Chemical Synthesis Method for Production of Silica Gel as a Sorbent Material

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Abstract

The ever increasing world population and the demand for continuous development acquire production of products with better quality in increasing amounts. However, in order not to encroach on ecological systems, eco-responsible or green vision should be integrated in every front of life. For this purpose, eco-innovative means and the green chemistry (GC) movement appear to be the best tools. GC provides the desired ends without making compromises on the ecosystems. In this study, principles of GC are used to synthesize silica xerogels, which are used as drying chemicals, sorbents, catalysts, animal litter, in glass equipments, in food industry, by using hexadecyl trimethyl ammonium bromide, which is a cationic surfactant used as an inexpensive precursor and structure template, monitoring of experiment at room temperature and regeneration of the ion exchanger after the experiment rendered the process energy efficient and eco-friendly and provided particles with very small size and almost homogeneous size distribution. Thus, in this study GC was employed as an eco-efficient and effective way of producing silica gel which offers promising results in many areas in animal husbandry, such as food preserving, controlling humidity in the animal houses and as animal litter.

Key words: Green chemistry, silica gel, xerogels, ion exchanger

1. Introduction

The remarkable economic and population growth of the 20th century, which was based on continuous growth and development rather than sustainability, was closely coupled to substantial increases in the extraction and consumption of natural resources. This caused increasingly-damaging negative environmental impact. If the economic growth rate is not decoupled from the rate of natural resource consumption, by 2050, approximately 140 billion tons of minerals, ores, fossil fuels and biomass per year, which is three times the current rate, would be needed [1]. This is far beyond what is likely sustainable if realized at all given finite world resources and *its impact on our water supply, air quality, forests, climate, biological diversity, and human health would be severe.* Today 40% of deaths worldwide are due to water, air and soil pollution [2]. It should be kept in mind that already the world is running out of cheap and high quality sources of

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some essential materials such as oil, copper and gold, the supplies of which, in turn, require ever-rising volumes of fossil fuels and freshwater to produce. Therefore, it is a must that the rate of resource productivity, which is doing more with less, should be improved faster than the economic growth rate. However, economic growth globally was faster than growth of the rate of consumption of natural resources. This indicates that without depleting the natural resources and causing negative impact on the environment and humans and economic growth can be realized. As mentioned in the UNEP International Resource Panel, globally, about 25% less material input was required in 2002 compared to 1980 to produce one unit of real GDP, and some negative environmental impacts have been reduced [1]. In other words, some 'dematerialization' of the world economy has occurred spontaneously. Accelerating this process of decoupling economic activity from consumption and environmental impacts is fundamental to future human well-being. Thus, in order to enable decoupling to support sustainable development more effectively further sustainability-oriented innovations are urgently required. Hence, more transformative change and a more resource efficient and Green Economy, in which economic growth, social equity and human development are interlinked with environmental security, business and industry is required to meet the size of the challenge.

*S*ustainable consumption and production models and *patterns* should be adopted and devised to promote social and economic development within the carrying capacity of ecosystems. Therefore, economic growth should be delinked from environmental degradation through improving efficiency and sustainability in the use of resources and production processes; and reducing resource degradation, pollution and waste. Thus, *i*t has come to be recognized in recent years, that the science of chemistry is central to addressing the problems faced today. The utilization of various sub-disciplines of chemistry and the molecular sciences has increased an appreciation in Green Chemistry (GC) which is needed to design and attain sustainable development [3, 4]. A central driving force for this increasing awareness is that GC accomplishes both economic and environmental goals simultaneously through the use of sound, fundamental scientific principles. The drive towards clean technology in the chemical industry, with an increasing emphasis on the reduction of waste at source, will require a level of innovation, new technology and designing clean or 'green' chemical transformations and processes including synthesis, catalysis, analysis, monitoring, and separation and reaction conditions.

The GC revolution provides an enormous number of opportunities to discover and apply new synthetic approaches using alternatives, feed-stocks, eco-friendly reaction conditions, energy minimizations and the design of less toxic and inherently safer chemicals. Briefly, green chemistry is based on 12 basic principles (Fig. 1) of hazard, energy and waste minimization or prevention which would be the key driving factors for achieving the necessary decoupling [1, 2]. UNEP International Resource Panel revealed five major findings for which GC should be exploited to procure the means to realize them:

1) Assessing biofuels: towards sustainable production and use of resources on;
2) Decoupling natural resource use and environmental impacts from economic growth;
3) Metal Stocks in Society;
4) Recycling Rates of Metals; and
5) Priority products and materials: assessing the environmental impacts of consumption and production.

According to these findings as stated in the GC approach when materials and goods are to be designed and produced it should be kept in mind that they are multi functional and multi-purpose and the approach to be taken should be “cradle to cradle”. A good example of such a material is silica gel.

Silica gel was widely used in World War I and II and in many different sectors including industry, husbandry, military, broadcasting, and health. Some of the usage areas of silica gel are indicated in Table 1. It also provides high quality broadcasting. If excessive moisture builds up within a waveguide it can cause arcing inside the waveguide and this damages the power amplifier which feeds it. Also, the beads of water that form and condense inside the waveguide change the characteristic impedance and frequency, degrading the signal. Therefore, small compressed air system is used to circulate the air inside the waveguide over a jar of silica gel.

Greenness of a material also requires its production process to be green as well. However, in the production process of silica gel, which has such a wide variety of usage areas, ammonium tetrachlorocobaltate (II) $(NH_4)_2CoCl_4$ or cobalt chloride $CoCl_2$ are used. These substances are toxic and carcinogenic, and were reclassified by the European Union in July 2000 as a toxic material and $CoCl_2$ is carcinogenic. Therefore, in production silica gel development of greener production processes have gained much importance.

Sol gel chemistry is an attractive alternative to other synthetic methods for many reasons. The method is cost and energy effective and can generally be performed under room conditions with general lab equipments; making the processing quite convenient. Historically sol-gel technique involves the use of metal alkoxides as precursors which readily undergo catalyzed hydrolysis and condensation to form a sol of metal oxide particles with sizes in nano scale dimensions [5, 6].

The overall process involves hydrolysis and polycondensation reactions of the organometallic (silicon alkoxides) or inorganic (silicic acid) compounds. Polymerization followed by condensation of siloxane bonds results in the formation of a gel which is generally defined as a continuous solid frame work embedded in a large volume fraction liquid phase. Further processing results in the formation of dried gels which are named depending on how the solvent is removed from the gel i.e. supercritical drying produces aerogels (aero stands for air), ambient drying yields xerogels (xero stands for dry) and freeze drying generates cryogels (cryo stands for freeze). Aerogels are known to possess the highest surface area (above 1000 m2/ g) and a very low density which makes them the lightest solids on earth [7]. Synthesis of silica gels involving silicon alkoxide has proven to be quite efficient and successful but there is a problem of some alkoxides being expensive and some are quite sensitive [8], further still, several alkoxides are not commercially available or are difficult to obtain, thus hindering the momentum of research. So a cheaper and easily available material like water glass, rice hull ash or clay is needed to synthesize silica gels.

Textural properties of the silica gels can be improved by controlling the precursor concentration, treatment, pH of the precursor mixture, temperature of the reaction mixture, aging time and most importantly evaporation of solvent during the drying stage. Extensive work has been already conducted to improve the textural properties of the silica gels derived from Na-Si precursor [9-13]. Achieving smaller particle size and higher surface area had been a point of major concern to many groups and it was observed that Na-Si based gels can have high surface area and smaller pore size only if an ion-exchanger is used to remove the Na ions from the precursor [14]. Another problem faced during the drying of the gels is the capillary pressure created by the evaporating solid which results in the collapse of the gel structure. It has been discovered that exchanging water with some organic solvent having low surface tension can help reduce the generation of cracks in the dried gel [14]. In this work, we have selected water soluble inexpensive inorganic reagent sodium silicate as the silica precursor instead of expensive and more hazardous organic precursors. To obtain smaller sized particles, it is converted to silicic acid (H_2SiO_3) by passing it through a cation exchanger to exchange the Na^+ ions in sodium silicate with the H^+ ions of the ion exchanger which is later converted to silica gel through a process with minimum energy consumption and hazard production. Throughout the experiment water is used as a solvent which has a low boiling point and creates no pollution/hazard.

2. Materials and Method

Sodium silicate was purchased from Scharlau, Spain. 35% pure ammonium hydroxide was supplied by Fischer Scientific; Hexadecyl trimethyl ammonium bromide (CTAB) was provided by BioWorld while Amberlite IR 2000 (ion-exchanger) was supplied from Merck. All chemicals were used without further purification. Throughout the experiment deionized water was used.

Characterization Studies were made by the SEM, FT-IR, TGA analysis of the prepared sorbent. The FT-IR studies were carried out in absorbance mode with 28 scan per sample, using Thermo Scientific Nicolet 6700 FTIR spectrophotometer in the range of 4000 to 400 cm^{-1}. Thermal properties of the samples were analyzed in Mettler Toledo TGA/SDTA 851e at a temperature range of 0-1000^oC at a heating rate of 10^oC per minute. XRD spectrum was recorded using PANalytical X'Pert Prodiffractometer equipped with Nickel-filtered Cu Kα radiations. Data was recorded using a step size of 0.04^{o}at a scanning rate of 2 theta per second and in a scanning range between 10-80 ^{o}2 theta. Tube voltage was 40 kV and the tube current was 30 mA. A JSM-5910 Scanning Electron Microscope was used to determine the surface morphology of the gold sputter coated xerogels at 5 kV.

2.1. Synthesis

4% solution of sodium silicate was prepared by dissolving sodium silicate in deionized water. Then the solution was slowly passed through the ion exchanging column, which is made from a 63.5x 5.08 cm pyrex column filled with Amberlite IR-2000. After passing through the ion exchange column, the solution was collected in a polypropylene beaker. The pH of the collected silicic acid was determined via pH meter. 17.5 ml of the effluent was drop wise added to 5 ml of 1% CTAB solution with magnetic stirring. Then 0.05M ammonium hydroxide was slowly added to the mixture with continuous stirring until the pH was 5. Then the silica sol was stirred for about 30 minutes and was then kept at 50^oC for an hour. Then it was covered with aluminum foil and was cooled to room temperature so that gelation proceeded smoothly. After the gel was formed within an hour it was left for aging for 2 days so that the gel network became stronger and stable. Then the solvent was exchanged with ethanol for 4 consecutive days replacing ethanol after every 24 hours. On the fourth day, ethanol was allowed to evaporate first at room temperature and later at 60^oC until the gel was completely dry. The dry gel was divided into two parts. One was labeled as SXGCT and the other part was calcined in a muffle furnace at 600^oC for 3 hours under a temperature gradient of 5^oC per minute. This sample was named as SXGCT_C. The overall sequence of reactions is displayed in Fig. 6. After the experiment, the ion exchanger was regenerated via washing with 5% NaOH solution, then with 5% HCl solution and lastly with de ionized water so that it can be reused.

2.2.Sample Characterization

Surface morphology of the calcined xerogels was studied. Scanning Electron Microscope (SEM) and the micrographs of the sample taken at different magnification as are shown in Fig. 2. Thermogravimetric Analysis **(**TGA) thermograms of as-synthesized silica are shown in Fig. 3. Infra Red (IR) spectra of both the calcined and uncalcined xerogels obtained by Fourier Transform (FT)-IR analysis are shown in Fig. 4

2.3. Theory/calculation

A major problem faced by the gels, during the process of evaporation of the solvent is the capillary pressure created by the evaporating solvent which results in the creation of cracks on the surface [6]. This phenomenon is controlled by using a low boiling point solvent which evaporates faster than water. In this case, water is exchanged by ethanol as a solvent which helped reduce the creation of cracks during the evaporation process. Almost the whole process is carried at room temperature or at a temperature slightly higher than room temperature, which proves the energy efficiency of the whole synthesis.

3. Results

3.1. Figure captions

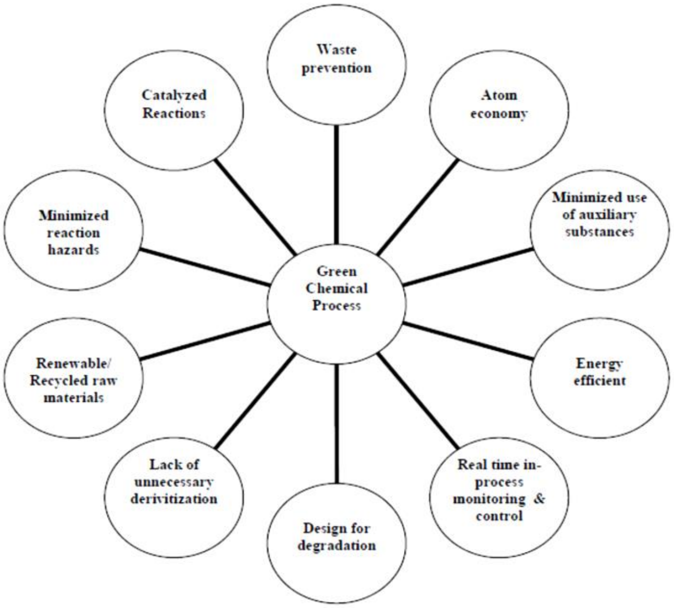

Fig. 1. The 12 Principles of Green Chemistry.

In Figure 1 the main pillars of GC is presented.

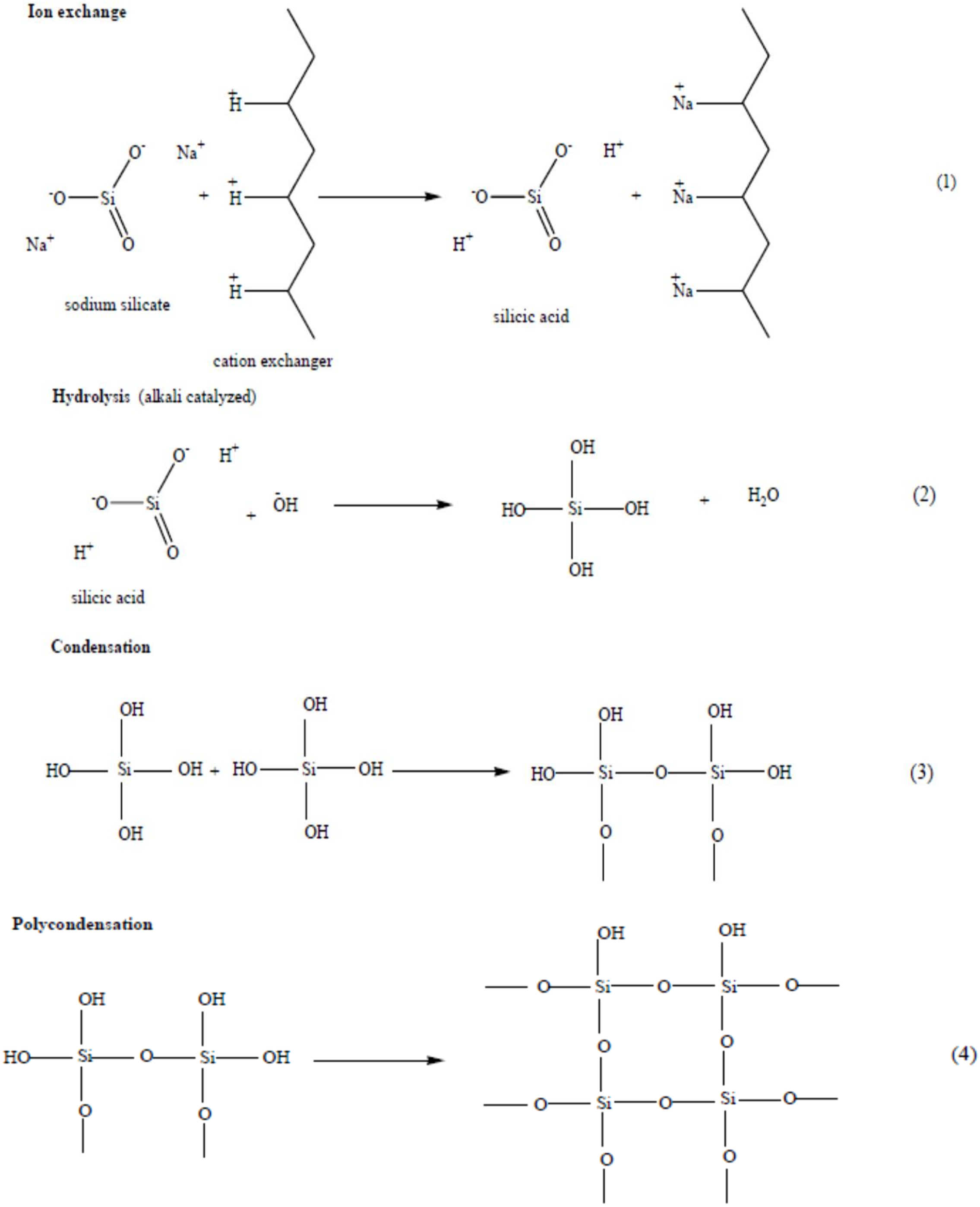

Figure 2. Sol-gel synthesis routes

In Figure 2 the sol-gel synthesis routes are presented

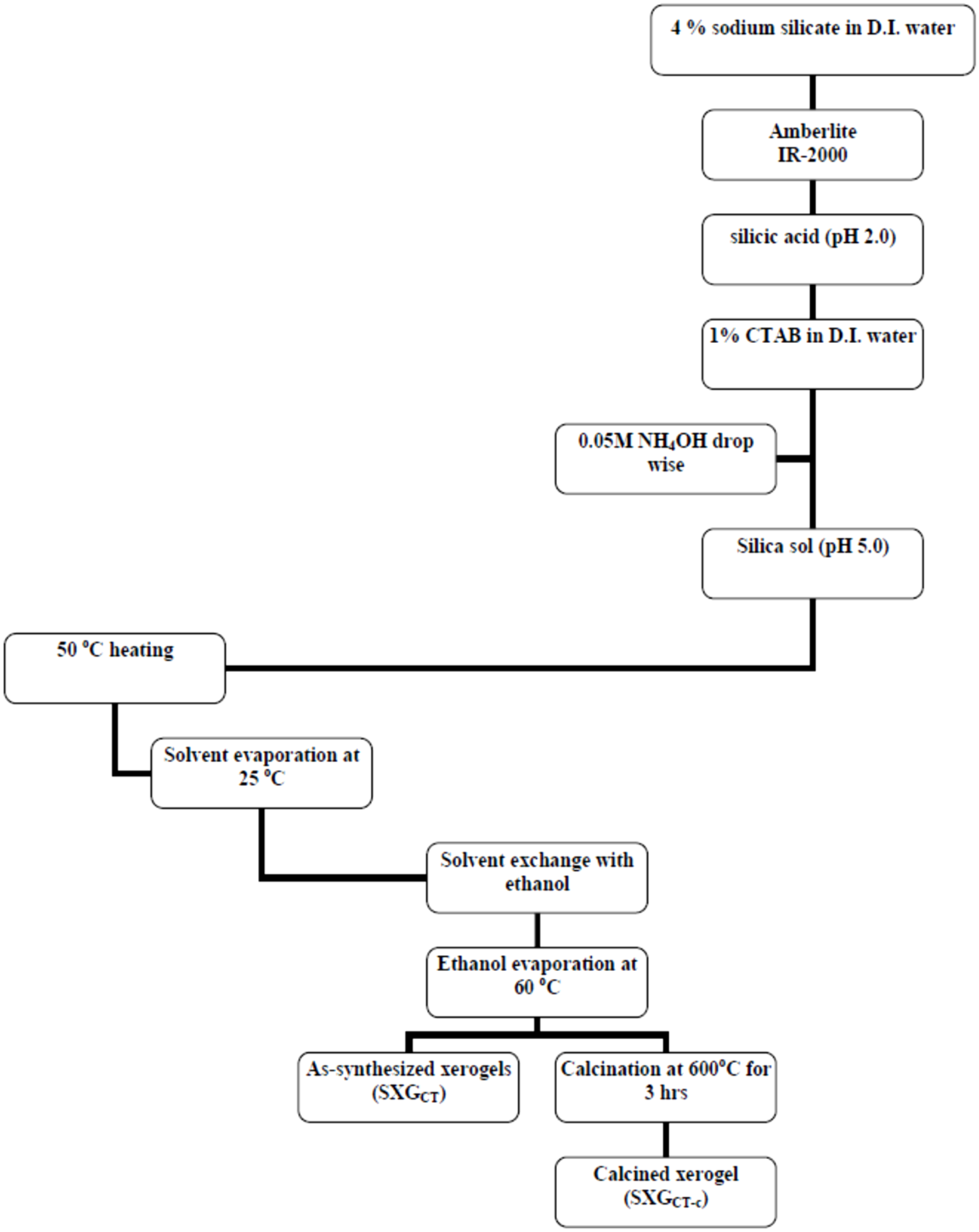

Figure 3. Reaction scheme.

The synthesis route is presented in Figure 3.

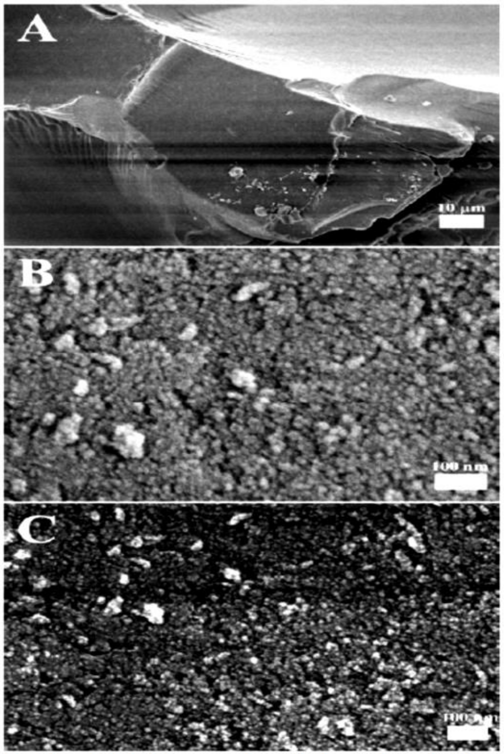

Figure 4. SEM Micrographs of the calcined silica xerogel. (A) at a low magnification, (B) and (C) show the morphology at high magnification

In Figure 4 it can be seen that the surface is quite smooth and the tiny particles are not visible at low magnification (Fig. 4 A) but at higher magnifications, the surface of the xerogel seems to comprise of very small particles of diameter lesser than 100 nm. The particle size is mostly homogeneously distributed and most of the particles seem to lie in the same size range i.e. 2-50 nm.

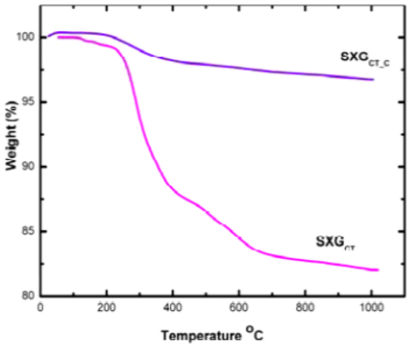

Fig. 5. TGA Thermograms of calcined (SXGCT_c) and uncalcined (SXGCT) xerogels.

As shown in Figure 5, the thermograms show that almost 20% of the sample weight is contributed by CTAB which is completely removed at 600^{o}C leaving behind only silica which stays stable even when heated upto 1000^{o}C. On the other hand, the calcined silica shows a minimal weight loss at about 200^{o}C.

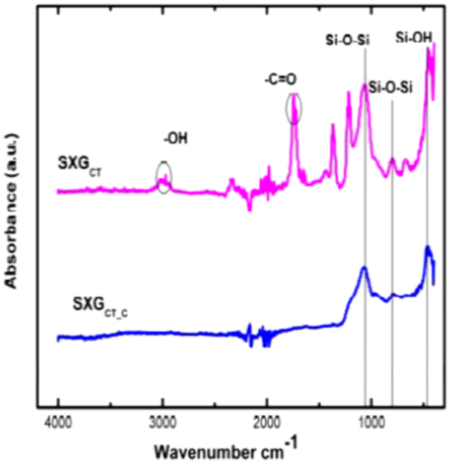

Fig.6. FTIR spectra of calcined (SXGCT_c) and uncalcined (SXGCT) xerogels.

In Figure 6 the typical peaks shown by silica are labeled in both the samples while SXGCT shows additional peaks. The calcined silica mainly shows these three prominent peaks while uncalcined sample shows additional peaks at 1220, 1365 and 1730 cm^{-1}, the main peak in the FTIR spectra of both xerogels appears at 1090 cm^{-1}.

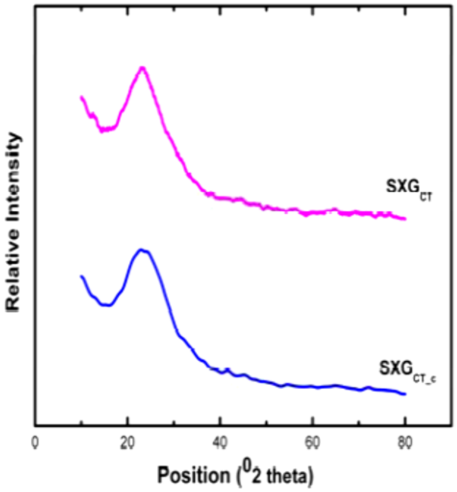

Fig.7. X-ray diffractograms of calcined (SXGCT_c) and uncalcined (SXGCT) xerogels. Both types of XRD patterns indicate amorphous nature of the xerogels.

In Figure 7 the diffractograms show a wide peak at 2θ value of around 24^{o} which is a characteristic of amorphous silica [14].

3.2. Tables

In Table 1 the most common areas where silica gel is used are presented.

Table 1. Some usage areas for silica gel

- adsorption of vapors and gases in gas mask canisters
- protecting military equipment from moisture damage
- maintaining the desired relative humidity in humidors, keeping tools or other materials rust-free in damp environments or long-term storage
- preserving dried food.
- acts as a fluid cracking catalyst for the production of high octane gasoline
- acts as a catalyst support for the manufacture of butadiene from ethanol
- feedstock for the synthetic rubber program
- dry the air in industrial compressed air systems adsorbs moisture from the air, preventing damage at the point of use of the compressed air due to condensation or moisture.
- dry the compressed air on railway locomotives, where condensation and ice in the brake air pipes can lead to brake failure
- animal litter
- İn keeping medicine dry
- diagnostic test strips, inhalation devices, syringes, drug test kits and hospital sanitation kits
- Separation science: Chromatography columns
  can be functionalized to afford specialty silica gels that exhibit unique stationary phase parameters
- functionalized silica gels are used in organic synthesis and purification as insoluble reagents and scavengers
- functionalized silica gels are used for removing metal ions selectively from aqueous media.

4. Discussion

The results of the experiment show that most of the particles seem to lie in the mesoporous size range i.e. less than 50 nm in size according to IUPAC classification of mesopores. Generation of mesopores can be attributed to the creation of empty space, which was occupied by the eliminated template (CTAB), before the process of calcination. The calcination process also helped to break any sort of bonds between silica xerogel and CTAB, which resulted in the generation of particles with very small diameter.

The TGA results offered an idea about the composition of the as synthesized xerogels since CTAB is completely removed if heated below 600^{o}C while silica stays stable at temperatures as high as 1000 ^{o}C. The weight loss of the the calcined silica at about 200^{o}C may be due to the chemically adsorbed water in the sample; otherwise the sample stays stable till 1000^{o}C (Fig. 3). Absence of a prominent weight loss in the calcined gel indicates complete removal of CTAB from the sample.

The FT-IR spectra of both the xerogels shows a main peak which may be associated with the anti-symmetric stretching action of Si–O–Si bonds in the SiO_2 matrix [13]. The bands at around 800 cm^{-1} and 460 cm^{-1} are respectively assigned to bond symmetric stretching and the bond rocking vibration of the Si–O–Si bonds in the three-dimensional SiO_2 network. The additional peaks observed with SXGCT may be due to the surfactant and residual water or alcohol (-OH peak) and the additional peaks observed with the uncalcined sample may be generated because of CTAB in the sample.

In the diffractograms of the silica gels surprisingly the as-synthesized xerogel does not show any other peak indicating the existence of amorphous structure of the xerogel even when the surfactant present in the gel (Fig. 5). Although some working teams have reported presence of ordered mesostructures in surfactant templated silica [17]; however evidence for the existence of thoroughly amorphous nature of surfactant templated silica is also observed in some cases [18]. It is mainly dependent on the reaction conditions particularly pH and catalysis which decide the nature of silica. Amorphous structures are usually reported when reaction pH is close to neutral conditions [19].

The results indicate that GC offers a much eco-efficient, greener and safer sol-gel synthesis method for silica.

Conclusions

A new green chemical synthesis method was developed for production of silica gel as a sorbent material for employing in different areas of industry including but not limited to husbandry, environmental protection, water industry, pharmaceuticals. Mesoporous silica xerogels are obtained by using a cost effective green chemistry approach. Choice of an inexpensive precursor, monitoring of experiment at room temperature and regeneration of the ion exchanger after the experiment made the process not only energy efficient but also cost effective. Use of catalyst helped to speed up the process while using CTAB as a template has resulted in the formation of particles with very small size which can be used as sorbents or catalysts in a variety of processes [17]. Green chemistry can efficiently be used to meet the requirements and needs set forth in the UNEP International Resource Panel and meet the needs of different industries and people without encroaching neither on the economies nor on the ecology.

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