also be noted that for samples made with 68 % Mg and 32 mol % Ca (PSS-MgCa-68/32); 75 mol % and 25 mol % Ca (PSS-MgCa-75/25) exhibited even higher S BET than the samples containing the single metal. The S BET of PSS-MgCa-68/32 and PSS-MgCa-75/25 are nearly the same, and have a better S BET compared with the rest of the samples prepared. The S BET of the samples decreased from 373 m²/g (PSS-MgCa-68/32) to 257 m²/g (PSS-MgCa-50/50) when Ca content was 50 mol % and it continues to dramatically decrease to 63 m²/g (PSS-MgCa-0/100) when Ca content was 100 mol %. The variation in S BET with the Mg/Ca ratio can be explained by referring to the XRD analysis. It can be observed from Fig.9 that samples that had crystalline compounds shows less S BET (Table 2). Lin and co-workers (Ren-Bin et al. 2003) prepared 3CaO·2SiO2·4H2O sorbents with various ratios of Ca/SiO2. It was shown that the sorbent composed of two particles types, either open thin foils of 3CaO·2SiO2·4H2O or some particles being more compact or sorbent compose of both particles types based on the Ca/SiO2 ratio. Magnesium silica hydrates, have also been shown to consist of agglomerates of thin plate particles (Brew et al. 2003). In this work the formation of compact plate like particles of calcium silicate hydrate were more abundant in the sample prepared with 100 mol % Ca and therefore reducing the accesses of nitrogen into some of the pores. This can be partly explained by the bigger diameter of the Ca-atoms. When the Ca mol % is reduced to 50 and Mg increased to 50 mol %, the amount of compact particles of 3CaO·2SiO2·4H2O is reduced and the introduction of Mg results in the formation of porous agglomerates of magnesium silicate particles in the sorbent consequently increases the surface area and the volume of pores. For the PSS-MgCa-68/32 sorbent the amount of magnesium silicate increased and the S BET increased accordingly. According to the results in Table 2, the V tot follow the same pattern as does the S BET with the exception of PSS-MgCa-75/25, which had similar S BET as PSS-MgCa-68/32, but the results of the V tot was contrary to the S BET.

The amount of micro- and mesopores in the MgCa-sorbents has further been calculated via t-plots by the Harkins and Jura equation (Rouquerol et al. 1996). The t-plots are shown in (Fig.5b in Paper I) and the corresponding parameters shown in Table 2. The presence of micropores in the sorbents prepared is confirmed by the fact that the linear region of the t-plot intercepts the y-axis in these plots. The micropore volumes (V mic) of the samples are derived
from the y-axis intercept of the extrapolated linear region and mesoporous area ($S_{\text{mes}}$) from the slope in these plots. Given this, the $V_{\text{mic}}$ and $S_{\text{mic}}$ of sorbents with $\geq 75$ mol % of Mg are relatively large compared with the rest of the samples. The $S_{\text{mic}}$ contributions to the respective $S_{\text{BET}}$ are for PSS-MgCa-0/100: 14%, PSS-MgCa-50/50: 5%, PSS-MgCa-68/32:12%, PSS-MgCa-75/25: 18% and PSS-MgCa-100/0: 30%. The $V_{\text{mic}}$ follows similar pattern as does the $S_{\text{mic}}$. It can be concluded that sorbents prepared have mesopores occupying large portions of their pore structure. It’s worth noting that PSS-MgCa-68/32 has a relatively large $S_{\text{mes}}$ and $V_{\text{mes}}$ compared with the rest of the samples. This can be explained by the fact that PSS-MgCa-68/32 from SEM image has it constituent primary particles size being much smaller and homogenous. Therefore the mesopores originated from intraparticle spaces between the homogenous primary particles is much more distributed throughout the PSS-MgCa-68/32 structure than the rest of the samples.

![Fig.12](image)

Fig.12 N$_2$ isotherm curves (A) and (B) the corresponding NLDFT pore size distribution assuming cylindrical pore geometry
Fig. 12 - Geo with 2–4 nm and mesopore diameter centered at about 2.4 nm, distribution.

Samples sizes exhibit pores in size range of 1.4 nm to 5 nm. The sorbents made with 100 mol % Mg have a wide PSD in the range of 1.4 nm to 30 nm with abundance of pores in the range of 5 nm to 30 nm. It is evident from these results that the sorbent made with various Mg/Ca mol % contains micropores of cylindrical shape and mesopore pillared clay-like shape and probably other irregular pore shapes. From Fig. 12b, the MgCa-silica sorbents prepared show an interconnected bimodal pore distribution in the micro- and mesopore region. The PSS-MgCa-50/50 and PSS-MgCa-75/25 exhibited a narrow pore size range with micropore diameter centred at about 1.4 nm and mesopore diameter centred at about 2.4 nm, whereas PSS-MgCa-68/32 shows a sharp wide PSD with micropore diameter centred at about 1.4 nm and 5.4 nm for mesopore diameter. The PSD of PSS-MgCa-68/32 further confirmed the existence of an interconnected heterogeneous mesopore size distribution as observed from wide hysteresis loop in its isotherm. The sharp PSD of PSS-MgCa-68/32 may be due to the fact that pores arise from smaller and homogenous silica particles as observed in the SEM images. The pores in this case will be quite large. This explains why PSS-MgCa-68/32 shows a wide PSD in the range of 1.4 nm to 30 nm with abundance of pores in the range of 5 nm to 20 nm. On the other hand PSS-MgCa-75/25 which shows smaller and inhomogeneous particle sizes exhibits pores in size range of 1.4 nm to 5 nm. The sorbents made with 100 mol % Mg

Table 2 Textural properties of sorbents prepared with various Mg- and/or Ca molar ratios and sorbents impregnated with 8 wt% KOH

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( S_{\text{mic}} ) (m²/g)</th>
<th>( S_{\text{mes}} ) (m²/g)</th>
<th>( V_{\text{tot}} ) (cm³/g)</th>
<th>( V_{\text{mic}} ) (cm³/g)</th>
<th>( V_{\text{mes}} ) (cm³/g)</th>
<th>( d_{\text{mic}} ) (nm)</th>
<th>( d_{\text{mes}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSS-MgCa-0/100</td>
<td>63</td>
<td>9.0</td>
<td>53.6</td>
<td>0.17</td>
<td>0.003</td>
<td>0.167</td>
<td>1.40</td>
<td>1.33</td>
</tr>
<tr>
<td>PSS-MgCa-0/100</td>
<td>64</td>
<td>10</td>
<td>54</td>
<td>0.22</td>
<td>0.005</td>
<td>0.215</td>
<td>1.40</td>
<td>1.33</td>
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<tr>
<td>PSS-MgCa-50/50</td>
<td>267</td>
<td>13</td>
<td>254</td>
<td>0.41</td>
<td>0.003</td>
<td>0.408</td>
<td>1.37</td>
<td>1.33</td>
</tr>
<tr>
<td>PSS-MgCa-50/50</td>
<td>259</td>
<td>12</td>
<td>247</td>
<td>0.43</td>
<td>0.004</td>
<td>0.426</td>
<td>1.37</td>
<td>1.33</td>
</tr>
<tr>
<td>PSS-MgCa-50/50-KOH</td>
<td>221</td>
<td>6</td>
<td>215</td>
<td>0.55</td>
<td>0.003</td>
<td>0.547</td>
<td>1.61</td>
<td>1.41</td>
</tr>
<tr>
<td>PSS-MgCa-68/32</td>
<td>373</td>
<td>45</td>
<td>328</td>
<td>0.65</td>
<td>0.021</td>
<td>0.625</td>
<td>1.41</td>
<td>1.29</td>
</tr>
<tr>
<td>PSS-MgCa-68/32</td>
<td>372</td>
<td>49</td>
<td>323</td>
<td>0.63</td>
<td>0.020</td>
<td>0.610</td>
<td>1.41</td>
<td>1.29</td>
</tr>
<tr>
<td>PSS-MgCa-68/32-KOH</td>
<td>312</td>
<td>30</td>
<td>282</td>
<td>0.59</td>
<td>0.012</td>
<td>0.578</td>
<td>1.41</td>
<td>1.29</td>
</tr>
<tr>
<td>PSS-MgCa-75/25</td>
<td>374</td>
<td>66</td>
<td>308</td>
<td>0.53</td>
<td>0.031</td>
<td>0.499</td>
<td>1.36</td>
<td>1.28</td>
</tr>
<tr>
<td>PSS-MgCa-75/25</td>
<td>371</td>
<td>60</td>
<td>311</td>
<td>0.52</td>
<td>0.030</td>
<td>0.490</td>
<td>1.36</td>
<td>1.28</td>
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<tr>
<td>PSS-MgCa-75/25-KOH</td>
<td>361</td>
<td>23</td>
<td>338</td>
<td>0.58</td>
<td>0.009</td>
<td>0.571</td>
<td>1.71</td>
<td>1.47</td>
</tr>
<tr>
<td>PSS-MgCa-100/0</td>
<td>368</td>
<td>113</td>
<td>255</td>
<td>0.51</td>
<td>0.054</td>
<td>0.456</td>
<td>1.40</td>
<td>1.17</td>
</tr>
<tr>
<td>PSS-MgCa-100/0</td>
<td>347</td>
<td>109</td>
<td>238</td>
<td>0.55</td>
<td>0.046</td>
<td>0.504</td>
<td>1.40</td>
<td>1.17</td>
</tr>
<tr>
<td>PSS-MgCa-100/0-KOH</td>
<td>320</td>
<td>19</td>
<td>227</td>
<td>0.22</td>
<td>0.010</td>
<td>0.21</td>
<td>1.70</td>
<td>1.57</td>
</tr>
</tbody>
</table>

\( S_{\text{BET}} \) - BET specific surface area, \( S_{\text{mic}} \) - t-plot micropore surface area, \( S_{\text{mes}} \) - mesopore surface area, \( V_{\text{tot}} \) - total pore volume, \( V_{\text{mic}} \) - micropores volume, \( V_{\text{mes}} \) - mesopores volume, \( d_{\text{mic}} \), \( d_{\text{mes}} \) - micro-and mesopore maxima peaks in DFT pore size distribution, \( d_{\text{HK}} \) - micropore pore size obtained from Horvath-Kawazoe (H-K) equation.

The quantitative analysis of various pore size distributions (PSD) in the MgCa-silica sorbents have been derived by both DFT and HK models for comparison purposes (see Fig. 7 of paper I). NLDFT for pillared clay and \( N_2 \) - Cylindrical Pores-Oxide surface models and HK models were adopted assuming cylindrical pore geometry for both models, as it was found that these geometries best fitted the adsorption raw data (see Fig. 1 and 6 of Paper I). Nevertheless both cases give similar values of pore size. One can observe that when using \( N_2 \)-Cylindrical Pores-Oxide surface model, sharp peaks appeared in the micropore size range and a less sharp or broad peak in the mesopore size range. However, when the NLDFT pillared clay model is assumed, reverse results are obtained. It is evident from these results that the sorbent made with various Mg/Ca mol % contains micropores of cylindrical shape and mesopore pillared clay-like shape and probably other irregular pore shapes. From Fig. 12b, the MgCa-silica sorbents prepared show an interconnected bimodal pore distribution in the micro- and mesopore region. The PSS-MgCa-50/50 and PSS-MgCa-75/25 exhibited a narrow pore size range with micropore diameter centred at about 1.4 nm and mesopore diameter centred at about 2.4 nm; whereas PSS-MgCa-68/32 shows a sharp wide PSD with micropore diameter centred at about 1.4 nm and 5.4 nm for mesopore diameter. The PSD of PSS-MgCa-68/32 further confirmed the existence of an interconnected heterogeneous mesopore size distribution as observed from wide hysteresis loop in its isotherm. The sharp PSD of PSS-MgCa-68/32 may be due to the fact that pores arise from smaller and homogenous silica particles as observed in the SEM images. The pores in this case will be quite large. This explains why PSS-MgCa-68/32 shows a wide PSD in the range of 1.4 nm to 30 nm with abundance of pores in the range of 5 nm to 20 nm. On the other hand PSS-MgCa-75/25 which shows smaller and inhomogeneous particle sizes exhibits pores in size range of 1.4 nm to 5 nm. The sorbents made with 100 mol % Mg...
or 100 mol% Ca also did exhibit a narrow PSD range of 1 to 5 nm. They have their micropore and mesopore diameter centred at about 1.4 nm and 2.3 nm for PSS-MgCa-100/0 and 1.4 nm and 2.4 nm for PSS-MgCa-0/100 respectively. A similarity observed amongst PSS-MgCa-50/50, PSS-MgCa-68/32 and PSS-MgCa-75/25 is the presence of a sharp peak appearing at a pore diameter centred at ca. 25 nm on PSD curve. This kind of pores originates from spaces between relatively large particles.

Besides the DFT method, the micropore size distribution for the sorbents has been calculated with the Horvath-Kawazoe (H-K) (Saito-Foley) method from the adsorption branch assuming cylindrical –shaped geometry of the pores (Horvath and Kawazoe 1983). The H-K equation parameters (Larsen et al. 2000) used in this evaluation are given in Table 3 in paper I. Micropore size distributions obtained for sorbents prepared with different Mg and/ or Ca molar ratio is shown in Fig.7 in paper I and values in Table 2. All the sorbents were found to have micropores having distributions with maxima positions at about 1.17 nm and 1.3 nm and show a very good agreement with the maxima position of micropore size obtained from NLDFT PSD curves. This suggests that the micropore size of the samples prepared can be represented by either cylindrical or pillared clay-like geometries.

6.2.2 Surface areas and pore volume of SNP materials

Fig.13 shows the physisorption isotherms and the corresponding physicochemical parameters are summarized in Table 1 in paper V. The isotherms are of type IV with a type H4 hysteresis loop, indicating the presence of narrow slit-like pores (Sing et al. 1985). The SNP-SA exhibit a high surface area of 432 m² g⁻¹, and the pore size distributed in the range of 1 -100 nm with a maximum peak centred at about 47 nm as shown in Fig.13b. The S⁻¹⁰⁰ and pore size of the SNP-OA were slightly lowered with the variation of the acid type. A similar pore size was obtained by (Rao et al. 2002) when glycerol was used as drying control chemical additives in aerogel preparation (Rao et al. 2002). The variation of acid type from oxalic acid to sulphuric acid affected the density and the porosity, decreases from 0.122 to 0.077 g/cm³ whereas the porosity increase from 95 to 97% respectively. Such high surface area and homogeneous pores can be attributed to glycerol-silica clusters via formation of hydrogen bond. The glycerol thus provides a steric shielding around the colloidal particles, preventing rapid precipitation. A delay in precipitation reaction would results in small homogenous particles which provide large surface area. Moreover, the presence of glycerol in the SNP pore system shift the pore size distribution to large mean pore sizes, which reduce the degree of drying stress caused by differential pressures. Thus the SNP-SA with large pore size has a less tapped density as there was less stress or shrinkage during drying. The mean pore sizes of the SNP materials are smaller than the mean free path of air (~70 nm) under ambient conditions, indicating that the SNP’s can retard the gaseous heat conduction even under ambient condition in accordance with Knudsen number (Baetens et al. 2010; Quenard et al. 2005)
6.2.3 Surface areas and pore volume of carbon-silica composites

In preparing carbon-silica sorbents, PSS-MgCa-68/32 was selected as silica source due to its wide PSD (1.4 nm to 30 nm) with abundance of pores in the range of 5 nm to 20 nm which will serve as a good channel for gas entrapment. The composite was made by adding CAC at different stages of PSS-MgCa-68/32 preparation. The maximum amount of carbon that can be incorporated is 16 wt% for carbon particles sieved to a size < 500 micron and 45 wt% when particles size < 150 micron was used. With a carbon particle size < 500 micron, solid pellets were formed when carbon content was lower than 16 wt%. Above 16 wt% of carbon, disintegrated pellets consisting of powder-like composites were obtained. A similar scenario was observed for samples obtained when carbon content was above 45% of fine carbon (particle size < 150 microns). The N₂ sorption isotherms and PSD for composites obtained via route I with different carbon compositions and CAC are shown in Fig.14. The isotherms for composites prepared via route II and III are shown in Paper IV. The corresponding physicochemical parameters are summarized in Table 4. The PSC samples exhibits Type IIb isotherms as in PSS-MgCa-68/32, and show high nitrogen uptake as carbon content increases especially in the p/p° range 0.003-0.3, typical of microporous material. The steep increase in nitrogen uptake was more pronounced in PSC (I)-45F. The composite materials prepared show an increase in BET surface area in all routes and the increase was almost linear with carbon content. The effect of carbon content on the BET surface areas S_BET has further been analysed. The dashed line in Fig.15a shows the expected S_BETs of mechanical mixtures of pure PSS-MgCa-68/32 with different wt % of carbon. When the S_BETs of PSC composites (the solid line in Fig.15a) were plotted as a function of carbon content, no linear correlation with expected S_BET was obtained. Thus by following route I, the composites obtained exhibits surface area significantly higher than the expected values when 8 or 16 wt% of CAC of particle size less than 500 microns were used. When 8 or 16 wt % of CAC of particles less than 150 microns were used, the composites gave slightly less S_BET than the expected values. However from 32 wt% carbon contents the composites exhibits S_BET higher than the expected values. In contrast to composites obtained by route I, the composites obtained by route II and III give surface area below the expected values of mechanical mixtures of PSS-MgCa-68/32 and CAC (Fig.15a dashed line). The total pore volume in route I shows a maximum value (0.74 cm³/g) at 16 wt % carbon and started decreasing (0.68 cm³/g) when carbon content...
reached 32 wt %. The total pore volume was 0.65 cm$^3$/g when carbon content was raised to 45wt %. Further the total pore volumes obtained by following route II with carbon content 16 wt % was similar to total pore volume value of PSS-MgCa-68/32. With 32 wt % carbon content in route II, the total pore volume decreases and start increasing gradually when carbon content raised to 45 wt %. These features were better than carbon-silica composites prepared by impregnation of silica pore system with polyfurfuryl alcohol (PFA) followed by carbonization of PFA. Those composites exhibit a decrease in surface area and total pore volume upon filling the pores with more carbon content (Leboda 1992; Glover et al. 2008; Leboda 1993). Moreover, detailed analysis of pore volume indicates that microporosity volume increases with decreasing mesoporosity volume and with increase in carbon content in both route II and III (see Paper IV). Overall it can be concluded from Fig.15c that the microporosity in the PSC composites increases as carbon content increases. Therefore it is reasonable to assume that most of the carbon contained in PSC composites resides in the pores as porous filling and is easily accessible. For composites via route I, carbon was added after the pore system was formed and addition of carbon did not affect the pore structure. The adsorptive properties were rather increased as higher surface area and pore volume could be observed for samples obtained via this route. In case of PSC(II) and PSC(III) the carbon was present in either salt or silica solution before precipitation. This may have in a way prevented or reduced the formation of total pore volume as well as mesopores as observed in Table 3. This effect was predominant in route II as the materials obtained do not display strong signs of mesoporosity.

It is also worth noting that composites prepared with CAC2 of particles <150 microns exhibits high microporosity and slightly less BET surface area when compared to composites prepared with CAC1 of particles <500 microns even though the two carbons exhibits similar textural properties.
Fig. 14 N$_2$ sorption isotherms of (A) carbon and silica material in their original form and (B) the composites formed via route I with different carbon contents. Corresponding NLDFT pore-size distribution curves of (C) carbon and silica material and (D) composites samples are shown below.

The curves of PSD for the carbon-silica composites are shown in Fig. 14 and in Paper III and IV. It follows that the PSD of these composites is dependent on the synthesis route and carbon content. When route I and III are employed, the PSC(I) and PSC(III) samples exhibit wide PSD of 1 to 30 nm as in parent PSS-MgCa-68/32, whereas PSC(II) samples exhibit narrow PSD of 1 to 4 nm (see Paper III and IV). When comparing the PSD curves of composites materials, a significant difference was noted in the micropore range. When carbon content is 8 wt % or 16 wt %, composite exhibits similar pore size distribution (1-30 nm) as in the parent silica structure but micro pore diameter centred at 1.4 nm shows an increase in micropore volume. Moreover, when increasing the carbon content a pore centred at 1.14 nm was introduced. Thus, depending on the carbon content two distinct micropore dimensions are identified. By following route I and III, PSC with carbon loadings below 16 wt % have micropore size centred at about 1.4 nm whereas PSCs with carbon content 32 wt % or more shows micropore diameter centred at 1.14 nm. Moreover following route II, micropore size centered at 1.17 nm was observed when carbon content was 32 or 45 wt % (see Fig. 2 in Paper IV). These micropore diameters were unique when compared to parent CAC (1.22 nm) and PSS-MgCa-68/32 (1.4 nm). The micropore diameter presented here was similar to that obtained in the work of Liu et al. (Liu and Komarneni 1995) concerning carbon-silica composites formed with Xerogel and porous carbon powder. In their work the silica-carbon obtained was predominantly microporous with pore size found to be centred on 1 nm. In
contrast to effect of carbon content on micropore diameter, the synthesis routes had effects on the mesopore region of PSD.

In route I, samples obtained shows slight change in the mesopores region and shows similar abundance pores of diameter from 5 to 20 nm as in pure PSS-MgCa-68/32 (Fig.12b). In route III however, the mesopore in the same region (5-20 nm) exhibits a decrease rather in volume. Further such mesopores (5-20 nm) practically disappear from the PSC composites when route II was followed. The PSD of carbon is narrow (1-2 nm). Therefore it appears that in PSC(I) and PSC(III) samples, the pore system was apparently subjected to silica pore structure whereas in PSC(II) the pore structure was dominated by carbon pore system. It can be observed from Fig.2 in Paper III that the PSC(II) maximum pore size (2.4 nm) is located at an almost average position between maximum pore size 2 nm for carbon and 5.4 nm for pure PSS-MgCa-68/32.

Fig.15 Plot of (A) BET surface area of PSC composites (solid lines) and expected mechanical mixtures of parent silica and CAC (dashed line), (B) change of total pore volume and (C) micro-meso pore volume change (from t-plots) versus carbon content wt %
6.2.3.1 Spontaneous ignition temperature analysis

When selecting an adsorbent for a specific application other factors may be equally important besides the obvious demand for adsorption performance. One such factor may be the fire hazard due to the flammability of the adsorbent or due to an erroneous installation giving insufficient cooling or too exothermic reactions due to high VOC concentrations.

In this thesis TG data has been used to assess the spontaneous ignition temperature (SIT) of carbon-silica composites. From Fig.6 in Paper IV it can be seen that the SIT value of PSC(I) – 45F is around ~509 °C and is higher than CAC with value around ~ 477 °C while PSC (I)-8F do not show any evident SIT. This indicates that SIT values are higher for composites compared to CAC and that data may correlate to the carbon amount. The data for the Al-C composite is less clear and seem to indicate a multiple stage weight loss, probably related to its constituents.

Table 3 Surface areas and Pore Properties of Parent Silica and Carbon and their Composites obtained via routes I-III

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$S_{mic}$ (m$^2$/g)</th>
<th>$S_{mes}$ (m$^2$/g)</th>
<th>$V_{tot}$ (m$^3$/g)</th>
<th>$V_{mic}$ (m$^3$/g)</th>
<th>$V_{mes}$ (m$^3$/g)</th>
<th>$d_{mic}$ (nm)</th>
<th>$d_{mes}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PSS</td>
<td>372</td>
<td>44.5</td>
<td>327.5</td>
<td>0.63</td>
<td>0.021</td>
<td>0.609</td>
<td>1.41</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(I)-8</td>
<td>469</td>
<td>46</td>
<td>423</td>
<td>0.67</td>
<td>0.021</td>
<td>0.649</td>
<td>1.39</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(I)-8F</td>
<td>388</td>
<td>137</td>
<td>251</td>
<td>0.65</td>
<td>0.040</td>
<td>0.610</td>
<td>1.40</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(I)-16</td>
<td>512</td>
<td>82.5</td>
<td>429.5</td>
<td>0.70</td>
<td>0.042</td>
<td>0.658</td>
<td>1.39</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(I)-16F</td>
<td>431</td>
<td>150</td>
<td>281</td>
<td>0.74</td>
<td>0.065</td>
<td>0.675</td>
<td>1.39</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(I)-45F</td>
<td>769</td>
<td>480</td>
<td>289</td>
<td>0.65</td>
<td>0.198</td>
<td>0.452</td>
<td>1.14</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(II)-8</td>
<td>394</td>
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<td>0.59</td>
<td>0.034</td>
<td>0.556</td>
<td>1.41</td>
<td>2.4</td>
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<tr>
<td>PSC(II)-8F</td>
<td>386</td>
<td>126</td>
<td>261</td>
<td>0.59</td>
<td>0.045</td>
<td>0.545</td>
<td>1.41</td>
<td>2.4</td>
</tr>
<tr>
<td>PSC(II)-16</td>
<td>391</td>
<td>86.3</td>
<td>304.7</td>
<td>0.55</td>
<td>0.049</td>
<td>0.501</td>
<td>1.41</td>
<td>2.4</td>
</tr>
<tr>
<td>PSC(II)-16F</td>
<td>393</td>
<td>222</td>
<td>171</td>
<td>0.54</td>
<td>0.092</td>
<td>0.448</td>
<td>1.41</td>
<td>2.4</td>
</tr>
<tr>
<td>PSC(II)-32F</td>
<td>523</td>
<td>296</td>
<td>227</td>
<td>0.61</td>
<td>0.126</td>
<td>0.484</td>
<td>1.17</td>
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</tr>
<tr>
<td>PSC(II)-45F</td>
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<td>0.158</td>
<td>0.442</td>
<td>1.17</td>
<td>2.4</td>
</tr>
<tr>
<td>PSC(III)-8</td>
<td>374</td>
<td>59</td>
<td>315</td>
<td>0.62</td>
<td>0.023</td>
<td>0.597</td>
<td>1.40</td>
<td>5.3</td>
</tr>
<tr>
<td>PSC(III)-8F</td>
<td>399</td>
<td>107</td>
<td>292</td>
<td>0.61</td>
<td>0.047</td>
<td>0.563</td>
<td>1.36</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(III)-16</td>
<td>408</td>
<td>65</td>
<td>277.4</td>
<td>0.58</td>
<td>0.039</td>
<td>0.547</td>
<td>1.41</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(III)-16F</td>
<td>381</td>
<td>177</td>
<td>204</td>
<td>0.64</td>
<td>0.073</td>
<td>0.567</td>
<td>1.36</td>
<td>5.4</td>
</tr>
<tr>
<td>PSC(III)-32F</td>
<td>509</td>
<td>337</td>
<td>172</td>
<td>0.60</td>
<td>0.141</td>
<td>0.459</td>
<td>1.13</td>
<td>16.6</td>
</tr>
<tr>
<td>PSC(III)-45F</td>
<td>596</td>
<td>410</td>
<td>186</td>
<td>0.62</td>
<td>0.167</td>
<td>0.453</td>
<td>1.14</td>
<td>16.6</td>
</tr>
<tr>
<td>Al-C</td>
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<td>146</td>
<td>0.29</td>
<td>0.108</td>
<td>0.182</td>
<td>1.31</td>
<td>6.7</td>
</tr>
<tr>
<td>CAC1</td>
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<td>828</td>
<td>193</td>
<td>0.50</td>
<td>0.423</td>
<td>0.077</td>
<td>1.54</td>
<td>2.2</td>
</tr>
<tr>
<td>CAC2</td>
<td>1056</td>
<td>955</td>
<td>101</td>
<td>0.47</td>
<td>0.410</td>
<td>0.060</td>
<td>1.22</td>
<td>2.0</td>
</tr>
</tbody>
</table>
6.2.4 Effect of impregnation on Surface Areas and Pore Size distribution of MgCa-Silica sorbents

For high gas filtration rate and better performance, the MgCa-silica has been impregnated with different impregnates. The MgCa-silica is not effective in removing sulphur dioxide and hydrogen sulphide by physical adsorption, but it can be when impregnated with chemicals that do react with these contaminants. In this case the MgCa-silica serves as a carrier of impregnates and by providing a surface on which the chemical reaction(s) can proceed. Addition of impregnates to the adsorbent improve the uptake capacity and give it some degree of specificity. This is also associated with changes in the porous structure of the adsorbent. It is important that the benefits obtained by of impregnates chemicals are not to reduced due to pore entrance blockage or vice versa. Table 4 presents the surface area and pore volume of both the KOH and KMnO₄ impregnated MgCa-silica. The different amounts of impregnates that were added to the MgCa-silica substrate and samples denotations are explained in section 5.1.4.

The interior surface area reduction was observed for all the chemisorbents prepared. When 8 wt % KOH was incorporated into PSS-MgCa-68/32 substrate, there was about 16% and 7% reduction of surface area and pore volume, respectively. The isotherms and pore size distributions of impregnated PSS-MgCa-68/32 indicated in Fig.16 did not show any significant changes when compared to the starting substrate. As further evident in Fig.16 however, incorporation of 8 wt % KOH did affect the shape of isotherms and PSD of the rest of the samples. Further examination indicates that impregnation tend to increase the pores and shift the maximum pore peak to larger pore diameter. Thus for example, PSS-MgCa-100/0, PSS-MgCa-75/25, and PSS-MgCa-50/50, which exhibited narrow pore size range, tend to get a broader pore size distribution with larger maximum pore diameter located at 3.7, 3.5, and 25.4 nm respectively. This resulted in the increase of the pore volumes in that region and the total pore volume as a whole. With the exception of PSS-MgCa-100/0-KOH, the pore size was shifted to 3.7 nm but the total pore volume decreased. These findings indicate that PSS-MgCa-68/32-KOH sorbent porosity is more stable than the rest of the samples when a KOH impregnation is added. The KMnO₄ impregnation has therefore been performed only on PSS-MgCa-68/32 substrate via two routes.

Fig.16 N₂ sorption isotherms (A) and (B) pore size distribution of PSS-MgCa-sorbents impregnated 8 wt% KOH. The PSD have been determined by N2-Cylindrical Pore-Oxide surface model and assuming cylindrical pore geometry.
The effect of KMnO4 impregnate on PSS-MgCa-68/32 pore structure has therefore been viewed from two sides; the effect as results of the preparation routes and the effect of loading amounts. The effect of the preparation routes on PSS-MgCa-68/32 pore properties (Table 5) becomes clear when compared PSS(I)-8 (8.4 wt%) and PSS(II)-8 (7.6 wt%) as they were prepared with similar KMnO4 content but via different routes. Overall, all impregnated PSS obtained exhibit a completely reversible type II isotherm similar to the parent PSS-MgCa-68/32 structure. Furthermore the PSS-MgCa-68/32 before and after impregnation exhibits the same wide range of pore size distribution, between 1 to 32 nm (see Fig. 4 in Paper II) with maximum micropore and mesopore pore diameter centred at ~1.4 and ~5.4 nm respectively. Although decrease in BET surface area and pore volume was observed for KMnO4 impregnated samples, the effect of preparation route was not apparent in the BET surface area. However, the effect was obvious in the total pore volume. Chemisorbents obtained via route I, PSS(I)-8 and PSS(I)-13 exhibits a total pore volume reduction of about 19 % and 23 % respectively. By following route II however, the total pore volume reductions were 24 % and 26 % for PSS(II)-8 and PSS(II)-13 respectively. Further analysis of the mesopore volume which occupied large portion of the pore structure also indicates a reduction in a case where II route was followed. The mesopore volume reductions were about 22 % and 24 % for PSS(II)-8 and PSS(II)-13 respectively. By following route I however, the mesopore volume reductions were about 19 % and 22 % for PSS(I)-8 and PSS(I)-13 respectively.

The difference in chemisorbents pore parameters could be related to the route of impregnation. In chemisorbents obtained via route I (PSS(I)-8 and PSS(I)-13) the KMnO4 has been introduced by mixing with the silica coagulum. In this way most of the KMnO4 may end up in the pore walls and few on the pore wall surface. It is reasonable to speculate that with ~8 wt% KMnO4 addition, most KMnO4 resides in the pore walls and few on the pore wall surfaces as illustrated in Fig. 17. Hereby with ~11 wt% KMnO4 (PSS(I)-13) (see Table 5), the same amount of KMnO4 as in pore walls of PSS(I)-8 may reside in the pore walls of PSS(I)-13 and the rest on the pore wall surfaces. In the case of PSS(II), KMnO4 is introduced via soaking into the pore channels. In this way more of impregnates end up in the pore volume and on wall surfaces than in the first scenario. The higher the percentage of KMnO4 on pore wall surface the further the reduction in pore volume and surface area available in the pore channels may be. This effect was much more evident in route II since the chemisorbents obtained do display higher reduction of total pore volume as well as mesopore volume. Therefore, the most significant change observed in PSS (II) chemisorbents is the decrease in

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ 2$\text{m}^{-2}$</th>
<th>$S_{mic}$ 2$\text{m}^{-2}$</th>
<th>$S_{mes}$ 2$\text{m}^{-2}$</th>
<th>$V_{tot}$ 3$\text{cm}^{-3}$</th>
<th>$V_{mic}$ 3$\text{cm}^{-3}$</th>
<th>$V_{mes}$ 3$\text{cm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSS 60</td>
<td>385</td>
<td>28.6</td>
<td>356</td>
<td>0.610</td>
<td>0.0135</td>
<td>0.603</td>
</tr>
<tr>
<td>PSS(I)-8</td>
<td>320</td>
<td>10.3</td>
<td>310</td>
<td>0.493</td>
<td>0.0032</td>
<td>0.490</td>
</tr>
<tr>
<td>PSS(I)-13</td>
<td>284</td>
<td>9.2</td>
<td>275</td>
<td>0.469</td>
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<td>PSS</td>
<td>372</td>
<td>44.5</td>
<td>329</td>
<td>0.630</td>
<td>0.0210</td>
<td>0.609</td>
</tr>
<tr>
<td>PSS(II)-8</td>
<td>310</td>
<td>13.4</td>
<td>297</td>
<td>0.478</td>
<td>0.0048</td>
<td>0.473</td>
</tr>
<tr>
<td>PSS(II)-13</td>
<td>281</td>
<td>10.7</td>
<td>270</td>
<td>0.465</td>
<td>0.0035</td>
<td>0.462</td>
</tr>
<tr>
<td>PSS-MgCa-50/50-KOH</td>
<td>221</td>
<td>6</td>
<td>215</td>
<td>0.550</td>
<td>0.003</td>
<td>0.547</td>
</tr>
<tr>
<td>PSS-MgCa-68/32-KOH</td>
<td>312</td>
<td>30</td>
<td>282</td>
<td>0.590</td>
<td>0.012</td>
<td>0.578</td>
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<tr>
<td>PSS-MgCa-75/25-KOH</td>
<td>361</td>
<td>23</td>
<td>338</td>
<td>0.580</td>
<td>0.009</td>
<td>0.571</td>
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<tr>
<td>PSS-MgCa-100/0-KOH</td>
<td>320</td>
<td>19</td>
<td>227</td>
<td>0.220</td>
<td>0.010</td>
<td>0.210</td>
</tr>
</tbody>
</table>

$S_{BET}$ - BET specific surface area, $S_{mic}$ – t-plot micropore surface area, $S_{mes}$ – mesopore surface area, $V_{tot}$ – total pore volume, $V_{mic}$ – micropores volume, $V_{mes}$ – mesopores volume, KOH-potassium hydroxide, KMnO4-potassium permanganate.
the mesoporosity compared to route I. The influence of loading amounts of KMnO$_4$ on textural properties of PSS chemisorbents is studied by comparison of chemisorbents prepared via route I. The N$_2$ isotherm and NLDFT pore size distribution for the chemisorbents PSS(I)-8 and PSS(I)-13 are shown in Fig. 4 in paper II. The main difference observed in the isotherms is the nitrogen uptake as the KMnO$_4$ content increases in MgCa-silica substrate. The steep decrease in nitrogen uptake was more pronounced in PSS(I)-13 (11.2 wt %). In the PSD, the increase in impregnate amount of the chemisorbents did not result in any significant difference in terms of pore diameter positions when compared to the starting substrate. Moreover, an increase in KMnO$_4$ content from 8 to 11 wt% (as in PSS(I)-8 &13 respectively) caused more decrease in pore volume between 1 and 15 nm. These similar scenarios were also observed in PSS(II) chemisorbents. The above developments suggest that the pore entrances have neither been blocked nor shifted by KMnO$_4$ amount but rather disperse uniformly on the pore walls surfaces thereby reducing the surface area and pore volume available. The chemisorbents prepared here had a more stable pore diameter than similar chemisorbents prepared by Lu et al. (Lu et al. 2010). Further the chemisorbents with KOH show stability in water and show no sign of KOH dissolution in water, as no pH change was observed. The pellets did not soften, swell or disintegrate when immersed into water at 23°C for 24h.

Fig. 17 Illustration of KMnO$_4$ distribution in the pore walls and on pore wall surfaces
7. Application of the materials prepared

7.1 The thermal conductivity of mesoporous silica, SNP

The thermal conductivity for the SNPs under study as a function of the tapped density, obtained by TPS is shown in Fig. 18 and summarised in Table 1 in paper V. The first important result is that the trends observed by both materials as a function of tapped density are very different (Fig. 18). The thermal conductivity of SNP-OA is low (0.0284 W (m. K)$^{-1}$) at 0.092 g/cm$^3$, and then slightly increases with density. On the contrary, the SNP-SA at 0.064 g/cm$^3$ tapped density, the thermal conductivity is 0.0314 W (m. K)$^{-1}$, then decreases slightly as the powder is compressed. The best thermal conductivity (0.0294 W (m. K)$^{-1}$) is then obtained at 0.146 g/cm$^3$ tapped density at final compressing.

The foregoing phenomena can be explained as follows. The modelling of the effect of particle packing on total thermal conductivity has been shown by many studies (Evans et al. 2008; Yi 2008; Agento et al. 1996) and proven that contact areas and the contact resistances have a significant effect on the conductive properties when the particles volume is reduced by external load. Firstly, the theoretical dependence of the thermal conductivity on the external load is influenced merely by a compaction of the powder. Under external load or pressing of the powder, the porosity will be decrease which influences the grain-to-grain geometric and contact resistance. Secondly, upon gradual compressing of SNP-OA powder, the plate and spherical particles (see Fig. 11) may begin to overlap and the gap between the particles will be lowered. The increased contact areas and reduced gap will make the system behave like a homogenous material. The temperature gradient and hence heat flux is almost uniformly distributed and consequently promotes rapid conduction which reaches the maximum value that represent the dense powder. In the case of SNP-SA, where the particles are spherical aggregates, the compressing of the powder will lower the pores or gaps between the particles and the tendency of overlapping may be reduced or eliminated (see Fig. 12d).

![Graph: Total thermal conductivity of SNP powder samples versus their densities](image)
The conductivity of the powder will therefore be determined by the space between the conducting particles which can be considered as a resistor network that retards gas conduction. The reduction of the gap by compression will therefore result in lowering the total thermal conductivity as seen in SNP-SA thermal conductivity values. The thermal conductivity depending on the tapped density and porous structure was also affected by the acid type.

Obviously, the SNP with lower density and higher $S_{\text{BET}}$ are better thermal insulators.

Although the thermal conductivity is higher for our SNP powders than for aerogels and fumed silica as reported by (Alam et al. 2011; Baetens et al. 2010; Hüsing and Schubert 1998; Quenard et al. 2005), our technique is simple, inexpensive and environmentally friendly, and may be used in large-scale thermal insulating applications at low pressures such as VIP.

7.2 Composite and chemisorbents for dynamic adsorption of H$_2$S, SO$_2$ and Toluene

7.2.1 Carbon-silica composite as sorbent for dynamic adsorption of Toluene

The carbon-silica composites under study were challenged with an air stream (50% RH at 23 °C) containing either ~4870 ppb (in Paper III) or ~80 ppm (in Paper IV). It is worth to note that the adsorbents prepared or obtained were used without degassing to reflect real life scenario. Fig.19a,b shows the 80 ppm upstream concentration and the corresponding downstream concentration of toluene gas with time for PSC composites with 32 wt % carbon, PSC composites with 45 wt % carbon and commercial alumina-carbon composite (Al-C). Fig.19c,d shows the corresponding removal efficiency [%] in relation to adsorbed amount in wt % (grams toluene/grams adsorbents). From Fig.19a,b it can be observed that all the PSC composites prepared exhibit a much lower downstream concentration of toluene when compared to PSS-MgCa-68/32 (see Fig.3 in paper III). Among the composites prepared it was observed that the uptake capacity was in the order of PSC(I)>PSC(III)>PSC(II). Hereby the uptake capacity of toluene was dependent on the synthesis route and also the amount of carbon in the composite. The results further shows that PSC(I)-45F exhibits a better uptake performance than the rest of the composites. From Fig.19c,d when comparing the uptake by composites of 45 wt % and by that of 32 wt % carbon at 0% efficiency, it was obvious that composites with 45 wt % carbon have an uptake capacity based on carbon content to be in the range of ~22 to 28 wt % whereas the latter have ~19 to 26 wt % after 22 hours before reaching 0% efficiency. This is evident from Fig.19a,b in which PSC-32F composites shows a higher downstream concentration between 20 to 70 ppm compared to that of the PSC-45F composites. Interestingly enough, the PSC composites with 32 wt % carbon shows better performance over the commercial composite Al-C which has the same carbon content, 32 wt %. The poor performance of Al-C can be observed from Fig.19a where the downstream concentration of Al-C traces the upstream concentration and efficiency drops just after 8 h. The difference in the dynamic performance of these two composites are therefore not based solely on the carbon content but are also influenced by other factors such as pore parameters which is discussed in the next section. It is important to note that the Al-C is impregnated with 5 wt % KOH and this may also affect the uptake of toluene. From Fig.19c and d if the toluene uptake capacity (wt %, grams of toluene/grams of adsorbents) is compared at the 50% breakthrough (i.e. at 50% efficiency), the uptake capacities are summarized in Table 6 as capacity A. From Fig.3 in Paper III, the maximum uptake by pure MgCa-silica was 0.08 wt % at 0% efficiency. It is therefore obvious that the uptake by the composites were mainly contributed by the carbon composition. In line with this argument, capacity B is calculated based on the carbon content of the adsorbents.
Table 5 Uptake capacity of carbon-silica composites as well as commercial CAC and alumina-carbon composite

<table>
<thead>
<tr>
<th></th>
<th>PSC(I)-32F</th>
<th>PSC(II)-32F</th>
<th>PSC(III)-32F</th>
<th>PSC(I)-45F</th>
<th>PSC(II)-45F</th>
<th>PSC(III)-45F</th>
<th>Al-C</th>
<th>CAC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, wt %</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>32</td>
<td>100</td>
</tr>
<tr>
<td>Toluene capacity A, wt %</td>
<td>4.8</td>
<td>3.0</td>
<td>3.0</td>
<td>7.4</td>
<td>5.9</td>
<td>6.1</td>
<td>0.75</td>
<td>29.1</td>
</tr>
<tr>
<td>Toluene capacity B, wt %</td>
<td>15.1</td>
<td>9.4</td>
<td>9.4</td>
<td>16.4</td>
<td>13.1</td>
<td>13.6</td>
<td>2.3</td>
<td>29.1</td>
</tr>
<tr>
<td>Toluene capacity C, wt %</td>
<td>26.3</td>
<td>20.3</td>
<td>19.4</td>
<td>27.6</td>
<td>22.7</td>
<td>22.0</td>
<td>9.5</td>
<td>31.1</td>
</tr>
<tr>
<td>Time to 50% Breakthrough, hr</td>
<td>4.6</td>
<td>3.0</td>
<td>3.5</td>
<td>7.2</td>
<td>5.4</td>
<td>5.5</td>
<td>1.7</td>
<td>24.7</td>
</tr>
</tbody>
</table>

Capacity A- based on the grams of toluene uptake at 50% efficiency per grams of composite adsorbents; Capacity B- based on the grams of toluene uptake at 50% efficiency per grams of carbon content in the composite adsorbents; Capacity C - based on the grams of toluene uptake at 0% efficiency per grams of carbon content in the composite adsorbents.

The values are shown in Table 5, and presents high uptake capacity (up to 16 wt % for PSC(I)-45F). The uptake capacity at 50% efficiency for CAC consisting of 100% carbon is 29.1 wt %. When comparing the uptake capacity at 0% efficiency (capacity C) even much higher capacities values are obtained for the carbon-silica composites. This indicates that the carbon deposited in the pore system of MgCa-silica was porous and accessible to a great extent. These capacity values of carbon-silica composites (19-28 wt % relative to carbon content) are competitive compared with results obtained for commercial coconut activated carbon (31.1 wt %) and better than the alumina-carbon composite (9.5 wt % relative to carbon content).

Fig.19 Comparative performance of carbon-silica composites with 32 or 45 wt % carbon vs. Commercial alumina-carbon composite (Al-C). I, II and III indicates different routes by which the composites were prepared.
7.2.2 Desulphurisation by MgCa-silica chemisorbents

Although the sorbents prepared have calcium-magnesium silicates which are believed to have basic sites (Ren-Bin et al. 2003; Rodriguez et al. 2000) for chemisorption of acidic gases at higher temperature, at room temperature however, no practical uptake has been reported (Ahmed and Attia 1998). The sorbents obtained has therefore been impregnated with potassium hydroxide to provide basic site for acid-base reaction to occur (i.e. sulphur dioxide) or potassium permanganate as catalyst for oxidation of hydrogen sulphide to occur at room temperature.

7.2.2.1 Chemisorbents with KMnO₄ for H₂S uptake

The uptake performance of chemisorbents with KMnO₄ for H₂S adsorption is shown in Fig.20. The corresponding uptake capacities values at 50% efficiency are calculated and summarized in Table 6. Among all the KMnO₄ containing chemisorbents, PSS(I)-13 shows superior H₂S uptake performance in comparison with the others whereas PSS(I)-8 exhibits the lowest uptake of H₂S among KMnO₄ chemisorbents prepared. This poor performance of PSS(I)-8 is evident from Fig.20a,b where the downstream concentration of PSS(I)-8 traces the upstream concentration and display almost zero adsorption after ~30 h (at 0.2 s contact time). The PSS(I)-8 uptake performance was not different when contact time was increased to 0.4 s as after ~60 h almost zero adsorption was observed. Similar scenario was observed for PSS(II)-8 as increase of contact time did not have any improving effect on its uptake performance. The effect of 0.4 s contact time was however observed in chemisorbents with KMnO₄ content above 11 wt% as a slight increase in H₂S uptake capacity was seen in PSS(I)-13 and PSS(II)-13 (Table 6). The uptake capacity was in the order of PSS(I)-13>PSS(II)-13>PSS(II)-8>PSS(I)-8. It is obvious that the uptake performance of H₂S is dependent on a combined effect of chemisorbent preparation route and the amount of KMnO₄ in the chemisorbent. Hereby the main factor is the amount of KMnO₄ available for chemical reaction and not just the content of KMnO₄.

The influence of KMnO₄ content on the H₂S removal performance is listed in Table 6 and displayed in Fig.6 in paper II. The increase in KMnO₄ from 8.4 wt% in PSS(I)-8 to 11.2 wt% in PSS(I)-13 resulted in a superior uptake performance in the latter. The increment in chemisorbents prepared by route II (PSS(II)) however, did not show any improved effect when run at 0.2 s but rather at 0.4 s contact time. Because of some reason not identified, the performance of the PSS(II)-8 is similar to that of PSS(II)-13 at 0.2 s contact time. The comparison of uptake capacity of PSS(I)-13 of 11.2 wt% KMnO₄ to that of PSS(II)-13 of 13.6 wt% KMnO₄ indicate that the former has better performance than the latter. Hereby KMnO₄ content above 11 wt% is detrimental to the H₂S removal performance. Similar results have been reported by Muller et al. (Muller et al. 2006) and (Nguyen et al. 2005) who have compared different oxidants for removing H₂S on inorganic porous materials. In both works, the results suggest that extreme oxidants resulted in destruction of micropores and consequent blockage of pores by large clusters formed. In PSS(II)-13 chemisorbent, the excessive KMnO₄ reduced the total pore channels volume (Fig.4B in paper II) and surface area available for H₂S reaction.

The effect of the chemisorbents preparation routes on H₂S uptake performance is clearly seen when compared PSS(I)-8 and PSS(II)-8. Several possible reaction routes with different mechanisms are reported for KMnO₄ and H₂S removal. One mechanism suggested (Lindahl 2010) for KMnO₄ impregnated alumina is:

\[ 3\text{H}_2\text{S} + 8\text{KMnO}_4 + 4\text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 3\text{K}_2\text{SO}_4 + 2\text{KOH} + 6\text{H}_2\text{O} \quad (6) \]
Theoretically the uptake capacity of PSS(I)-8 (8.4 wt% KMnO₄) calculated from the stoichiometric reaction (eq.6) is 4.83 wt%. If the removal of H₂S follows the stoichiometric reaction and directly related to the KMnO₄ amount, then we could expect PSS(I)-8 to exhibit similar or higher uptake capacity than PSS(II)-8 (7.6 wt% KMnO₄). Instead the former has the lowest uptake capacity (see Fig.6 in paper). This suggests that even though high levels of KMnO₄ may be present in the chemisorbent, it may not be available for reaction due to restrictions imposed by the preparation route. This supports the previous claim that most of the 8 wt% KMnO₄ impregnated in PSS(I)-8 ended up in pore walls with few on the internal pore surfaces available for reaction. In line with this the content of KMnO₄ consumed or accessible for reaction has then been calculated based on the amount of H₂S removed and summarized in Table 6. It is obvious from Table 6 that PSS chemisorbents with high accessible content of KMnO₄ exhibit superior uptake capacity.

Fig.20 Uptake performance of PSS-MgCa-68/32 impregnated with KMnO₄ and NaHCO₃ for hydrogen sulphide
Table 6 H₂S uptake performance of PSS-MgCa-68/32 impregnated with different routes and KMnO₄ wt %

<table>
<thead>
<tr>
<th>KMnO₄ content, wt%</th>
<th>PSS(I)-8</th>
<th>PSS(I)-13</th>
<th>PSS(II)-8</th>
<th>PSS(II)-13</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO₄ consumed A, wt %</td>
<td>8.4</td>
<td>11.2</td>
<td>7.6</td>
<td>13.6</td>
</tr>
<tr>
<td>KMnO₄ consumed B, wt %</td>
<td>0.18</td>
<td>5.32</td>
<td>3.05</td>
<td>3.02</td>
</tr>
<tr>
<td>H₂S uptake Capacity A, wt%</td>
<td>0.10</td>
<td>3.06</td>
<td>1.75</td>
<td>1.74</td>
</tr>
<tr>
<td>H₂S uptake Capacity B, wt%</td>
<td>0.10</td>
<td>3.21</td>
<td>1.49</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Capacity and consumed A is the uptake capacity of chemisorbents run at 0.2s contact time. Capacity and consumed B is the uptake capacity of chemisorbents run at 0.4s contact time.

7.2.2.2 Chemisorbents with KOH for SO₂ uptake

Although KMnO₄ chemisorbents performed better, the use of KMnO₄ as impregnate chemical poses however health hazards for both humans and the environment when it comes to reuse or recycling of the worn out doped materials. Potassium hydroxide (KOH) which is an alternative environmentally friendly impregnate chemical has been used as an alternative impregnate. However when MgCa-silica impregnated with 8 wt % KOH is challenged with H₂S the material did not exhibit any uptake performance while SO₂ uptake was observed for KOH chemisorbents Fig.21. The non-removal of H₂S by chemisorbents with KOH is interesting, considering the fact that KOH is known to have excellent selective adsorption toward acidic gases (Lee et al. 2002). Depending on the type of adsorbent and the surface chemistry, adsorbed H₂S is believed to go through a number of transformations (Bandosz 2002):

\[
H₂S_{gas} \rightarrow H₂S_{ads} \quad (7)
\]

\[
H₂S_{ads} \rightarrow H₂S_{ads-liquid} \quad (8)
\]

\[
H₂S_{ads-liquid} \rightarrow HS⁻_{ads} + H^+ \quad (9)
\]

\[
HS⁻_{ads} + O^+_{ads} \rightarrow S_{ads} + OH^- \quad (10)
\]

\[
HS⁻_{ads} + 3O^+_{ads} \rightarrow SO₂_{ads} + OH^- \quad (11)
\]

On the other hand, when basic hydroxide is present it catalyses oxidation (eq. 10 and 11) of H₂S to elemental sulphur or sulphur dioxide until all the base is worn out (Bandosz 2002). In the case of the KOH-chemisorbents, it is reasonable to speculate that when H₂S is adsorbed; it does not able to oxidize to SO₂ which is easily chemisorbed by the KOH-chemisorbents. This may be due to less oxygen groups on the pore surface needed to facility oxidation. The O⁺ₐₙ₃ (dissociatively adsorbed oxygen) likely from air is not enough for catalytic oxidation. Surface chemistry has to be studied to ascertain the pore surface sites of KOH-chemisorbents.

The comparative uptake performance of MgCa-silica with Ca mol% > 50 and 100 mol% Mg and impregnated with 8 wt % KOH (PSS-KOH) has been shown in Fig.21a,b. The PSS-MgCa-0/100 sorbent has not been impregnated because of its poor pore parameters when compared to the rest of the samples. Uptake performance compared at 50% efficiency indicate uptake capacity in the order of PSS-MgCa-68/32-KOH > PSS-MgCa-75/25-KOH > PSS- PSS-MgCa-50/50-KOH > PSS-MgCa-100/0-KOH. The MgCa-68/32-KOH has a highest uptake capacity value of about 3 wt% whereas PSS-MgCa-100/0-KOH with lowest uptake capacity is about 1.2 wt%. Just for
uptake comparison, the commercial media has about 0.5 wt% uptake (see Fig. 21b). Thus the capacity values of MgCa-silica-KOH obtained are significantly better than a commercial chemisorbent CP-8 at 50% efficiency.

All the impregnated PSS-MgCa-sorbents have the same amount of potassium hydroxide content in their pore system and the following reaction is expected to be dominant in the interior pores of MgCa-Silica sorbents when SO$_2$ is adsorbed.

$$\text{SO}_2 + \text{KOH} \leftrightarrow \text{KHSO}_3 \quad (12)$$

$$\text{KHSO}_3 + \text{KOH} \leftrightarrow \text{K}_2\text{SO}_3 + \text{H}_2\text{O} \quad (13)$$

It would be reasonable to expect a similar SO$_2$ uptake if the above stoichiometric reaction is followed. The difference in the uptake capacities of MgCa-silica-KOH must then be the results of the differences in the pore parameters. This is further examined in the next section.

![Fig. 21 Comparative performance of MgCa-silica sorbents impregnate with 8 wt% KOH](image)

### 7.2.3 Effect of Pore Structure Parameters on Dynamic Adsorption Performance

As shown in the previous section, the uptake capacities of the composites or chemisorbents containing KMnO$_4$ or KOH were not merely based on the amount of carbon or the impregnate chemicals in them but also the pore structure plays a vital role. The carbon-silica composites micropore volumes and total pore volumes have been related to toluene uptake capacities and depicted in Fig. 22a,b. Including in the Figure are also the commercial coconut activated carbon (CAC) and alumina-carbon composite (Al-C). As shown in Fig. 22b sorbent with a large total pore volume do not necessarily have a large uptake capacity. On the other hand the presence of micropores shows a direct correlation to an increase in toluene uptake capacity as indicated in (Fig. 22a). Micropores are mostly responsible for the adsorption of low concentrations of gas molecules owing to the overlap of attractive forces from opposing pore walls (Sing et al. 1985). This can be established by comparing the micropore volume of CAC and that of the composites sorbents and their respective uptake capacities (Fig. 22a). It is obvious that the micropores volume of CAC was larger than those of the carbon-inorganic composites and so were their uptake capacities. Hereafter, it is reasonable to speculate that the large toluene uptake by the composites was directly adsorbed into the microporosity introduced into the inorganic adsorbent pore system by CAC addition. Another reason for the composites high uptake capacity...
is the increased in their mesopore area as well as total surface area. Further the pore size and pore size distribution also play vital role in the toluene uptake by the composites materials .This can further be observed when comparing composites with the same carbon content but prepared via different routes. This is evident in PSC(II)-45F sample, whose mesopore size is slightly smaller (2.4 nm) than that of PSC(I)-45F, (5.4 nm) and at the same time has less micropore volume, mesopore area as well as BET surface area, exhibits low toluene uptake capacity. Not merely large mesopore diameter that is important but rather the combined contribution from the micropore volume, mesopore area as well as BET surface area. This combined contribution can be seen in PSC (I)-45F which shows large uptake capacity over PSC(III)-45F and Al-C, even though all the three samples have similar mesopore diameter. Hereby the large uptake of PSC(I)-45F is derived from a synergetic effect between the micropores and the broad mesopore size distribution. This bimodal pore system is vital for effective toluene removal as micropores are essential for the trapping of the toluene molecule of diameter 0.85nm (Hernandez et al. 2005) and at the same time have mesopore diameters large enough to allow for bulk diffusion. The large mesopore area of PSC(I)-45F further functions as an effective channel system to allow bulk diffusion to occur. This area also allows for multiple toluene molecules collisions to occur. In interior pore system, a statistically significant number of sufficiently energetic molecular collisions between the carbon and toluene occur before final entrapment in micropores. Moreover, microporous carbon embedded in the mesopores of PSS-MgCa-68/32 also adsorbs some of the toluene during the collisions process. Hence, PSC(I) composites with wide PSD (1-30 nm) gave a larger dynamic adsorption capacity than that of PSC(II) composites with narrow PSD (1-4 nm) due to the greater time toluene spent inside the broad mesopore pore size region before their final entrapment in micropores. These scenarios, mentioned above, were similar in other composites obtained in the same route I, II and III but with different carbon content.

The uptake performance of KOH or KMnO₄ containing chemisorbents did not show any correlation between the specific surface area, total pore volume as well as micropore volume. On the other hand, the SO₂ uptake capacities correlate well with the maximum mesopore size and their respective mesopore volume as demonstrated in Fig 10 in paper I. Although pore diameter itself does not show any strong relation, the combinations of mesopore diameter and high proportion of volume in that pore size region are important factors for SO₂ uptake. This is clearly seen when compared PSS-MgCa-75/25-KOH and PSS-MgCa-100/0-KOH to PSS-MgCa-68/32-KOH. The former has low uptake capacities due to their slightly smaller mesopore diameter (~3.5 and 3.7 nm respectively) and less mesopore volume in comparison to the latter which has large pore diameter (~5.4 nm) and high mesopore volume. The mesopore diameter and volume in relation to uptake capacity is in the order of MgCa-68/32> MgCa-75/25> MgCa-50/50> MgCa-100/0. The influence of large mesopore volume on SO₂ uptake capacity is further evidence in PSS-MgCa-75/25-KOH which has higher uptake capacity over PSS-MgCa-50/50-KOH even though the latter has larger mesopore pore diameter. Herewith the larger mesopore volume is a major contributing factor for the enhanced PSS-MgCa-75/25-KOH uptake performance. As indicated in Fig.10 in paper I, the larger SO₂ uptake by PSS-MgCa-68/32-KOH is as a result of cooperative effect of broad pore distribution and abundance of pores in the mesopore region. As mention early in the case of toluene uptake, the bimodal pore structure permits bulk diffusion in the large mesopore diameter and at the same time have micropore diameter for the trapping of the SO₂ molecules that will escaped the multiple SO₂ molecules collisions with the internal pore walls. The internal pore walls are tinted with [OH]- and due to the greater time SO₂ spent inside the broad mesopore pore size region, a sufficiently energetic molecular collisions between [OH]- and SO₂ occurs and results in achieving chemical reactivity and hereby attained large uptake of SO₂ by PSS-MgCa-68/32-KOH.
Fig. 22 Relationship between (A) the micropore volume and dynamic toluene capacity and (B) the total pore volume and dynamic toluene capacity for all samples including the commercial adsorbents. The filled square represent PSC(I) composites (■), filled triangle represent PSC(II) composites (▲), circles represent PSC(III) samples (O), triangle represent CAC2 (Δ) filled circles represent (●), filled diamond represent Al-C(●)

Similar scenario can be said of KMnO₄ containing chemisorbents as they were made from same substrate, PSS-MgCa-68/32 and have similar pore structure after impregnation. The large proportion of mesopore volume is not only vital for bulk diffusion but also for storage of reaction products. The reaction products K₂SO₃ or K₂SO₄ may gradually fill the pores beginning from the smaller pores and spread across the large pores. In this case having large proportion of pores in smaller pore diameter region as in PSS-MgCa-75/25-KOH will lead to reduced gas diffusion rate as more K₂SO₃ builds up. This is evident in PSS-MgCa-75/25-KOH whose efficiency was of the same magnitude as the PSS-MgCa-68/32-KOH materials up until 80% efficiency. Below this efficiency the build-up K₂SO₃ crystals begin to inhibit diffusion and as such reduced the SO₂ uptake as more crystals forms on the interior pore walls of PSS-MgCa-75/25-KOH. In the case of the KMnO₄ containing chemisorbents, they all have similar pore size distribution but differ in micro- and mesopore volume depending on the impregnate amount and the route of preparation. It follows logically that KMnO₃-chemisorbents with large amount of KMnO₄ on pore wall surface will have limited space for storage of oxidation products, [SO₄]²⁻ and Mn²⁺. Hereby the PSS(II)-13 with 13.6 wt% KMnO₄ will have less storage space and their pores will blocked early and subsequently loss it ability to absorbed further H₂S than PSS(I)-13 with 11.4 wt% KMnO₄. As such the latter has superior performance.
6. Conclusions

Two different nanoporous silica materials have been synthesised using sodium silicate and studied for molecular filtration and thermal insulation application. In the first synthesis, MgCa-silica sorbents had been prepared, where Mg and Ca ion were varied, and the effects of these parameters on the adsorptive parameters were investigated. MgCa-silica chemisorbents using either potassium hydroxide or potassium permanganate as impregnate chemicals were further developed and tested for SO$_2$ and H$_2$S adsorption. Within the thesis, synthesis routes for MgCa-silica-carbon composites were developed and the obtained composites were proved for VOC adsorption. For thermal insulation application, low density mesoporous silica has been developed using sodium silicate and glycerol as pore forming agent. The effects of synthesis parameters such as acid type on pore parameter, particle morphology, tapped density as well as thermal conductivity were investigated. The main conclusions drawn from the investigations can be summarised as follows:

- The variation of Mg/Ca molar ratios affects both the particle morphology and porous parameters. The results further reveal traces of crystalline compounds in nanoporous silica made with $> 50$ mol % Ca, i.e. PSS-MgCa-50/50 and PSS-MgCa-0/100. These nanoporous silica exhibited low specific surface area ($S_{BET}$) and total pore volume ($V_{tot}$). For sorbents with 100 mol% Mg (PSS-MgCa-100/0) a relatively higher $S_{BET}$ and $V_{tot}$ was found. Further, sorbents made with 68 mol% Mg and 32 mol% Ca (PSS-MgCa-68/32) and 75 mol% Mg and 25 mol% Ca (PSS-MgCa-75/25) exhibited even higher specific surface area and total pore volume. Sorbents consisting of Mg/Ca-silica exhibited bimodal porosity. With high amount of micropore area and volume observed in sorbents made with $\geq 75$ mol% Mg whereas PSS-MgCa-68/32 shows relatively high mesopore area and volume. The PSD of PSS-MgCa-68/32 exhibits wide pore distribution ranging from 1 to 32 nm whereas sorbent made with 75 mol% Mg and 25 mol% Ca together with 50 mol% Mg and 50 mol% Ca shows narrow pore size range of 1 to 5 nm.

- The PSS-MgCa-68/32 chemisorbents containing potassium hydroxide or potassium permanganate exhibited a decrease in both specific surface area and pore volume but pore distributed between 1 to 32 nm (as in parent PSS-MgCa-68/32) were stable. However, for other MgCa-silica chemisorbents containing potassium hydroxide, the impregnation tend to increase the pore and shift the maximum pore peak to larger pore diameter. Thus for PSS-MgCa-100/0, PSS-MgCa-75/25 and PSS-MgCa-50/50, which exhibited narrow pore distribution, tend to get a broader pore distribution.

- Carbon-silica composites with up to 45 wt % CAC were prepared by following three different routes. An increased in specific surface areas of all the composites were observed in comparison to the parent PSS-MgCa-68/32. The increases in specific surface areas were related to the amount of CAC and the route of synthesis. Composites obtained via route I exhibited highest surface areas and pore volume. The pore structure of the obtained composites is bimodal consisting of a high microporosity due to the CAC and a mesoporosity from the parent PSS-MgCa-68/32. The composites in route I and III exhibit a wide pore size distribution (1-30 nm) whereas in route II shows narrow pore size range (1-4 nm).

- For molecular filtration, chemisorbents and composites obtained were successfully employed for dynamic adsorption of SO$_2$, H$_2$S and toluene. The SO$_2$ adsorption behavior evaluated for chemisorbents containing potassium hydroxide indicates that the highest SO$_2$ uptake corresponds to PSS-MgCa-68/32-KOH and was determined by the combined synergetic effect of large mesopore diameter and extensive mesopore volume. The SO$_2$ capacity (3 wt %) obtained was about 6 times higher than uptake capacity of commercial
media compared. For chemisorbents containing potassium permanganate, the highest \( \text{H}_2\text{S} \) uptake capacity corresponds to chemisorbent with 11.4 wt% \( \text{KMnO}_4 \) and prepared by direct impregnation. The combined effect of the impregnation route, amount of \( \text{KMnO}_4 \) and its location in the pore system were the determining factors in achieving large \( \text{H}_2\text{S} \) uptake. The highest toluene uptake capacity (27.6 wt % at 0% efficiency) was obtained for carbon-silica composite obtained with the carbon content of 45 wt % and obtained via route I. The combined effect of both the pore distribution and the amount of micropores in the composites were the crucial factors that govern the large uptake capacity. The composites obtained while having a high ignition temperature had uptake capacity values that were competitive to commercial activated carbon (31.1 wt % at 0% efficiency) and better than results obtained for commercial alumina-carbon composite (9.5 wt % at 0% efficiency).

- With respect to the nanoporous silica for thermal insulation application, mesoporous silicas, SNP, with low density were successfully prepared using sodium silicate and glycerol as template. The use of glycerol as template resulted in formation of porous silica of homogenous pore structure and high specific surface area. The material obtained had a large total pore volume in the range of 1.4-1.8 cm\(^3\)/g and porosity in the range of 95-97%. The influences of the synthesis parameter such as type of acid on the textural and thermal conductivity properties were observed. The type of acid used in the synthesis determines the particle morphology, porous structure as well as the tapped density.

- Thermal conductivity measurements indicate that the trends observed by both materials as a function of actual density were very different. Whereas the lowest thermal conductivity 0.0284 (W/(m·K)) can be obtained at a density of 0.092 g/cm\(^3\) for SNP obtained by oxalic acid, for SNP obtained by sulphuric acid on the other hand, a low thermal conductivity 0.0294 (W/(m·K)) was obtained at a density of 0.146 g/cm\(^3\). Thus under compression, the specific density at which the smallest thermal conductivity can be obtained is particle morphology dependent. At higher compression, spherical particles will be more efficient in the reduction of the total thermal conductivity by forming small pore network and reducing gas conduction. Particle morphology should therefore be put into consideration in designing low density mesoporous silica for thermal insulation applications.
7. Future Research

There are several possibilities for future research and development work continuing what is presented in this thesis. Possible directions for future work concerning the preparation of MgCa-silica structure can be summarised as: (i) preparation of other metals-silica structure (e.g. transition metals); (ii) to further extend the synthesis of MgCa-silica to ordered MgCa-silica structure by employing various environmentally friendly organic compounds to be used as templates. Due to their active metal sites and ordered porosity, these sorbents could have a potential application in the area of catalysis.

The characteristics required in a sorbent are capacity, selectivity, regenerability, kinetics, and cost. Remarkable advances in capacity and selectivity have been achieved and it could be interesting to extend the work to other sorbent characteristics.

As shown, KOH modified MgCa-silica sorbent leads to adsorption of SO₂ but not H₂S. It would be interesting to study the surface features of the KOH modified MgCa-silica sorbents which may give information about their adsorption mechanism. In addition, alternative modified agents for H₂S removal certainly merits further investigation.

The carbon-silica composite prepared should be characterized in more detail, e.g. using X-ray photoelectron spectroscopy (XPS), Fourier transform Infrared (FTIR), etc., in order to understand their surface features and to evaluate their merits. Adsorption of H₂S and of other VOC's besides toluene by the carbon-silica composites is needed to study in order to evaluate the performance in comparison to other composite materials and other adsorbent materials on market. On the basis of the obtained dynamic adsorption results some further modification could be required in terms of further tailoring their composition, impregnates, etc.

MgCa-silica sorbent is a new type of adsorbent, and certainly their application beyond gas filtration needs investigation. Tailored MgCa-silica should be investigated for water filtration applications. In addition, the possibilities to employ the worn-out impregnate materials in other applications should be explored.

The synthesis route of SNP mesoporous material resulted in a material with promising thermal conductivity properties and will merit a further work to control the particle morphology and the pore size. The effect of other acid should be considered. The SNP obtained is hydrophilic and it could be interesting to hydrophobically modify the surface. The effect of hydrophobicity on pore structure, density and thermal conductivity should therefore be studied. Further detail studies of SNP pore structure using transmission electron microscopy (TEM) and Small angel X-ray scattering (SAXS) should be considered in order to understand their pore diameter effect on thermal conductivity. Addition of opacifies such as silicon carbide to pure silica has shown to reduce the thermal conductivity by 0.002-0.003 W/(m·K) (Alam et al. 2011) and it will be interesting to study the thermal conductivity of SNP with silicon carbide.

Further studies to modify SNP pore structure to function as both insulator and filter media in built environment will be remarkable. Mixture of such material with cement and sand may be employed as rendering or plaster material that may function as both insulator and molecular filter.
8. References


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