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**MASTER DEGREE THESIS**

**Two Novel Techniques of Drying Silica Aerogel at  
Ambient Pressure**

(两种常压干燥二氧化硅气凝胶的新技术)

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## ABSTRACT

The exceptional properties of silica aerogel make it one of the intensely investigated porous materials obviously because of its multiple and diverse applications. However, its commercial-scale production is often limited by a drying technique that critically embodies considerations such as cost, safety, time for production and effects on the environment. In an attempt to address these challenges two methods were developed in this work.

The first part of the work demonstrates the use of a switchable hydrophilicity solvent (SHS) for pore water solubilization of a sodium silicate (water glass)-produced hydrogel from a pressurized carbonation sol gel (PCSG) process, and the subsequent pore water extraction preceding silica aerogel production. Carbon dioxide (CO<sub>2</sub>) at atmospheric pressure (0.1 MPa) was significant in this process. A quick CO<sub>2</sub> reaction time (1 min) was discovered to be ideal for the maximum solubilization (72.8 %) of pore water as tests on the recovered filtrate showed. Filtered silica wet-gel were dried under ambient pressure whiles, the one-phase filtrate was also recycled for re-use. The N<sub>2</sub> adsorption-desorption analysis showed that, the produced aerogels exhibited a high Brunauer–Emmett–Teller (BET) surface area of 414.1-507.8 m<sup>2</sup>/g and Barrett–Joyner–Halenda (BJH) pore volume of 2.3 - 2.6 cm<sup>3</sup>/g. The pore volume as well as a narrow mean particle size distribution ( $D_{50} = 6.2\text{-}7.2 \mu\text{m}$ ) significantly affected the application as flattening agent (FA) culminating in the obtention of an extinction index ( $E_i$ ) of 61.7 and 52.8 % for hydrophobic and hydrophilic applications respectively. Again, a respective hydrophilic and hydrophobic film transmittance index ( $FT_i$ ) of 78.3 and 86.1 % were attained. These FA performance indices were relatively better than that of commercial silica which was simultaneously investigated. Furthermore, the recycled SHS with 6.2 % water content was exclusively used to re-synthesize aerogel. Besides the simplicity and quickness associated with process, the dual utilization of CO<sub>2</sub> both for the production of the hydrogel, and the aerogel clearly makes the process environmentally benign with good prospects for large-scale

industrial production.

In the second component of this work, we analyzed the ability of some selected thermal decomposable salts (TDS) for the production of silica aerogels by employing the same PCSG-produced hydrogels. Amongst trials of several TDS, one of them showed better prospects of producing silica aerogels. The high solubility of the chosen TDS in water as well as its precipitation effects in the presence of protic solvents was significant. Its resultant effect of salt crystallization confined to the pores formed large pores when decomposed. Relative technical parameters of varied hydrogel concentration (0.25-1.0 mol/L), TDS solution concentration (9.1-33.3 w/w%), stirring time (15-120 min) and protic solvents were thoroughly investigated. The identified optimal conditions were 0.5 mol/L, 28.6 w/w% and 30 min for hydrogel concentration, salt solution concentration and stirring time respectively while using isopropanol. Even though, surface modification agents were not employed, yet physicochemical attributes of high BET surface area (667.7 m<sup>2</sup>/g), high BJH pore volume (3.2 cm<sup>3</sup>/g) and narrow particle size distribution ( $D_{50}$ =6.5-7.0 μm) were attained after this salt-mediated drying. The produced aerogels were further characterized by X-ray powder diffraction, Fourier Transform Infrared spectroscopy and thermogravimetric analysis. Moreover, SEM and TEM studies confirmed the mesoporosity of the aerogels. It was revealed via the application of the produced aerogels as the FA that, the aerogels depicted improved performance indices over commercial samples. Accordingly, an  $E_i$  of 58.7 and 65.2 % were accomplished for the hydrophilic and hydrophobic applications respectively. Besides, the hydrophilic and hydrophobic  $FT_i$  of 86.5 and 96.2 % were as well attained for the synthesized products. These were as a result of the contributory effects of the pore volume and  $D_{50}$ .

**Keywords:** Silica, switchable hydrophilicity solvent, sodium silicate, carbon dioxide, pore water solubilization, thermal decomposable salts, ambient pressure drying, flattening agent, extinction index, film transmittance index

## 摘要

二氧化硅气凝胶因其优异的性能广泛应用于各个行业，成为多孔材料研究的热点之一。然而，工业化生产时往往受限于干燥技术，主要的影响因素包括成本、生产效率、安全性和对环境的影响程度等。本工作开发两种方法来解决这些问题。

第一种方法采用一种可变换亲水溶剂(SHS)溶解于二氧化硅水凝胶的间隙中，之后将间隙中的水萃取出来，其中二氧化硅水凝胶采用加压碳化溶胶-凝胶过程制得。引入常压  $\text{CO}_2$  与该 SHS 反应，发现快速反应（反应时间 1 分钟）就能使滤液内水的最大溶解度达到 72.8 %。滤液是单相溶液，并可以循环使用。滤渣是二氧化硅湿凝胶，可用常压干燥得到二氧化硅气凝胶。用氮气吸附-脱附仪测试可知，该气凝胶产品具有较大的比表面积（414.1-507.8  $\text{m}^2/\text{g}$ ）和孔容（2.3-2.6  $\text{cm}^3/\text{g}$ ）及很窄的粒径分布（ $D_{50}=6.2-7.2 \mu\text{m}$ ）。这些指标表明该产品很适合用于涂料消光剂。检测表明用于油性涂料中消光率达到 61.7 %，透光率达到 78.3 %；水性涂料中消光率达到 52.8 %，透光率达到 86.1 %。该消光剂的性能指标均比同等条件下检测的市售二氧化硅效果好。另外，回收的含有 6.2 % 水的该 SHS 可用于再次制备气凝胶二氧化硅。整个过程简单、快速，结合资源化利用  $\text{CO}_2$  生产水凝胶二氧化硅工艺，有望实现二氧化硅气凝胶的工业化生产。

第二种方法考虑采用可实现热分解的盐进行二氧化硅气凝胶的干燥，同样使用加压碳化法生产的二氧化硅水凝胶。实验尝试了几种盐，发现一种盐适合于制备干燥获取二氧化硅气凝胶。该盐在水中具有很高的溶解性，同时由于其可以通过质子溶剂沉淀出来，从而实现良好的干燥过程。在干燥中，孔道内结晶的盐加热分解，使二氧化硅保持孔道结构。考察的参数包括水凝胶浓度(0.25-1.0 mol/L)、盐溶液浓度(9.1-33.3 w/w%)、搅拌时间(15-120 分钟)及不同的质子溶剂。研究获得最合理的条件为：水凝胶浓度 0.5 mol/L、盐浓度 28.6 w/w%、30 分钟搅拌和采用异丙醇做溶剂。虽然过程没有加入表面改性剂，但干燥后二氧化硅气凝胶的比表面积达到 667.7  $\text{m}^2/\text{g}$ ，孔容达到 3.2  $\text{cm}^3/\text{g}$  及很窄的粒径分布（ $D_{50}=6.5-7.0\mu\text{m}$ ）。通过氮气吸附-脱附分析，XRD 衍射，傅里叶光谱分析及热重分析对产品进行表征，用 SEM 和 TEM 确认其孔结构。产品通用用于涂料消光剂，其在水性涂料中消光率为 58.7 %，透光率为 86.5 %；在油性涂料中消



光率为 65.2 %，透光率为 96.2 %，结果均优于市售的二氧化硅消光剂。这些优秀的性能主要得益于二氧化硅产品的孔容和粒径分布。

关键字：二氧化硅，可变换亲水溶剂, 硅酸钠，二氧化碳，增溶剂，热分解盐，常压干燥

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## ABBREVIATIONS AND SYMBOLS

APD	ambient pressure drying
SCD	supercritical drying
TMOS	tetramethoxysilane
TEOS	tetraethoxysilane
HMDS	hexamethyldisilazane
TMCS	trimethylchlorosilane
SHS	switchable hydrophilicity solvent
$\text{Na}_2\text{SiO}_3$	sodium silicate
EtOH	ethanol
MeOH	methanol
TDS	thermal decomposable salts
ODT	onset decomposition temperature
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
SEM	scanning emission microscopy
PSD	pore size distributions
TEM	transmission emission microscopy
XRD	X-ray powder diffraction
TGA	thermogravimetric analysis
FTIR	Fourier transform infrared
$E_i$	extinction index
$FT_i$	film transmittance index
FA	flatting agent
$T_c$	critical temperature
$P_c$	critical pressure
$P_{\text{cap}}$	capillary pressure
$D_{50}$	mean particle size distribution
nm	nanometer
$\mu\text{m}$	micrometer
h	hour
min	minute(s)

**TABLE OF CONTENTS**

<b>ACKNOWLEDGEMENTS</b> .....	<b>i</b>
<b>ABSTRACT</b> .....	<b>ii</b>
摘要 .....	<b>iv</b>
<b>ABBREVIATIONS AND SYMBOLS</b> .....	<b>vi</b>
<b>TABLE OF CONTENTS</b> .....	<b>vii</b>
<b>LIST OF FIGURES</b> .....	<b>x</b>
<b>LIST OF TABLES</b> .....	<b>xii</b>
<b>CHAPTER 1: INTRODUCTION</b> .....	<b>1</b>
1.1 General Background .....	1
1.2 Literature review .....	3
1.2.1 Porous materials.....	3
1.2.2 General preparation route of silica aerogel.....	10
1.2.3 Relevant reaction parameters.....	19
1.2.4 CO <sub>2</sub> responsive materials.....	21
1.2.5 Salts usage in silica synthesis .....	23
1.2.6 Flatting agent and its associated performance indices.....	25
1.3 Problem Statement, Motivation, Significance of Study, and Research Objectives .....	26
1.3.1 Problem statements and significance of study .....	26
1.3.2 Motivation.....	27
1.4 Research Objectives.....	28
1.4.1 Main objectives .....	28
1.4.2 Specific objectives .....	28
<b>CHAPTER 2: CO<sub>2</sub>-MEDIATED SWITCHABLE HYDROPHILICITY SOLVENT FOR PORE WATER EXTRACTION</b> .....	<b>29</b>
2.1 Introduction.....	29
2.2 Experimental .....	30
2.2.1 Materials and Chemicals.....	30
2.2.2 Synthesis of silica hydrogels.....	31
2.2.3 Extraction of pore water and drying .....	31
2.2.4 Process of recovery of the hydrophobic solvent.....	32
2.2.5 Characterization .....	33

## Table of Contents

2.2.6 Flating test.....	33
2.3 Results and Discussion .....	34
2.3.1 Influence of CO <sub>2</sub> reaction time on pore water solubilization.....	34
2.3.2 Effect of extracted water on textural properties.....	35
2.3.3 Morphology and microstructure of the as-produced aerogels .....	37
2.3.4 Nitrogen physisorption isotherms and pore size distributions.....	39
2.3.5 X-ray spectroscopy analysis .....	41
2.3.6 Infrared spectra of synthesized aerogels .....	41
2.3.7 Particle size distribution.....	42
2.3.8 Flating test.....	43
2.3.9 Recycling of the SHS and its re-use .....	45
2.4 Conclusion .....	45
<b>CHAPTER 3: SALT-MEDIATED DRYING TECHNIQUE IN PRODUCING SILICA AEROGEL.....</b>	<b>48</b>
3.1 Introduction.....	48
3.2 Experimental.....	49
3.2.1 Materials and Chemicals.....	49
3.2.2 Synthesis of silica hydrogel .....	50
3.2.3 Silica aerogel preparation .....	50
3.2.4 Characterization .....	51
3.2.5 Flating test process.....	52
3.3 Results and Discussion .....	52
3.3.1 Selection of appropriate salt.....	52
3.3.2 Aerogels produced with the salt and the influence of some reaction parameters .....	53
3.3.3 Morphological characteristics .....	58
3.3.4 N <sub>2</sub> physisorption studies on the produced aerogels .....	59
3.3.5 Particle size distribution.....	61
3.3.6 X-ray spectroscopy analysis .....	63
3.3.7 Infrared spectroscopy analysis on the as-synthesized aerogel.....	64
3.3.8 Thermal analysis on the silica aerogel.....	65
3.3.9 Re-use of salt solution and solvent recovery through an extended approach .....	66
3.3.10 Flating test analysis.....	68
3.4 Conclusion .....	69
<b>CHAPTER 4: GENERAL CONCLUSIONS AND RECOMMENDATIONS.....</b>	<b>71</b>
4.1 General Conclusions .....	71
4.1.2 Switchable hydrophilicity solvent produced aerogels .....	72
4.1.3 The salt-produced aerogels.....	72
4.2 Recommendations.....	72

**REFERENCES.....74**

厦门大学博硕士学位论文摘要库

## LIST OF FIGURES

Figure 1.1 Applications of aerogels .....	1
Figure 1.2 Schematic cross-section of a porous solid .....	4
Figure 1.3 Different classifications of aerogels.....	7
Figure 1.4 Sol-gel reaction for an alkoxy silane.....	9
Figure 1.5 General preparation route to prepare aerogel.....	11
Figure 1.6 (A) Schematic structure and (B) TEM of a solid and a liquid phase of a silica gel.....	12
Figure 1.7 Typical schematic apparatus of PCSG process .....	13
Figure 1.8 Schematic illustration of an autoclave for supercritical drying with ethanol.....	15
Figure 1.9 A possible cold CO <sub>2</sub> supercritical drying path in the Pressure ( <i>P</i> ) Temperature ( <i>T</i> ) phase diagram of CO <sub>2</sub> .....	16
Figure 1.10 Silylating of silica gel .....	17
Figure 1.11 Spring-back effect phenomena.....	18
Figure 1.12 Structure of CO <sub>2</sub> -switchable functional groups: A) tertiary amine B) amidine C) guanidine D) imidazole E) carboxylic acid.....	22
Figure 1.13 The phase behaviour of a mixture of water and SHS .....	23
Figure 2.1 Flow-chart of aerogel production.....	32
Figure 2.4 SEM micrographs of the samples produced in a reaction time of 1min using A) 0.25 mol/L B) 0.50 mol/L C) 0.75 mol/L and D) 1.0 mol/L .....	38
Figure 2.5 SEM micrographs of the 0.75 mol/L Na <sub>2</sub> SiO <sub>3</sub> samples produced in a reaction time of 1min at A) 500 nm and B) 200 nm.....	38
Figure 2.6 TEM images of as-synthesized silica powder produced with 0.75 mol/L Na <sub>2</sub> SiO <sub>3</sub> .....	39
Figure 2.7 N <sub>2</sub> adsorption/desorption isotherms of silica aerogels prepared with (a) 0.25 mol/L (b) 0.50 mol/L (c) 0.75 mol/L and (c) 1.0 mol/L Na <sub>2</sub> SiO <sub>3</sub> concentrations in a CO <sub>2</sub> reaction time of 1 min .....	40
Figure 2.8 XRD pattern for the as-produced aerogels with different concentration of Na <sub>2</sub> SiO <sub>3</sub> ...	41
Figure 2.9 FTIR spectra of silica aerogels produced using A) 0.25 mol/L B) 0.50 mol/L C) 0.75 mol/L and D) 1.0 mol/L Na <sub>2</sub> SiO <sub>3</sub> concentration .....	41
Figure 2.10 Particle size distribution for silica aerogel produced with A) 0.25 mol/L B) 0.75 mol/L C) 0.75 mol/L D) 1.0 mol/L Na <sub>2</sub> SiO <sub>3</sub> under CO <sub>2</sub> reaction time of 1min E) Commercial aerogels.	43
Figure 2.11 Relative absorbance of films formed with the as-produced aerogels and commercial products for both A) hydrophilic and B) hydrophobic applications.....	44
Figure 3.1 General preparation route (with an extension directed with dash-lines).....	51
Figure 3.2 Optical view of the as-synthesized silica powder .....	58
Figure 3.3 SEM images of as-synthesized silica powder produced from 0.50 mol/L hydrogel.....	59
Figure 3.4 TEM images of as-synthesized silica powder produced with 0.5 mol/L Na <sub>2</sub> SiO <sub>3</sub> solution.....	59
Figure 3.5 N <sub>2</sub> adsorption/desorption isotherms with their respective pore size distribution for silica aerogels prepared with (a) 0.25 mol/L (b) 0.50 mol/L (c) 0.75 mol/L and (c) 1.0 mol/L Na <sub>2</sub> SiO <sub>3</sub> concentrations .....	61
Figure 3.6 Particle size analysis for samples produced with A) 0.25 mol/L B) 0.50 mol/L .....	63
Figure 3.7 XRD patterns for 0.5 mol/L Na <sub>2</sub> SiO <sub>3</sub> produced with 28.6 w/w% of the salt solution ..	64

## List of Figures

---

Figure 3. 8 XRD patterns of produced aerogels at different concentration of $\text{Na}_2\text{SiO}_3$ .....	64
Figure 3. 9 FTIR spectra of silica aerogels produced using A) 0.25 mol/L B) 0.50 mol/L C) 0.75 mol/L and D) 1.0 mol/L $\text{Na}_2\text{SiO}_3$ concentration .....	65
Figure 3. 10 Thermal curves of samples produced A) before drying B) after drying at 120 °C C) after drying and calcination.....	66
Figure 3. 11 Relative absorbance of film formed with the as-produced aerogel and commercial products.....	69

厦门大学博硕士学位论文摘要库

**LIST OF TABLES**

Table 1.1 Definitions of terms used to characterize porous solids .....	3
Table 1.2 Identification of aerogel properties and features with their applications .....	6
Table 1.3 Precursor chemicals used in the production of silica aerogels .....	10
Table 1.4 Some solvents and their surface tension.....	21
Table 2.1 Physicochemical properties of solvents used in the study.....	31
Table 2.2 Effects of the reaction parameters on the textural properties of the as-synthesized silica aerogels .....	36
Table 2.3 $E_i$ and $FT_i$ for the synthesized aerogels at varied concentration and commercial aerogels .....	44
Table 3.1 Relevant physical properties, cost and description of produced products.....	52
Table 3.2 Textural properties of the products produced from the four samples .....	53
Table 3.3 General effects and contributions of the reaction parameters <sup>a</sup> on the as-produced silica aerogels .....	55
Table 3.4 Comparison of protic solvents.....	58
Table 3.5 $E_i$ and $FT_i$ for the synthesized aerogels at varied concentration and commercial aerogels .....	69



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