Synthesis of Calcium silicate nanoparticles and its catalytic application in Friedlander reaction

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Abstract

This work describes the nitric acid catalysed synthesis of wollastonite ($CaSiO_3$) nanoparticles (NP) from tetra ethyl ortho silicate and calcium nitrate tetra hydrate. The formed calcium silicate nanoparticles were characterized by Fourier transforms infra-red spectroscopy (FT-IR), Powder X-ray Diffraction (PXRD) and scanning electron microscopy (SEM) equipped with X-ray micro analysis. The $CaSiO_3$ NPs showed an excellent yield (93%) towards the synthesis of quinolines *via* Friedlander reaction. The synthesised compound 3-dimethyl-7-nitro-9-phenyl-3,4-dihydroacridin-1(2*H*)-one was characterized by various spectroscopic techniques.

Keywords

Calcium silicate, Particles, nanosized, Friedlander reaction, Spectroscopy

1. Introduction

Ceramic processing is the developing of chemical route for blending the powder materials [**1**]. The Wollastonite ($CaSiO_3$) is a significant material in ceramics, tile and cement manufacturing industries. A congregation of favourable properties such as low shrinkage, whiteness, lack of volatile constituents, good strength, fluxing characteristics, body permeability, and acicular shape render wollastonite useful in several ceramic and other applications [**2**]. Recently, the novel techniques such as spray pyrolysis sol–gel [**3-6**], hydrothermal [**7**], polymer pyrolysis [**8**], etc. has been successfully employed for synthesis of silicate-based phosphor. The ceramics of calcium silicates ($CaSiO_3$) are identifying as a hopeful bioactive materials for bone tissue engineering [**9**].

Heterocyclic compounds have considered as one of the important molecules in pharmaceutical applications. Today's severe environmental problem is to reduce the formation of inorganic wastes, solvent waste, and side products [**10-13**]. The chemistry field is moving towards the eco-friendly synthesis [**14, 15**]. Important research and development frontier in modern science is Nanoscience [**16**]. By reducing the catalyst's size, there will be a more surfaces has been exposed to the reactants for good yield [**17-19**]. In continuation of our earlier work, we have utilized $CaSiO_3$ as nanocatalysts for the formation of quinolines. We have developed inexpensive, economic and novel route for the synthesis of calcium silicate ($CaSiO_3$) NPs. The produced $CaSiO_3$ NPs then was used as a catalyst towards the synthesis of quinolines *via* Friedlander reaction.

2. Methodology

2.1. General procedure for synthesis of $CaSiO_3$ NPs

The following compounds were added to double distilled water in the sequential order: 1.0 M HNO_3, Tetra Ethyl Ortho Silicate (TEOS 99% purity) and soluble calcium nitrate tetra hydrate ($Ca (NO_3)_2.4H_2O$ 99% purity). 16.67g of TEOS was added to double distilled water under vigorous stirring. Then added 4.72g of [$Ca (NO_3)_2. 4H_2O$] that was dissolved in 12 ml of 1.0 M HNO_3 under stirring. After 30 min of hydrolysis, a homogeneous solution was obtained. Nitric acid was used to catalyse the TEOS hydrolysis using H_2O/TEOS molar ratio of 12:1 and H_2O/ HNO_3 volume ratio of 6:1. The round bottom (RB) flask containing solution was hermetically sealed and placed in an oil bath at different ageing temperature at 50 °C to 90 °C for 5 h. Finally, the gel was dried in an oven at 110 °C for 16 h. The dried gels were recovered from the oven and transferred into an alumina crucible and sintered at 900 °C for 2 h to obtain the $CaSiO_3$ catalyst.

As shown in **scheme 1**, an equimolar amount of (2-amino-5-nitrophenyl)(phenyl)methanone, 1 and 5,5-dimethylcyclohexane-1,3-dione, **2** were taken in an clean round bottom flask and 10 mol % $CaSiO_3$ NPs were added to the flask and the mixture was heated at 120 °C for 30 min. The movement of the reaction was supervised by thin layer chromatography test. The reaction mixture was allowed to room temperature and EtOAc (2*30 mL) was added. Then the reaction mixture was filtered and evaporated the filtrate followed by washing with hexane to afford the product as off-white solid with yield of 93 %. The used $CaSiO_3$ NPs was separated and dried for further utilized for the same reaction. The $CaSiO_3$ NPs has been reused five times without significant variation in the isolated yield and it was clearly stated in Figure 2.

We have carried out five replications, provided the isolated yields 93, 93, 91, 91 and 90 % respectively.

Characterization of 3, 3-*dimethyl-7-nitro-9-phenyl-3,4-dihydroacridin-1(2H)-one,* ***3***

The off-white solid; Yield 93 %; mp: 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 6H, -CH_3), 2.64 (s, 2H, -CH_2), 3.34 (s, 2H, -CH_2),7.20 – 7.22 (m, 2H, ArH), 7.57-7.59 (m, 3H, ArH), 8.19 – 8.22 (d, 1H, ArH), 8.45 – 8.46 (m, 1H, ArH), 8.51-8.54 (m,1H, ArH).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 32.2, 48.6, 54.1, 124.1, 124.8, 125.0, 126.7, 128.0, 128.5, 128.5, 130.4, 135.7, 145.5, 150.8, 152.8, 165.1, 197.1. HRMS: m/z calcd. for $C_{21}H_{18}N_2O_3$ 346.1317 found 346.1142.

3. Results & discussion

Fig. 1 shows the FTIR, Powder XRD and SEM – EDAX characterisation of CaSiO3 NPs. The XRD displays more noticeable development of 320, –432 and –921 hkl crystal planes of calcium silicate (JCPDS Card No. 27-0088) and it confirms the presence of crystalline nature of $CaSiO_3$ nanoparticles (**Fig. 1a**). In application point of view, we have optimized the Friedlander reaction conditions using $CaSiO_3$ NPs (10 mol %). In **Fig. 1b** the FTIR spectra shows the H-O-H deformation band observed at 1631cm^{-1} indicates the presence of incorporated water in the SiO_2 network. The hydroxyl band at 3450cm^{-1} was attributed to OH^- groups on the surface of silicone which could be due to the formation of silica gel through hydrolysis and condensation of TEOS (387). The bands at 470 and 810 cm^{-1} are attributed to the ring structure of the SiO_4 tetrahedral. The absorption sharp peak at 1086 cm^{-1} suggested the cross-linking of Si-O-Si bands that occurred via hydrolysis and condensation (385). This observation was further confirmed by the fact that the intensity of the band at 950 cm^{-1}, related to Si-OH stretching vibration is also found to be developed (**Fig. 1b**). From the SEM analysis (**Fig. 1c**), the particles are found to be spherically agglomerated, and the size of the particles are in the range of 200 nm. The elemental composition of calcium silicate powder was further evidenced by EDAX analysis in **Fig. 1d**. All the corresponding elements such as Ca and Si are confirmed from the spectra, and the Au peak has arisen from the gold substrate used for the analysis.

The spectroscopic assignment of the acridone, **3** was done and shown in (**Fig. S1**). In ^{1}H NMR of the compound, **3** there are three singlets, and it has 12 protons which include 6 methyl and 6 methylene protons. A singlet peak at δ 0.91 assigned to 6 methyl protons (2* -CH_3), another two singlets are appeared at δ 2.35 and δ 3.13 corresponding to the 6 methylene protons (3 * -CH_2). In the case of compound 1, there are 10 protons which include 8 aromatic protons and one –NH_2 protons. The –NH_2 proton appears at δ 6.06, and aromatic protons appear in the range of δ 6.67-7.61 (**Fig. S2**). The product **3** has 18 protons which include 6 methyl, 4 methylene and 8 aromatic protons. The 6 methyl protons (H-20 and H-21) shown at δ 1.21 (2 * -CH_3) and 4 methylene protons (2 * -CH_2) shown at δ 2.64 (H-4) and δ 3.34 (H-2). Then the remaining eight Ar-H were resonating in the range of δ 7.50 – 8.54 (8 ArH)

In ^{13}C NMR**,** there are 4 signals at δ 28.3, 32.2, 48.6, and 54.1 are corresponds to C-20, C-21, C-3, C-4 and C-2 respectively. The C-20 and C-21 appear at single signal due to their same environment and we are getting a peak at δ 197.1 is assigned for C-1 (-C=O carbon). The remaining protonated and non-protonated carbons resonate in their respective aromatic region. The compound **3** has two methyl carbons (C-20, C-21), two methylene carbons (C-2, C-4), one aliphatic methine carbon (C-3), seven aromatic non-protonated carbons, eight aromatic methine carbons and one carbonyl carbon (**Fig S3**). The assignment of aromatic carbon by using ^{13}C NMR alone is quite difficult. The assignment of carbon peaks is simplifying by recording DEPT -45, DEPT-90 and DEPT-135. The DEPT – 45 NMR of the compound **3** shows only protonated carbons. It shows 11 protonated carbon signals which is matching with the required product. The DEPT -90 NMR also recorded for compound 3, there are eight methine carbons complies with product's structure. We are getting 6 signals from DEPT -90 NMR, the C-14 and C-18 appears at δ 128.0 and C-15 and C-17 appears at 128.5 due to their same environment (**Fig. S3**). We also record the DEPT -135 NMR for compound **3** which provides the information about methyl, methylene and methine carbons attached to the compound. We are getting, one upward signal at δ 28.3 corresponds to C-20and C-21. Then two inverted signals at δ 48.8 and δ 54.1 are an assignment for C-3 and C-4 respectively. Usually, the methine carbons are not shown in DEPT-135 NMR.

4. Conclusions

We developed an easy and economic method to synthesize calcium silicate NPs. The calcium silicate NPs provide promising result towards the synthesis of quinolones *via* Friedlander reaction and 93 % of yield was achieved.

Supplementary Material

Supplemental data for this article can be accessed at the publisher's website.

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References

[1] Winterstein, J.P.; Carter, C.B. Electron beam damage and point defects near grain boundaries in cerium oxide. *J. Eur. Ceram. Soc*. **2014**, 34, 3007-3018.

[2] Rieger, K.G. Sintered apatite wollastonite glass-ceramics. *Ceram Int.* **2000**, 26, 779-785.

[3] Lin, J.; Sanger, V; Mennig, M.; Barner, K. Sol–gel deposition and characterization of Mn^{2+}-doped silicate phosphor films. *Thin Solid Films*. **2000**, 360, 39-45.

[4] Ahmadi, T.S.; Haase, M; Weller, H. Mater. Low-temperature synthesis of pure and Mn-doped willemite phosphor (Zn_2SiO_4:Mn) in aqueous medium. *Res. Bull.* **2000**, 35, 1869-1879.

[5] Zhang, H.X.; Buddhudu, V.S.; Kam, C.H.; Zhou, Y.; Lam, Y.L.; Wong, K.S.; Ooi, B.S.; Ng, S.L.; Que, W.X. Luminescence of Eu3+ and Tb3+ doped Zn2SiO4 nanometer powder phosphors. *Mater. Chem. Phys.* **2001**, 68, 31-35.

[6] Lenggoro, I.W; Iskandar, F.; Mizushima, H.; Xia, B.; Okuyama, K.; Kijima, N. One-Step Synthesis for Zn_2SiO_4:Mn Particles 0.3–1.3 µm in Size with Spherical Morphology and Non-Aggregation. *Jpn. J. Appl. Phys. Lett.* **2000**, 39, 1051-1053.

[7] Lu, S.W.; Copeland, T.; Lee, B.I.; Tong, W.; Wasgner, B.K.; Park, W.; Zhang, F. Synthesis and luminescent properties of Mn2+ doped Zn2SiO4 phosphors by a hydrothermal method. *J. Phys. Chem. Solids.* **2001**, 62, 777-781.

[8] Su, K.; Tilley, D.T.; Sailor, M.J. Molecular and Polymer Precursor Routes to Manganese-Doped Zinc Orthosilicate Phosphors. *J. Am. Chem. Soc.* **1996**, 118, 3459-3468.

[9] Patil, S.M.; Kulkarni, S.; Mascarenhas, M.; Sharma, R.; Roopan, S.M. A. Roychowdhury, DMSO–$POCl_3$: a reagent for methylthiolation of imidazo[1,2-a]pyridines and other imidazo-fused heterocycles, *Tetrahedron*. **2013**, 69, 8255-8262

[10] A) Eshghi, H.; Nasseri, M.A.; Sandaroos, R.; Molaei, H.R.; Damavandi, S. Ferric Hydrogensulfate-Catalyzed One-Pot Synthesis of Indeno[1,2-*b*]quinoline-7-ones. *Synth. React. Inorg. Met.-Org. Chem.* **2012**, 42, 573-578. B) Elango, G.; Kumaran, S.M.; Kumar, S.S.; Muthuraja, S.; Roopan, S.M. Green synthesis of SnO_2 nanoparticles and its photocatalytic activity of phenolsulfonphthalein dye. *Spectrochim. Acta A.* **2015**, 145, 176-180. C) Kalaiselvi, A.; Roopan, S.M.; Madhumitha, G.; Ramalingam, C.; Elango, G. Synthesis and characterization of palladium nanoparticles using Catharanthus roseus leaf extract and its application in the photo-catalytic degradation. *Spectrochim. Acta A.* **2015**, 135, 116-119.

[11] Roopan, S.M.; Khan, F.R.N. SnO_2 nanoparticles mediated non-traditional synthesis of biologically active 9-chloro-6,13-dihydro-7-phenyyl-5H-indolo [3,2-c]-acridine derivatives. *Med. Chem. Res.* **2011**, 20, 732-737.

[12] Roopan, S.M.; Khan, F.R.N. ZnO nanoparticles in the synthesis of AB ring core of camptothecin, *Chem. Pap.* **2010**, 64, 812-817.

[13] Roopan, S.M.; Maiyalagan, T.; Khan, F.R.N. Solvent-free syntheses of some quinazoline-4(3*H*)-ones derivatives. *Can J Chem.* **2008**, 86, 1019-1025.

[14] A) Palaniraja, J.; Roopan, S.M. UV-light induced domino type reactions: synthesis and photophysical properties of unreported nitrogen ring junction quinazolines. *RSC Adv.* **2015**, 5, 37415-37423. B) Roopan, S.M.; Patil, S.M.; Palaniraja, J. Recent synthetic

scenario on imidazo[1,2-*a*]pyridines chemical intermediate. *Res Chem Intermed.* **2016**, 42, 2749-2790.

[15] Bharathi, A.; Roopan, S. M.; Kajbafvala, A.; Padmaja, R.D.; Darsana, M.S.; Kumari, G.N. Catalytic activity of TiO_2 nanoparticles in the synthesis of some 2,3-disubstituted dihydroquinazolin-4(1*H*)-ones, *Chinese Chem. Lett.* **2014**, 25, 324-326.

[16] A) Kaur, N. Metal Catalysts for the Formation of Six-Membered N-Polyheterocycles. *Synth. React. Inorg. Met.-Org. Chem.* **2016**, 46, 983-1020. B) Roopan, S.M.; Palaniraja, J. Synthetic journey towards transition metal-free arylations. *Res Chem Intermed.* **2015**, 41, 8111-8146.

[17] A) Palaniraja, J.; Roopan, S.M. Iodine-mediated synthesis of indazoloquinazolinones via a multi-component reaction. *RSC Adv.* **2015**, 5, 8640-8646. B) Roopan, S.M.; Bharathi, A.; Palaniraja, J.; Anand, K.; Gengan, R.M. Unexpected regiospecific Michael addition product: synthesis of 5,6-dihydrobenzo[1,7]-phenanthrolines. *RSC Adv.* **2015**, 5, 38640-38645.

[18] Subashini, R.; Bharathi, A.; Roopan, S.M.; Rajakumar, G.; Rahuman, A.A.; Gullanki, P.K. Synthesis, spectral characterization and larvicidal activity of acridin-1(2*H*)-one analogues. *Spectrochim. Acta, Part A.* **2012**, 95, 442-445.

[19] Roopan, S.M.; Khan, F.R.N.; Mandal, B.K. Fe nano particles mediated C-N bond forming reaction: Regioselective synthesis of 4-[(2-chloroquinolin-3-yl)methyl]pyrimidin-4(3*H*)ones, *Tetrahedron Lett.* **2010,** 51, 2309-2311.

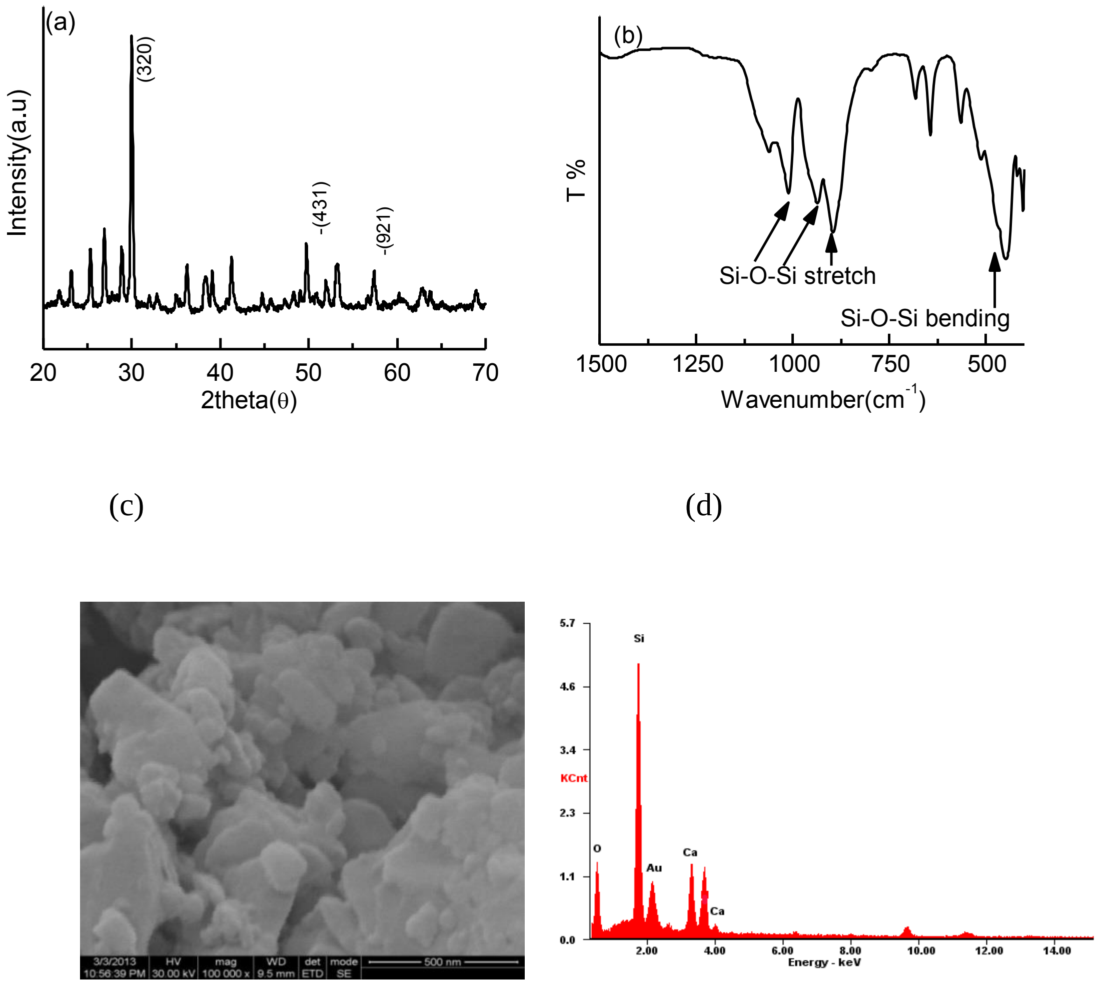


Fig. 1 XRD (a), FT-IR (b), SEM (c) and EDAX (d) analysis of calcium silicate nanoparticles `

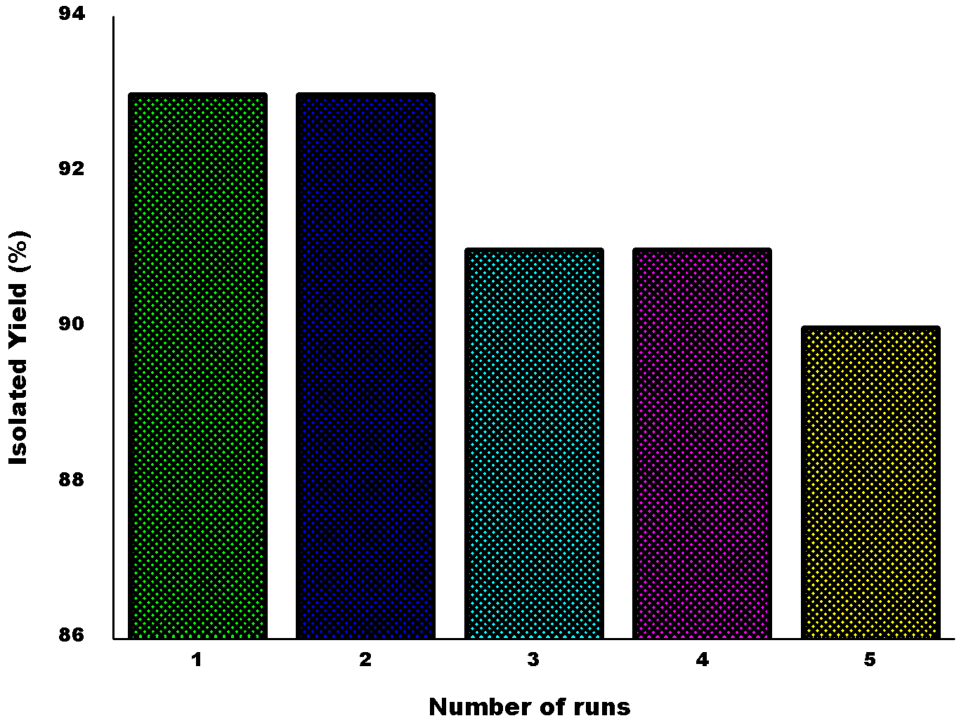
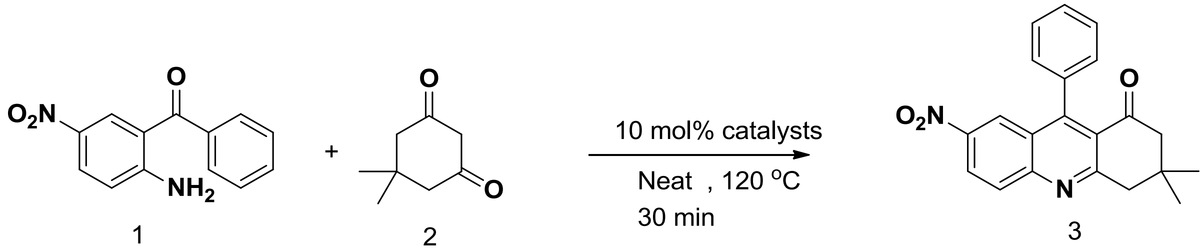


Fig. 2 Reusability of $CaSiO_3$ NPs towards a Friedlander reaction



Scheme. 1 Synthesis of 3,3-dimethyl-7-nitro-9-phenyl-3,4-dihydroacridin-1(2*H*)-one, **3**