Synthesis and characterization of nickel nitrate as additive into SiO$_2$ matrix by supercritical drying method.

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Abstract

In current report, the investigation of synthesis of silica aerogel composite by reinforcing metal oxide particle nickel nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O)] as a filler into SiO$_2$ matrix. In silica matrix with the help of tetraethoxysilane (TEOS),ethanol and oxalic acid catalyst ,using sol-gel technique followed by high temperature(N$_2$ gas) solvent extraction with supercritical drying technique. The obtained aerogel doped with nickel nitrate display a well developed porous structure, excellent physical properties with less volume shrinkage, extremely high specific surface area (794.3 m²/g), average pore size of 240 nm. The aerogel composite possessed a BET specific surface area even after calcinations of 500ºC for 4 hours by maintaining the pore shrinkage with the supporting skeletons nickel nitrate contents. The cross-linked aerogel composite, structural and physical properties were investigated by XRD (X-ray diffraction), field emission scanning electron microscopy (FE-SEM), Fourier- transform infrared-spectroscopy (FT-IR) and Brunauer, Emmett and Teller (BET) and BJH nitrogen gas adsorption-desorption.

Keywords: *TEOS, Nickel Nitrate, Porosity, supercritical drying, FTIR spectra.*

Introduction

In the world of nanoscience and nanotechnology, main attention are nano-materials. Aerogels are the highly porous nano-material which have a large surface area(`~1200 m^2 /g),high porosity (80-98%),low bulk density(~0.03gm/cm^2), extremely low thermal conductivity(0.005W/ mK) and unique acoustic properties(sound velocities as low as 100m/s)[1,2].Due to fascinating properties of nano-porous aerogels used in various areas as thermal super-insulators in solar energy systems, refrigerators, and thermal flasks[3], Internal Confinement Fusion (ICF) targets for thermonuclear fusion reactions[4],very efficient catalysts and catalytic supports[5],in radio luminant devices[6],in window insulating systems[7],in storage media for liquid for rocket propellants[8],for oil-spill cleanup [9].

The key issue of aerogel in various application is the fragility and brittleness of sample handling with naked condition. Few of researchers working on to improve toughness of pure aerogel. In current paper we have make aerogel with nickel nitrate as a nanofiller [Ni(NO$_3$)$_2$] to improve stiffness with maintaining the super properties of parent sample up to the maximum extend.

Inspite of unique properties of SiO$_2$ aerogel, their are limitation on application in various technical fields due to the fragility. By doping metal oxide like cobalt nitrate and nickel nitrate into the SiO$_2$ matrix used as the backbone of silica aerogel with colourful nature with maintaining parent level properties of silica aerogel like porosity, surface area, microstuctural and texture nature etc

2. Experimental methods

2.1. Materials

The chemicals were utilized for the preparation of alcosols were TEOS (tetraethylorthosilicate) as a main source of precursor, hydrolysis catalyst ammonium hydroxide (NH$_4$OH) ,ethanol (EtOH,C$_2$H$_5$OH) , oxalic acid(C$_2$H$_2$O$_4$)and metal oxide are nickel nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O].Diluted concentration of oxalic acid and ammonium hydroxide catalysts prepared by using double distilled water.

2.2. Preparation of Silica Aerogel composite by sol-gel technique

Silica aerogel composite were prepared by acid –base catalyzed sol-gel process followed by supercritical drying. The experimental steps followed for the aerogel synthesis have been shown in fig.1.Silica composite alcosols were prepared in three steps as follows: In the first step, tetraethoxisilane(TEOS),

Ethanol (EtOH,C$_2$H$_5$OH) were mixed under constant stirring condition for 30 min. under atmospheric condition. In stage second, after half an hour, oxalic acid(C $_2$H $_2$O$_4$) followed by nickel nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O] ,added into the solution while stirring for again half an hour. After the time interval of two days, the base catalyst (NH $_4$OH) was added drop by drop while constant stirring at atmospheric condition for 10 min. to the acid catalyzed sol. Initially colorless solution turns into superprising color means sky blue color as the addition of base catalyst ammonia. Then, the alcosols were made air-tight and kept for gelation at atmospheric (room) temperature. As the alcosols were sets (i.e.gelation), a small quantity of ethanol was added over the gels in order to prevent the (28.2C) evaporation of pore solvent and hence avoid shrinkage and cracking of gel. The alcogels were aged 12h in ethanol at room temperature (28ºC).In the next stage, the alcogels were subjected to supercritical conditions(240ºC,64 bar) for minimum 1 hour 15 minutes. In order to study physical and structural properties of a metal oxide silica aerogel compo...
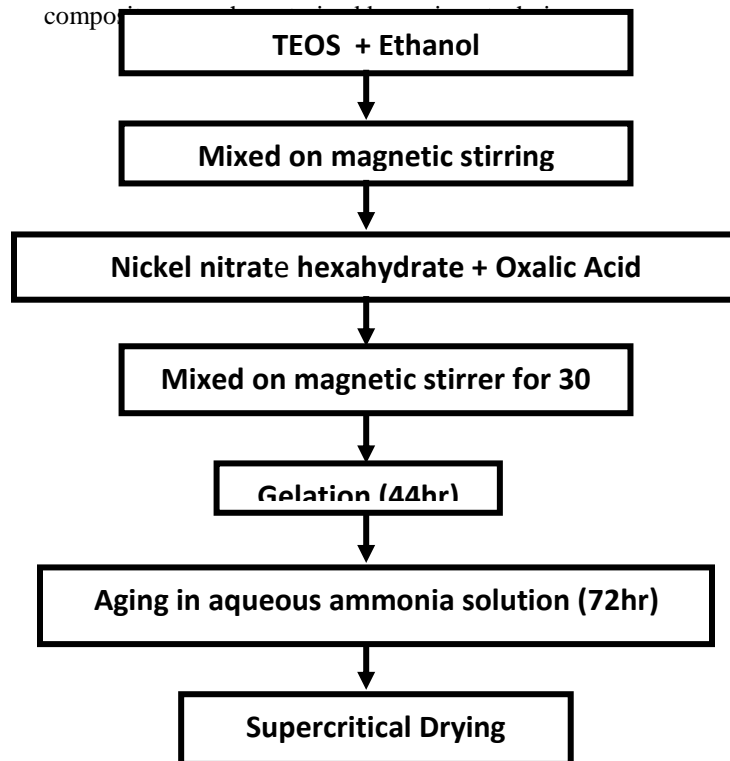
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┌──────────────────────────────────────┐
│           TEOS  + Ethanol            │
└──────────────────────────────────────┘
                   │
                   ▼
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│        Mixed on magnetic stirring    │
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│ Nickel nitrate hexahydrate + Oxalic Acid │
└──────────────────────────────────────────┘
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│      Mixed on magnetic stirrer for 30│
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│            Gelation (44hr)           │
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│ Aging in aqueous ammonia solution (72hr)     │
└──────────────────────────────────────────────┘
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                   ▼
┌──────────────────────────────────────┐
│          Supercritical Drying        │
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Fig.2: Photographs of a) pure aerogel b) silica aerogel composite nickel nitrate as a additive

2.2 Characterization methods

The effect of addition of nano-filler as metal oxide particles in silica hydro-sol on various properties of parent sample like microstructure and textual properties were investigated using described methods [10]. The apparent density of the monolithic silica aerogel was calculated from the ratio of measurement the mass of the aerogel by using an electronic micro-balance with an accuracy of up to 10^{-4} g, with the volume of the sample silica aerogel blanket. X-ray diffraction (XRD) of silica aerogel composite carried out to understand crystalline nature of sample. The Fourier Transform Infrared (FTIR) spectroscopy investigates the surface modification which shows the hydrophilic nature becomes hydrophobic using Perkin Elmer (Model number 760 400-4000cm^{-1}). The textual properties of the aerogel such as average pore diameter (P_d), BET surface area (S_{BET}) and pore volume (P_v) investigated by a BET N2 gas adsorption/desorption apparatus. The microstructure and morphology of the silica aerogel were studied by using a Scanning Electron Microscopy (SEM).

2.2.1 XRD

The spectrum in fig.3 shows the single broad peak at diffraction angle $2\theta=24°$ approx. and FWHM was found very large which indicates that the samples are amorphous in nature.
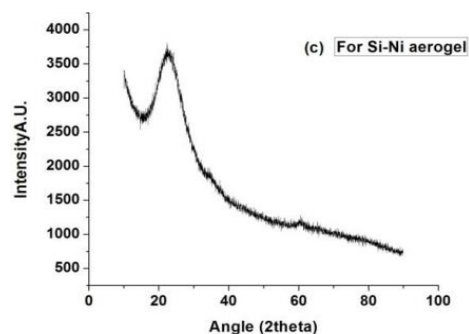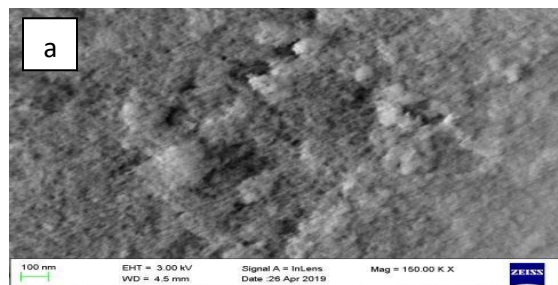

Fig.3: XRD spectrum of a) pure aerogel b) cobalt nitrate silica aerogel composite c) nickel nitrate silica aerogel composite

2.2.2 Microstructure of nickel nitrate silica aerogel composite

The microstructure of pure silica aerogel and silica aerogel composite observed by SEM shows in fig.3.The metal oxide particles as a nanofiller, merged in silica matrix structure whose preparation of alcosol acting as a backbone of skeleton which strengthen the silica aerogel. The metal oxide silica aerogels maintained porous structure with comparatively high porosity. The pore diameter is most probably lies within the mesoporous (2-50nm) range [11].
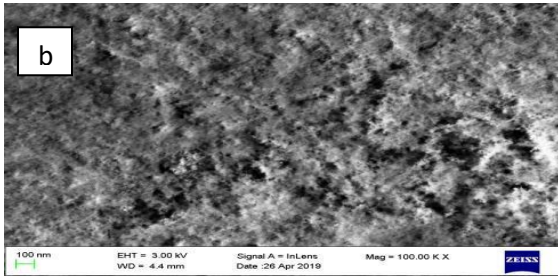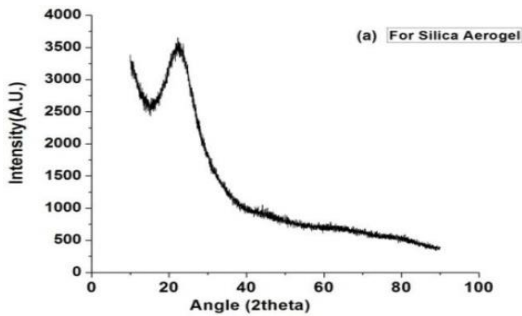
Fig.4: SEM micrographs of the a) pure aerogel b) nickel nitrate silica aerogel composite.

2.2.3 BET Analysis:

The impact of immerging metal oxide particles in silica gel on textural properties like average pore size, specific surface area, cumulative pore volume, N_2 gas

adsorption/desorption isotherms and pore size distributions (PSDs) and comparative study of pure silica aerogel and silica aerogel composite were analyzed by BJH method. Fig.4 and Fig.5 indicates the variations of pore volume and pore size of pure silica aerogel and N^2 (Nickel nitrate)--silica aerogel composites. The BET specific surface area obtained of N^2-silica aerogel are Ni-Si (794.3558m²/g) are less comparative to the pure silica aerogel (1,633.9191 m²/g). The pore volume and pore size of silica aerogel composite (pore diameter≅250A°) is less in comparision with the pure silica aerogel (pore diameter≅190A°) calculated from the BJH desorption isotherm. The

result indicates that there is decrease in porosity (%) of silica aerogel composite as decrease in pore diameter and surface area of pore. Mostly, in the silica aerogels the pronounced peak is lies in the mesoporous region (2-50 nm) [11]. It confirms that silica aerogel matrix and porosity is preserved by adding nickel nitrate into nano-porous silica matrix under supercritical drying technique.

Table 1

Effects of metal oxide nano-filler on textual properties of silica aerogel

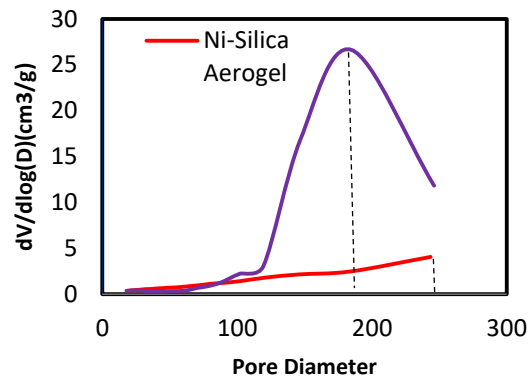| Samples	BET surface area (m²/g)	Pore Volume (cm³/g)	Pore size (Å)
Pure silica	1,633.9	7.714514	170
Si-Ni aerogel	794.3	2.032116	240

Fig.5: Cummulative study of pore size distributions of pure silica aerogel and N^2- silica aerogel composite
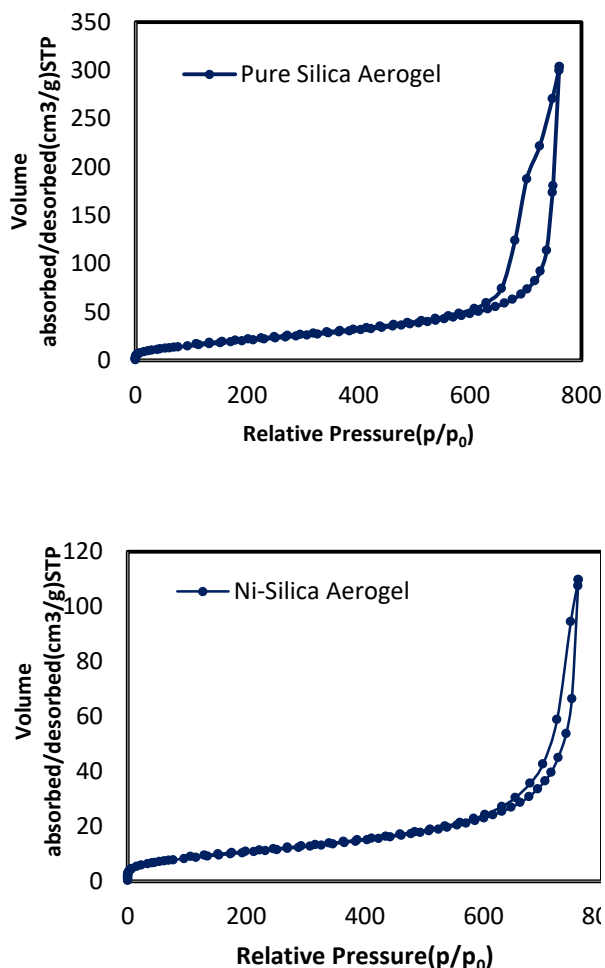
Fig.6: Cumulative study of N_2 absorption-desorption isotherms of pure silica aerogel and N^2-silica aerogel composite (calculated from BJH desorption data)

2.2.4 FTIR:

Normally, the surface modification verified with Fourier transforms infrared spectroscopy spectra.The chlorotrimethylsilane (TMCS) used as a surface modifying agents in which the lone pair electrons on the oxygen atom in the silica group (Si-OH) attack on the silicon atom in TMCS then to form Si-OSi $(CH_3)_3$ bonding .Thus reduced the concentration of Si-OH bonding and enhanced by replacing hydrophobic group(CH_3). In fig.6 indicates the peak at 1070 and 495 cm−1 represents the Si—O—Si bonds which examines the presence of silica network structure [12, 13]. The broad absorption peak centered at 3450 cm−1 and 1630 cm−1 corresponding to the O—H absorption band is possibly caused by physically adsorbed water [15, 16]. The peaks at, 1560 and 840 cm^{-1} indicate the —CH3 groups, which are results to surface modification, happened successfully [17, 18].
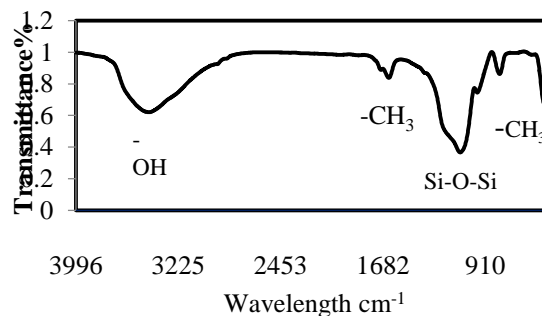

Fig.6: FTIR spectra of Nickel nitrate silica aerogel composite

4. Conclusion

Pure silica aerogel along with silica aerogels with nickel nitrate composite could be synthesized by the two step acid-base sol-gel polymerization of tetraethoxysilane (TEOS) followed by the supercritical drying. Using silica aerogel matrix as a host for Nickel nano-crystalline particles slightly decreases the surface area, surface volume, commutative pore volume and pore size of the pure silica aerogel matrix. FTIR spectra show surface modification done successfully which represents the hydrophobic nature of silica composite. Increasing the concentration of metal oxides affect the transparency of silica aerogel.

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