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Synthesis and characterization of a new amorphous hybrid silica using TEOS, TMSPA and CTAB

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ABSTRACT

A new amorphous organic-Inorganic hybrid silica materials have been prepared by the conventional sol-gel reaction of bis(gamma-trimethoxysilyl)propylamine (TMSPA) and Tetraethyl Orthosilicate (TEOS) in the presence of Cetyltrimethylammonium bromide (CTAB) as a structure directing agent. The hybrid was analyzed by using FTIR, TGA and SEM. The hybrid was also thermally stable at a temperature 800^o c. The hybrid material has the potentiality of adsorbing heavy metals from the aquatic environment which is under investigation in the laboratory condition.

Key words: TEOS, TMSPA, CTAB, FTIR, SEM, TGA, Hybrid Silica.

INTRODUCTION

In the past decade, a lot of work has been put into the synthesis of well defined porous materials, because of their potential applications in catalysis (1-3), separation science (4,5), and environmental remediation (6,7). The scope of porous materials was expanded in 1999 when several research groups reported on a new class of organic-inorganic hybrid composites, called periodic mesoporous organ silica materials (PMOs) (8-10). Silica/ carbon composites are an example hybrid material and are particularly versatile materials that find many possible uses for example in electrochemical devices (11), and solar absorbers (12). Silica/ carbon composites may be prepared via many methods including sol-gel techniques followed by carbonization (13), pyrolysis of suitable carbon precursors in a porous silica matrix (14) or carbonization of organo silica/ surfactant mesophases (15).

Silica/ surfactant and organosilica/ surfactant phases synthesized by sol-gel condensation of silica precursors and bridged silsesquioxanes have been used as precursors for the fabrication of a wide range of nanostructure materials under a flow of an inert gas (15-18). By heating mesostructured benzene – bridged PMO with crystal like pore walls for 4 hours at 900 °C in a stream of nitrogen, Pang *et al* obtained mesoporous carbon/silica nanocomposite materials with pore walls uniformly constructed from molecular carbon and silica units (15). Pinnavaia *et al* reported the formation of carbon nanotubes by in situ carbonization of a micellar non-ionic surfactant (Pluronic P123) under a flow of nitrogen (16). Urban *et al* synthesized multiwalled carbon nanotubes by graphitization of as-synthesized mesoporous silicas template by cetyltrimethylammonium bromide (17). Mokaya *et al* showed that periodic mesoporous organosilica surfactant mesophases can be transformed into silica/carbon nanocomposites and mesostructured forms of pure silica, carbon and silica carbide (18).

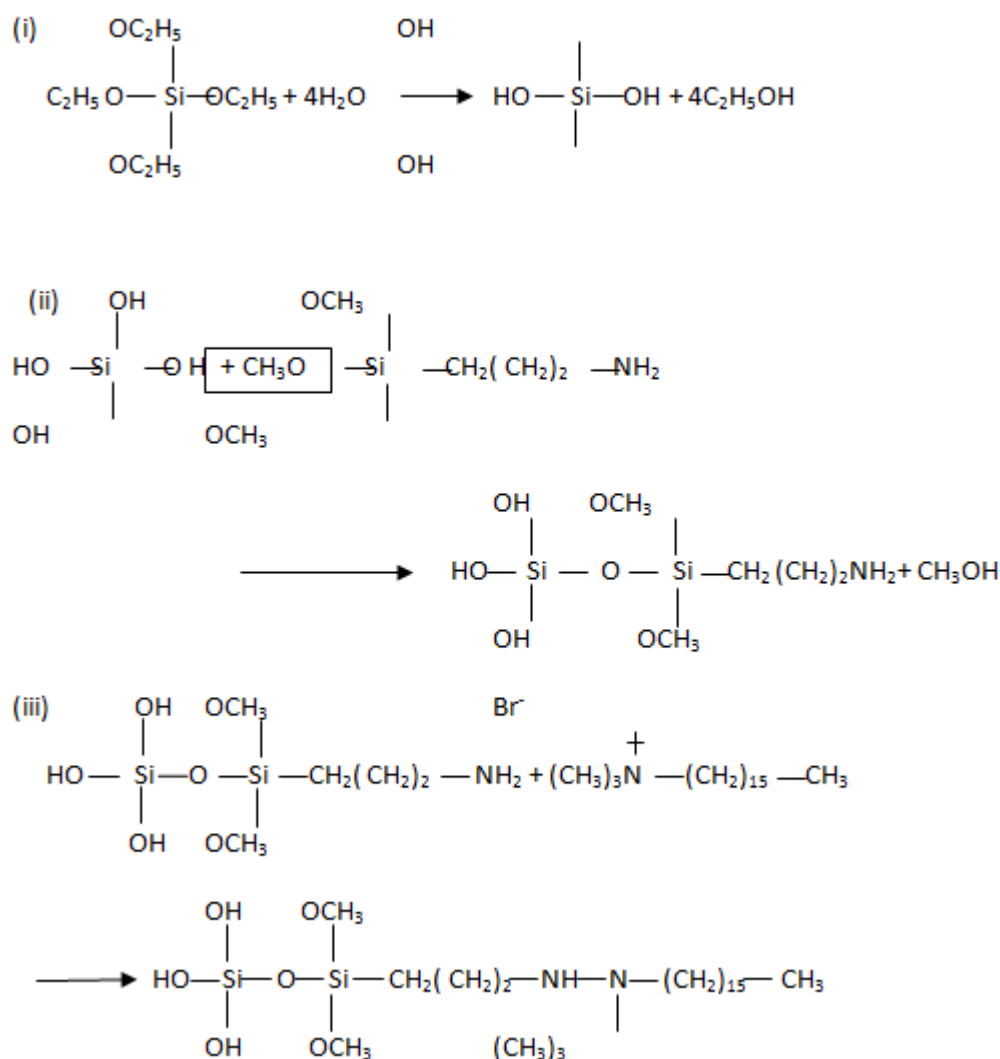
In this study, the sol-gel process was used for the synthesis of as-synthesized and surfactant extracted periodic mesoporous organosilica materials. Two different silica sources were used : tetraethyl orthosilicate (TEOS), and bis

[(3-trimethoxysilyl)propyl]-amine (BTMSPA). One structure directing agents were used, cetyltrimethylammonium bromide (CTAB).

Objective of Study:

- The chemical modification of silica gel surfaces with donor atoms such as N,S,O and p is primarily aimed at improving the adsorption and exchange properties of the Silica gel.
- Due to the presence of many reactive sites on silica gel large number of organic molecule could be immobilized on its surface to improve its sorption behavior by chemical bonding due to simple condensation.
- Analytical applications of the hybrid mesoporous organic – inorganic materials has been increased due to characteristics or large specific surface areas, pore sizes, thermal and chemical resistance, high adsorption capacity and easiness of functionalization.
- Recent works have shown increasing utility of hybrid mesoporous materials to produce sorbent for trace metal enrichment.
- In proposed work, we shall prepare new adsorbent materials by modification of silica using both commercial as well as newly synthesized silane based.

Reaction Scheme



Scheme 1: Preparation of hybrid mesoporous material for the combination of (TEOS)-3-Trimethoxysilylpropylamine using CTAB

MATERIALS AND METHODS

Tetraethyl orbusilicate (TEOS, 98%) bis gamma trimethoxysilylrpopyl amine (TMSPA), cetyltrimethyl ammonium bromide (CTAB) as a structure directing agent was purchased from Aldrich and used as received the demonized water and material were used as co-sulant. NaOH& HCL were used as catalysts.

0.4g of CTAB is dissolved in NaOH solution with constant stirring (Solution A). 5.0ml of silyl amine and 5.0ml of TEOS was taken in a separate beaker and constantly stirred for few minutes (solution B). The addition of solution A and solution B with constant stirring (24hrs) resulted in formation of white ppt. which was washed with demineralized water and subsequently dried in Vacuum-oven at 60°C.

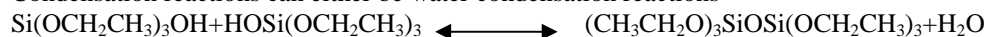
RESULTS AND DISCUSSION

HYDROLYSIS :

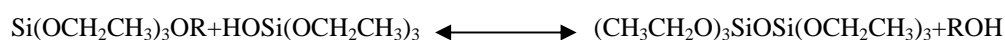
The first step in sol-gel processing of silica (SiO₂) is hydrolysis of silicon dioxide to form a hydroxylated product and a corresponding alcohol (Scheme 1). Scheme 1 Schematic representation of hydrolysis of tetraalkylorthosilicate. The process is catalysed by acids or bases resulting in different reaction mechanisms leading to the condensation reaction as shown in Scheme 1. The pH used therefore has an effect on the kinetics of the reaction which is usually expressed by the gel point of the sol-gel reaction.

CONDENSATION :

Condensation reactions can either be water condensation reactions



Or alcohol condensation reactions :



The material was characterized using FTIR, TGA and SEM (Fig-1) and the result are as follows.

1. The weak band near at 8400 cm⁻¹ is due to the absorbed water engaging with the silanol in hydrogen bonding.
2. The band at 1300 – 1700 cm⁻¹ come from the aminopropyl segment, some other organic groups such as –CH₃, –CH₂ – are assigned at peaks 1350 cm⁻¹, 1413 cm⁻¹ and 1470 cm⁻¹ due to deformation mode.
3. The bond at 930 cm⁻¹ are assumed to Si-O-C.
4. The bands at 785 cm⁻¹ is due to Si-C.
5. The peak 692 cm⁻¹ corresponds to the aminopropyl segment.
6. The band around 622 cm⁻¹ correspond to the bending vibration of Si-O-Si and a strong peak near at 1025 cm⁻¹ is attributed to the symmetric stretching mode of – Si-O-Si of cyclic structure.
7. The peak appeared at 1533 cm⁻¹ assigned to deformation mode (NH) of –CH-moiety from organofunctionalized silica gel material.

It can be seen that when the hybrid samples were prepared under constant sol concentrations at pH =12, the gelation time decreases with increasing mole concentration of TMSPA, suggesting that the gelation time is dominated by the concentration of TMSPA. The shorter gelation time for the TMSPA-rich hybrids may be in part due to transesterifications between the TMSPA and methanol because of the presence of OCH₃ groups [19]. The higher number of methoxy groups of the TMSPA molecule causes a much faster stabilization of the gel. Another possible reason may be that in the case of the reaction of aminosilanes with silica, the reagents themselves possess nucleophilic functions to promote the reaction [20].

THERMAL STABILITY:

Figure 2 shows the TGA curves in nitrogen atmosphere for the synthesized samples. The weight loss is observed mainly in three temperature regions. A significant weight loss occurred for each sample in the first temperature region from room temperature to around 100°C. This weight loss corresponds to the amount of water physisorbed as well as on the silanol surface.

The second significant weight loss in the TGA curves corresponds to the decomposition/ pyrolysis of the bridging organic groups. Depending on the kind as well as the amount and nature of the organic chains / groups degradation starts between 200°C. And 300°C and finishes between 500°C and 600°C. In the present work the temperature of degradation starts from near 250°C and finishes about 650°C. The additional weight loss occurred at higher temperature with a very slow rate due to further condensation of the silicate walls and the compression of the materials to a compacted silica network. It should be noted from the TGA curves of the hybrid materials that the thermal stability of the hybrid materials is higher as the TMSPA concentration is higher.

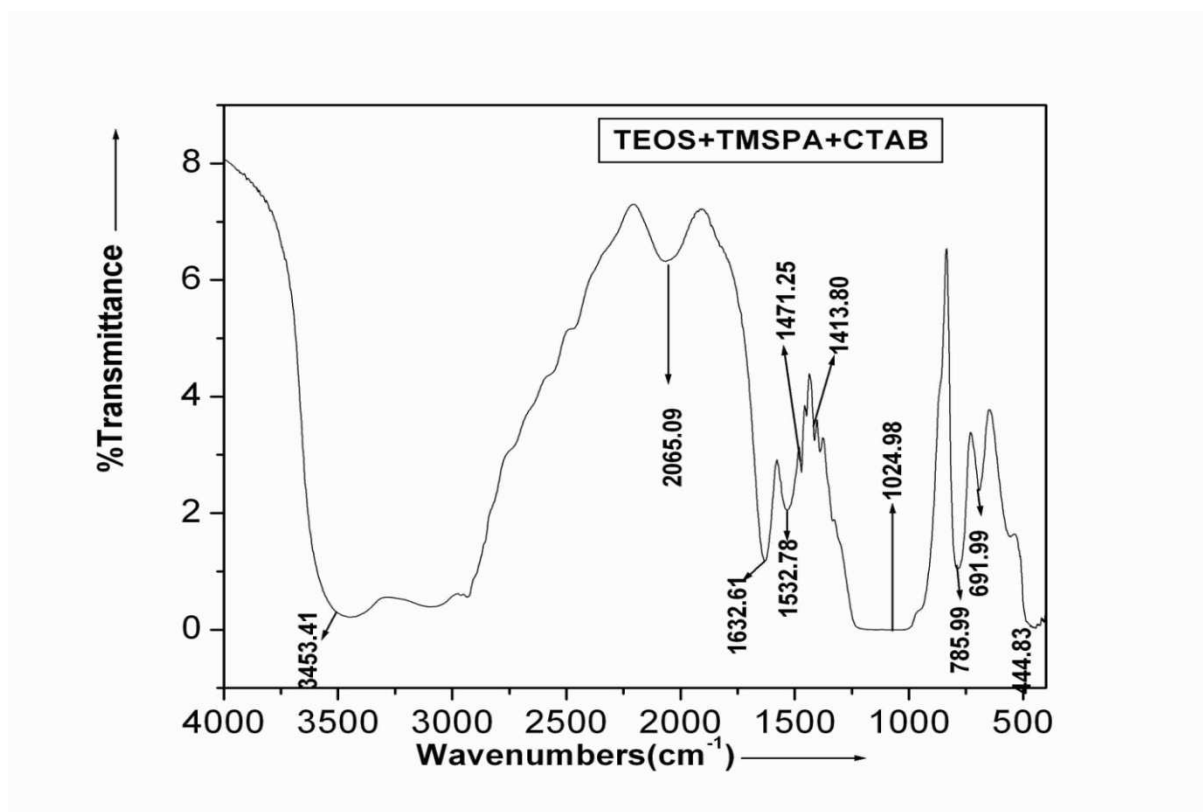


Fig 1: FTIR, TGA and SEM analysis of Hybrid Samples

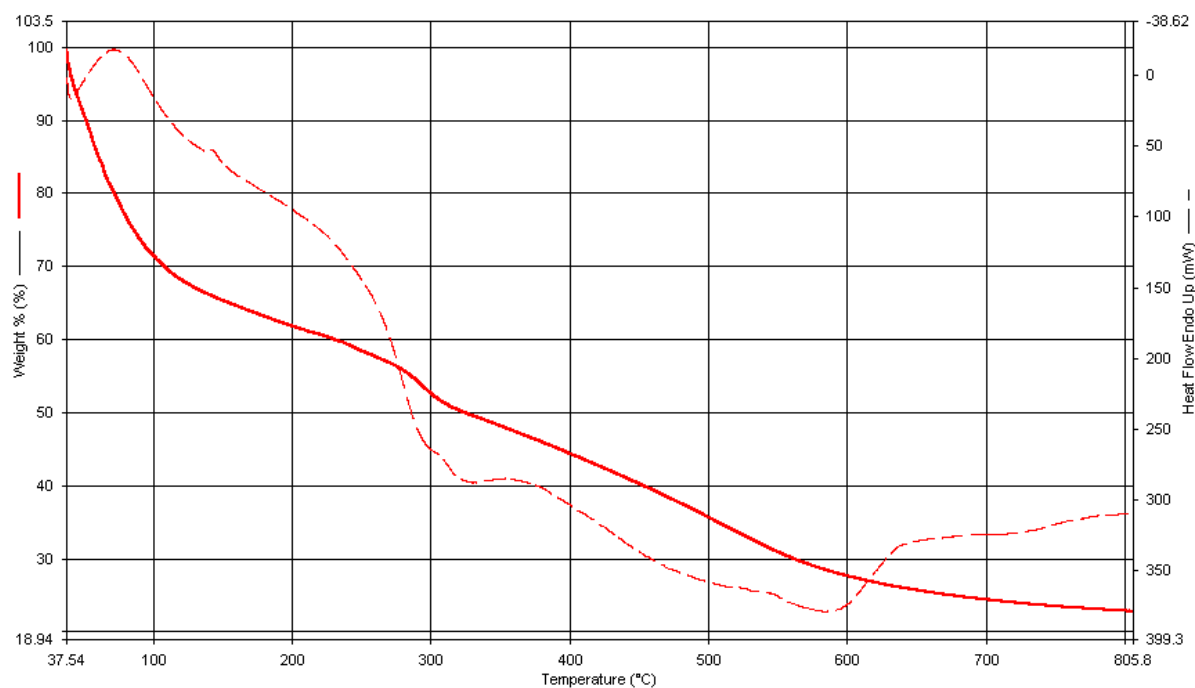


Fig 2: Weight loss and heat flow of hybrid sample in different temperatures

CONCLUSION

In this work, Amorphous hybrid silica materials structure have been successfully prepared by the sol-gel processing using the new precursor bis(gamma-trimethoxysilyl)proylamnine with tetraethyl orthosilicate under different experimental conditions. FTIR, TGA and SEM study demonstrate that the experimental procedure used in this work was successful in altering the chemistry of Silica based Organic-Inorganic hybrid material.

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