A review on silica aerogels for CO₂ capture applications

Karbondioksit yakalama uygulamaları için silika aerojeller üzerine derleme

Bora YAYAÇ, Nilay GIZLI

†CMS Jant ve Makina Sanayi AŞ, İzmir, Turkey.
‡Department of Chemical Engineering, Engineering Faculty, Ege University, İzmir, Turkey.

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* Corresponding author/Yazışlan Yazar.
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Abstract
In recent years, greenhouse gases known as, CH₄, N₂O, O₃, CFC and especially CO₂ are released into the atmosphere through activities such as combustion, industrial emission or anaerobic decomposition and they cause an increase in surface temperature and global climate changes due to their high heat absorption capacities. Both political and scientific studies gained momentum as the countries of the world set the priority for the reduction of CO₂ emissions. Developing methods for reducing global carbon emissions; are known as carbon capture and storage known as (CCS) technologies. They are mainly classified as pre-combustion, post-combustion and oxyfuel combustion processes. Adsorption, physical and/or chemical absorption, membrane and cryogenic process can be considered as the most common CCS technologies. Porous solid sorbents can be also used for the physical adsorption of carbon dioxide from flue gases, as well. However, these processes are also known to have weaknesses in terms of both selectivity and cyclic operation. More recently, modification of mesaporous materials with amine groups have been shown to be efficient solid sorbents for CO₂ capture. With this review, current scientific studies on the recent advances in carbon sorption applications of silica aerogels has been investigated. The review consists of three main sections: preparation and modification of silica aerogels, literature studies on CO₂ sorption performances and future perspectives. As a result, it has been concluded that amine-modified silica aerogels are promising materials for the carbon capture for the post combustion processes with their superior properties.

Keywords: Silica aerogel, CO₂ capture, Adsorption, Supercritical drying, Ambient pressure drying

1 Introduction
The hazard of global warming is increasing day by day due to the greenhouse gases released to the atmosphere and almost 60% of the emissions of these harmful greenhouse gases are generated by carbon dioxide [1]. The concentration of CO₂ in the atmosphere has reached the value of 400 ppm with very serious consequences of environment such as, climate change in terms of rise both in sea level and global mean temperature [2]. To moderate the future climate change due to CO₂ emissions, the International Energy Agency (IEA) offers Carbon Capture and Storage (CCS) Technologies as powerful solutions [3]. Many CCS technologies (Figure 1). Have been developed for the capture of CO₂ such as absorption [4]-[8], physical/chemical adsorption [9]-[15], membrane [8],[16],[17] cryogenic processes [18],[19], and combination of two or more of them, named as hybrid processes [20]. According to the literature, the chemical absorption, using aqueous alkanolamine solution has been stated as the most suitable technology for capturing CO₂ among these methods [21]-[23]. However, corrosion damage of the alkanolamine aqueous solution for the equipment [24], high energy consumption during regeneration and high-volume absorbent requirement make this process disadvantageous. To avoid the drawbacks of amine scrubbing process, the development of solid supported amine-based sorbents has attracted much attention [25],[26]. Amine species are incorporated on to porous supports in order to increase the adsorption capacity and mass transfer surface area [27]. In this context, the application of silica aerogels for CO₂ capture processes as solid support has become a focus of great interest...
due to their superior properties such as high porosity large specific surface area, large pore volume and mesoporous structures [28],[29]. Moreover modification of silica aerogels with amine compounds improves the CO₂ sorption capacity and selectivity by combining the reaction properties of amine species (high CO₂ selectivity) and porous structure of silica aerogels (high surface area) [30]-[32]. Up to now, many researches have mainly focused on the synthesis of amine containing silica aerogels and evaluation of their CO₂ sorption properties [29].

The objective of this paper is to review the technologies of silica aerogel as adsorbents that impregnated or grafted with amine functional groups for CO₂ capture from post-combustion streams. Within this scope, synthesis of silica aerogels is firstly introduced then application of them for CO₂ adsorption processes are reviewed and finally future perspectives are discussed.

2 Aerogel synthesis by using sol-gel process

Aerogels can be synthesized by using sol-gel technique in three critical steps as sol preparation, gel aging and drying [34]. A nanostructured solid network of silica is formed as a result of a hydrolysis and condensation reactions of the silica precursor. Final properties of aerogels (specific surface area, porosity, density, etc.) are highly depend on the sol–gel process parameters. The most common sol-gel precursors are tetraethylorthosilicate (TEOS), tetraethyl orthosilicate (TMOS), Polyethoxy Disiloxane (PEDS). Beside silica precursors, different solvents such as alcohol, acetone, dioxane are used to homogenize the mixture [35]. Depending on the desired properties of aerogels, various routes can be followed as shown in Figure 2.

In the followings, the critical synthesis steps in aerogel preparation are outlined.

2.1 Sol-Gel process

In the sol-gel process, firstly, homogeneous solutions of very pure starting materials are prepared. Then hydrolysis is carried out by adding and mixing alkoxy-water. If the solution pH is different from 7, the hydrolysis reaction proceeds in a considerably accelerated manner. Therefore, the addition of acid or base to the reaction media accelerates this process. The reaction proceeds by hydrolysis of the alkoxide precursors under acidic or basic conditions and by polycondensation of the hydroxylated monomers to form a porous gel. The acidity of the solution after hydrolysis is increased about pH of 7, which promotes gelation [37]. Hydrolysis and condensation reaction rate with respect the pH of the solution can be shown in Figure 3.
2.2 Drying of alcogel
The final step after formation of the cross-linked wet alcogel is the exchange of the liquid solvent confined into the pores of the silica network with air. The evaporation of the solvent by natural drying of the wet alcogel causes the pore structure to collapse due to the interface tension between the solvent and the air upon formation of the vapor-liquid interface. Therefore, drying of the gel is a critical step. The purpose of the drying process is to prevent the build-up of the gel structure against collapse and to minimize the shrinkage [41]. There are various methods of drying alcogels. These methods may depend on the gel structure produced, the area of use and the production conditions. Alcogels can be dried either by supercritical drying or ambient pressure drying or by freeze-drying methods.

2.2.1 Supercritical drying
The main principle of supercritical drying is the transformation of solvent from liquid to gaseous state, passing through the supercritical region without any phase boundary (Figure 4). Density of the liquid phase and the gas phase are equalized at the critical point of the drying. Most organic solvents are dangerously flammable and explosive at critical pressures of the critical point of the drying. Most organic solvents are dangerously flammable and explosive at critical pressures of 50-600 atm at high critical temperatures between 300-600 °C. Therefore, supercritical drying at high temperature requires special safety precautions.

2.2.2 Ambient pressure drying
The production of aerogels in supercritical conditions has some disadvantages in terms of high cost and flammability and explosiveness. Drying at ambient pressure has been widely used and achieved successful results in recent years to as it provided both cost and volume shrinkage reduction and safer use. In processes which liquid carbon dioxide is used as the solvent, the chemical stability of the aerogel decreases considerably during supercritical drying. To overcome this problem, Brinker and Scherer introduced a commercially attractive ambient pressure drying method to produce silica aerogels [42].

2.2.3 Freeze drying
Another option to eliminate phase boundaries between the gas and liquid phase during drying is called freeze drying. The liquid sublimes by freezing and the phase transformation is completed. There are many studies that produce aerogels by using this method. In addition, to stabilize the gel network, the aging period must be extended, the solvent should be replaced with a solvent with a low expansion coefficient and a high sublimation pressure and the salt should be added to achieve low freezing temperatures. Another disadvantage of this method is that the network structure can be damaged by crystallization of the solvent in the pores. Therefore, aerogels which are produced by freeze drying called as “cryogel” [43].

3 CO2 capture by adsorption
The solid adsorption process can be an alternative method for capturing CO2 since the aqueous amine adsorption process has some limitations due to low contact area between liquid and gas, low CO2 selectivity, high energy requirement for regeneration and equipment corrosion problems [44]. To overcome the afore-mentioned drawbacks, many studies have been focused on the CO2 capture by involving solid adsorbents [45],[46]. Proper adsorbents for CO2 capturing should have the properties of low raw materials cost, low heat capacity, fast kinetics, high CO2 adsorption capacity, high CO2 selectivity and thermal, chemical, and mechanical stabilities under extensive cycling. However, many materials have been developed for this purpose, the interest in aerogels among these materials is increasing day by day.

3.1 Silica aerogels for CO2 capture
Silica aerogels are special materials that have superior features such as large surface area, high porosity volume and low density. Moreover, the sorption performance of them can be improved by modifying with amine species. Synthesis of amine modified silica aerogel (AMSA) consists of two steps. Firstly, gels are produced by sol-gel method. Then prepared gels are absorbed into the amine initiators at suitable temperatures. Amine initiators diffuse into the gel with capillary forces and reach the gel surface with the aid of covalent bonds, Van der walls bonds, π bonds or hydrogen bond forces.

Table 1: Precursor types and properties for silica aerogels.

| Hydrophilic precursors | Hydrophobic precursors |
|------------------------|------------------------|
| Tetramethoxysilane (TMOS) | Methyltrimethoxysilane (MTMS) |
| Tetraethoxysilane (TEOS) | Methyltriethoxysilane (MTES) |
| Sodium Silicate (Na2SiO3) |  |

Properties of aerogels:
- High optical transmission (>90 %)
- Density <0.1 g/cm³
- Hard and brittle
- Opaque
- Density >0.1 g/cm³
- Soft and flexible

Figure 4: Pressure-temperature phase diagram for solid-liquid-vapor transformation.
Red arrow shows the supercritical drying, where the green arrow shows the ordinary drying and the blue arrow shows the two-phase changing freeze-drying in Figure 4.
Many studies show that amine modified silica aerogels can be used for CO$_2$ capture efficiently. In their study, Yong Kong et al. used tetraethoxysilane (TEOS) as silica precursor and aminopropyltriethoxysilane (APTES) as amine source. They followed the sol-gel procedure as given in Figure 5 and obtained aerogel after supercritical drying.

Nick Lineen et al. studied CO$_2$ capture with amine modified aerogels [48]. They produced and modified aerogels with amine precursor tetraethylenepentamine (TEPA). After producing aerogel, characterization processes and CO$_2$ capture analysis have been done. They examined the sorption capacities with cyclic experiments with the material which denoted the best performance. This type of aerogel exhibited 5.1 mmol/g CO$_2$ adsorption capacity [49]. They used a different silica precursor such as ((3-aminopropyl) trimethoxysilane (Mono-A-PTMS) and (3-trimethoxysiloxypropyl) diethylenetriamine (Tri-A-PTMS) and they examined the effect of amine ratios on the sorption performances. They also used tetramethyloctadecylsilicate (TMOS) as silica precursor and methanol, water, as co solvents and hydrochloric acid as catalyst. They concluded that the tri amine modified aerogel resulted in better sorption capacity of 0.81 mmol/g but less than other studies [49].

In Nick Lineen’s study, silica aerogels were grafted with amine in 3 different mole ratios. They reported that tri amine grafted aerogel specimen gave the best CO$_2$ adsorption result with the capacity of 2.61 mmol/g. The experiment was repeated 100 times to verify the results and an excellent stability was obtained with an average adsorption capacity of 2.30 mmol/g [50].

Hongyu Fan et al. used Methyltrimethoxysilane (MTMS), ethanol dimethyldimethoxysilane (DMDMS), (3-aminopropyl) triethoxysilane (APTES), acetic acid, urea, cetyltrimethylammonium chloride (CTAC) and methanol for the preparation of amine modified aerogel. The molar ratio of APTES to MTMS were set as 1:1, 1:2, 1:3 and 1:4, and the samples were abbreviated as Si-1, Si-2, Si-3 and Si-4 and dried by ambient pressure drying method. Time dependent CO$_2$ adsorption capacities of the aerogels prepared at different amine ratios were given in the Figure 6 [51].

Yong Kong et al., examined the effect of alcohol type on CO$_2$ adsorption capacity. They used three different type of alcohols such as acetone, ethanol, methanol and isopropanol in sol-gel reactions and they applied supercritical drying process to prepare amine grafted aerogel. They obtained the CO$_2$ sorption capacities of various types of aerogels (Figure 8). [52].
They concluded that the amine modified aerogels prepared in the presence of acetone exhibited the highest sorption capacity. They also studied the effect of temperature on the CO\textsubscript{2} sorption performances within the range of 25-75 °C and concluded the adverse effect of temperature as shown in Figure 9.

![Figure 9: CO\textsubscript{2} adsorption capacities at different temperature](image)

CO\textsubscript{2} capture experimental set up that used by many researchers can be illustrated as in Figure 10.

![Figure 10: CO\textsubscript{2} capture experimental set up.](image)

Finally, there are several studies on silica aerogels for CO\textsubscript{2} capture. If we compose them in one table, it can be tabulated on Table 2.

### 4 Conclusion and future perspectives

Silica aerogel hold great promise owing to their superior features of provided with nano sized pores filled with air and a solid network structure. The pore properties of aerogels can be tailored by sol gel parameters and type of precursors. Therefore, selection of the appropriate precursor and optimum parameters are very important for the quality of aerogels. The drying of aerogels can be carried out in three different methods. These methods are supercritical drying, ambient pressure drying and freeze drying. The drying method should be selected according to the desired morphological characteristics of the silica aerogels and target application area.

Amine grafted silica aerogels are the promising candidates in the CO\textsubscript{2} capture applications for the post combustion streams. Amin content of the silica aerogels determines the sorption performance of amine modified silica aerogel.

In recent studies, ionic liquids have attracted attention with their unique properties such as low vapor pressure, good thermal stability, high polarity, and non-toxicity. For CO\textsubscript{2} capture, IL can be used to absorb CO\textsubscript{2} by either physical absorption or chemical absorption. It can provide different advantages for future aerogel studies [53].

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### Table 2: Some remarks of previous studies for the CO\textsubscript{2} capture by using silica aerogels.

| Reference                  | Aerogel Type       | Drying Type   | Characterization Method | CO\textsubscript{2} Adsorption Condition | CO\textsubscript{2} Adsorption Capacity (mmol/g) |
|----------------------------|--------------------|---------------|-------------------------|-----------------------------------------|-----------------------------------------------|
| Yong Kong et al. [24]      | Silica (Amine Hybrid) | Supercritical | SEM-TEM-BET-XPS         | 1 atm-110 °C                             | 4.43 (Humid) - 3.57 (Dry)                      |
| Nick Lineen [25]           | Silica Aerogel (TEPA)  | Supercritical | TGA-BET                 | 1 atm-75 °C                              | 5.1 mmol/g                                    |
| K. Wörmeyer [26]           | Silica (Amine Grafted) | Supercritical | TGA-ATR-IR              | 250 Pa-70 °C                             | 0.87 mmol/g                                   |
| Nick Lineen [27]           | Silica (Amine Grafted) | Ambient       | BET-FTIR                | 1 atm-100 °C                             | 2.61 mmol/g                                   |
| Hongyu Fan et al. [28]     | Silica (Amine Grafted) | Ambient       | FTIR-SEM-BET            | 1 atm-25 °C                              | 6.45 mmol/g                                   |
| Yong Kong et al. [29]      | Silica (Amine + Alkohol) | Supercritical | FTIR-SEM-BET            | 1 atm-25 °C                              | 5.50 mmol/g                                   |
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