

## MWCNT incorporated silica aerogel prepared by ambient pressure drying: A recyclable catalyst for multicomponent synthesis of benzylpyrazolyl coumarin at room temperature

Isak Rajjak Shaikh<sup>a,f,\*</sup>, Noor Mahmad Nabisaheb Maldar<sup>b</sup>, Caroline Sunyong Lee<sup>c</sup>, Rajendra Charandeo Pawar<sup>c</sup>, Hyung-Ho Park<sup>d</sup>, Uzma Khwaja-Husain Bangi<sup>e,\*</sup>

<sup>a</sup>School of Chemical Sciences, Swami Ramanand Teerth Marathwada University (SRTMU), Vishnupuri, Nanded – 431 606 (Maharashtra) India

<sup>b</sup>School of Chemical Sciences, Solapur University, Solapur-Pune National Highway, Kegaon, Solapur – 413 255 (Maharashtra) India

<sup>c</sup>Hanyang University ERICA campus, 5<sup>th</sup> Engineering Building, 55 Hanyangdaehak-ro, Sangrok-gu Ansan-si, Gyeonggi-do 426-791, South Korea

<sup>d</sup>Department of Materials Science and Engineering, Yonsei University, Seodaemun-gu, Seoul 120-749, Republic of Korea

<sup>e</sup>School of Physical Sciences, Solapur University, Solapur-Pune National Highway, Kegaon, Solapur – 413 255 (Maharashtra) India

<sup>f</sup>Razak Institution of Skills, Education and Research, Nanded (Maharashtra) Republic of India

Received: 21 December 2016, Accepted: 18 November 2017, Published: 18 November 2017

### Abstract

Multiwalled Carbon Nanotube (MWCNT) reinforced silica aerogel was synthesized in a very simple and cost effective sol - gel method. The process was followed by ambient pressure drying, and then the aerogel material was characterized by XRD, BET, SEM, EDX and FT-IR.  $2.3 \times 10^{-3}$  wt% MWCNTs were successfully incorporated in sodium silicate based silica aerogel. This metal-free nanocomposite catalyzed a four component organic reaction among 4-hydroxy coumarin, benzaldehyde, phenyl hydrazine, and ethyl acetoacetate for synthesizing medicinally important benzylpyrazolyl coumarin at room temperature. The MWCNT/silica aerogel composite material having easy accessible active sites and high catalytic activity was easily recovered and reused. The aerogel composite when impregnated with ceria offered very efficient and selective reaction methodology.

**Keywords:** MWCNT/silica aerogel synthesis; ambient pressure drying; heterogeneous catalysis; multicomponent reaction; benzylpyrazolyl coumarin.

### Introduction

Multicomponent reactions (MCR) with atom economy, cost and energy savings, selectivity to desired product, easy work-up, catalyst recyclability and

the avoidance of metals and hazardous chemicals are of increasing importance among the wide range of methodologies explored in greening organic chemistry for the design and syntheses of biologically active molecules [1]. Partha P. Ghosh et

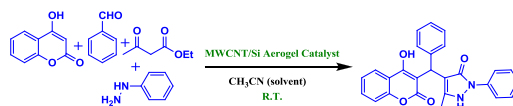
\*Corresponding author: Isak R. Shaikh & Uzma Bangi

Tel: +91 (800) 7000736, Fax: N/A

E-mail: isak@india.com, uzma.phys@gmail.com

al [2] reported one such MCR for the combinatorial synthesis of highly functionalized benzylpyrazolyl coumarin scaffolds. That was a four-component reaction catalyzed by glacial acetic acid in water under reflux condition. Herein, we focus our attention on developing an aerogel based composite to catalyze this useful convergent reaction protocol. Aerogels are low density, porous and high surface area materials wherein the liquid component inside the wet gel is exchanged by air without damaging the solid microstructure [3-4]. Aerogels provide the framework for nanomaterial to exist in a three dimensional space. And so, new possibilities to tailor the composition and the structure of the aerogels' nanostructured composite matrix opened up a new universe of

possibilities and provided new proving grounds for the scientific fraternity in using such materials in a broad spectrum of applications including adsorption [5] and catalysis [6-9]. Off late, silica aerogels and metal-modified aerogels have been widely employed as catalyst support and catalysts [9-13]. Similarly, carbon [14] and the advanced material thereof like the Carbon Nano Tubes (CNTs) [15-19] can substitute conventional catalyst supports and can perform catalysis and separation [20]. Uzma K. H. Bangi *et al* used the Multi Walled Carbon Nanotubes (MWCNTs) as reinforcement to improve the mechanical properties of silica aerogels [21]. MWCNT/Silica aerogel composites are useful hybrid aerogels [22-23] and are easier to modify or fabricate than the pure carbon aerogels.



**Scheme 1.** Benzylpyrazolyl coumarin synthesis over the MWCNT incorporated silica aerogel

In this work, sol - gel method was employed to prepare MWCNT incorporated silica aerogel with  $2.3 \times 10^{-3}$  wt% of MWCNTs. This ambient pressure dried aerogel nanocomposite was characterized by XRD, BET, SEM, EDX, FT-IR, etc and evaluated as a catalyst in the MCR of phenyl hydrazine, ethyl acetoacetate, benzaldehyde and 4-hydroxycoumarin at room temperature within short time in acetonitrile solvent to yield medicinally relevant benzylpyrazolyl coumarin. It is evident from the characterization that there is no metal impurity responsible for this catalytic property.

## Experimental

### Catalyst preparation

The chemicals used for the synthesis of MWCNTs incorporated silica aerogel

are: sodium silicate (s-d fine chemicals, India,  $\text{Na}_2\text{SiO}_3$  content 36 wt%,  $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.33$ ), citric acid-hydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , Merck, India), methanol (MeOH), hexane (Merck, India), trimethylchlorosilane (TMCS, Fluka, Pursis grade, Switzerland), multiwalled carbon nanotubes (MWCNTs, D-20 nm, L-0.1  $\mu\text{m}$ , purity-99%, Mollad, Mumbai) and Tween 80 (Polyethylene oxide (20) sorbitan monooleate, Fluka). Sodium silicate is a water soluble inorganic compound and produces an alkaline solution having pH in the range of 11-12.5. In a typical experiment, the dispersion of MWCNTs ( $2.3 \times 10^{-3}$  wt%) was carried out by subjecting the mixture of MWCNTs, de-ionized water and Tween 80 to ultrasonication for 4 h. Thereafter, the gel was formed by mixing sodium silicate, MWCNTs and citric acid.

During the synthesis, the H<sub>2</sub>O:Na<sub>2</sub>SiO<sub>3</sub> molar ratio and the concentration of MWCNTs were kept constant at 146.67 and 2.3x10<sup>-3</sup> wt% respectively and gel aging, solvent exchange, silylation and drying were subsequently performed. Factually, similar materials were reported earlier by Bargozin, H. et al. [21] from Iran and by our colleague [23] with a little difference in the preparation method (with different wt% MWCNTs incorporated within silica aerogel).

#### **Catalyst characterization**

The composition of synthesized aerogel was determined by X-ray diffraction (XRD) pattern using Ultima IV model (Rigaku, Japan) X-ray Diffractometer. For the analysis, Cu K $\alpha$  radiation with a wavelength of 1.541 Å ranging from 10° to 100° was applied. Elemental analysis performed by the Scanning electron microscopy (SEM; Hitachi S4800) analyzed the morphology of the aerogel composite. Energy-Dispersive X-ray spectroscopy (EDX) is shown in weight% and atomic%. The surface area, pore volume and average pore diameter of the aerogel were measured using BET analyser (Micromeritics Tristar 3000) from the amount of N<sub>2</sub> gases adsorbed at various partial pressures. The surface area, pore volume and average pore diameter of the as synthesized aerogel were determined using nitrogen adsorption-desorption isotherms with a Quantochrome machine cooled to liquid nitrogen temperatures (AS1). To determine the chemical bonds present in the aerogels, Fourier transform infrared spectroscopy (Nicolet iS10 Mid Infrared, Thermo Electron Scientific, USA) was used. The bulk density and % porosity are calculated using the formulae reported elsewhere [24].

#### **The four-component reaction**

The catalytic property of the MWCNT incorporated silica aerogel was studied by employing 15 mg of material in the four-component reaction of phenyl hydrazine (1.0 mmol), ethyl acetoacetate (1.0 mmol), benzaldehyde (1.0 mmol) and 4-hydroxycoumarin (1.0 mmol) in the presence of acetonitrile as the solvent at room temperature and it afforded 60% yield of the desired benzylpyrazolyl coumarin product within 40 minutes.

#### **Various techniques for characterizing organic reaction products**

Thin Layer Chromatography (TLC) was performed on GF 25U (Anal Tech) plates and silica gel glass-backed plates. Silica gel of 100-200 mesh was used column chromatographic separation. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on varian Gemini spectrometer 300 MHz. Melting points were determined on electrothermal Gallenkamp apparatus. Infra-red spectra of organic products were recorded on Nicolet Fourier Transform spectrometer. Mass spectra were recorded on VG Autospec Mass spectrometer.

#### **Results and discussion**

##### *Preparation and characterization of the MWCNT incorporated silica aerogel catalyst*

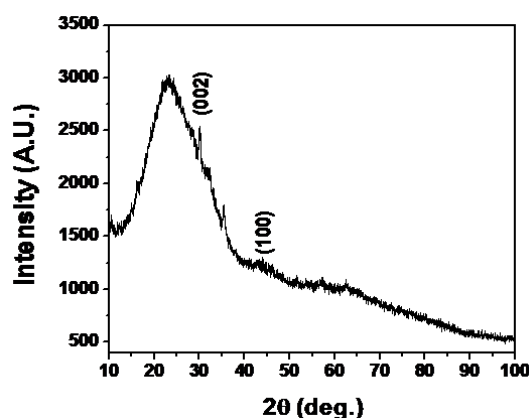
The aim of this work was to prepare MWCNT (2.3 x 10<sup>-3</sup> wt%) incorporated silica aerogel material by ambient pressure drying. Herein, low density (0.056 g/cc), highly porous (97%), large surface area (645.65 m<sup>2</sup>/g), semitransparent and super hydrophobic (148°) MWCNT incorporated silica aerogel. This composite offers scope for its utility in organic reactions because of high

silicon content and hydrophobic nature due to surface  $-\text{CH}_3$  groups.

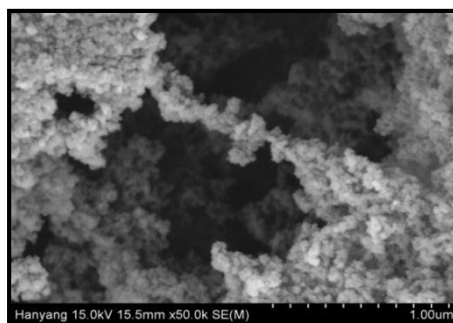
The broad peak in the XRD pattern (Figure 1) indicates the nanostructured nature of the silica aerogel with two small peaks at  $2\theta$  of around  $30.04^\circ$  and  $43.9^\circ$  corresponding to (002) and (100) planes of MWCNTs [25]. This clarifies that MWCNT is incorporated well in silica aerogel. The specific surface area, pore volume and pore size were derived from the  $\text{N}_2$  adsorption–desorption isotherm at 77 K (cf. Supporting Information). The catalyst exhibited type IV isotherms with a type H1 hysteresis loop, typical for mesoporous materials. Further, the material showed broad asymmetrical pore size distributions in the micro-mesopore range with more mesopores. The catalytic material exhibits a very high BET surface area of  $645.65 \text{ m}^2/\text{g}$ , Langmuir surface area  $1406.3 \text{ m}^2/\text{g}$ , BJH surface area  $740.60 \text{ m}^2/\text{g}$ , pore volume  $2.0113 \text{ cc/g}$  and the pore size of  $12.46 \text{ nm}$ . The FE-SEM image (Figure 2) manifests the agglomeration of silica particles on the sidewalls of MWCNTs. The elemental analysis from EDX

(Table 1) confirms the presence of Si, O and C atoms. There were no metal impurities present within MWCNTs or the MWCNT incorporated silica aerogel. The presence of high atomic percentage of carbon (50.87 %) is due to the surface methyl groups and MWCNTs. The hydrophobic surface was generated by replacing the H atoms from surface  $-\text{OH}$  with hydrophobic  $-\text{CH}_3$  groups in trimethylchlorosilane.

The MWCNTs form bonds with silica particles. The chemical bondings present in the MWCNT/silica aerogel nanocomposite were analyzed accurately by FT-IR spectroscopy (Figure 3). Transmittance peaks near  $3410$  and  $1615 \text{ cm}^{-1}$  are due to weak OH stretching and bending vibrations. The IR band near  $1065 \text{ cm}^{-1}$  is due to O–Si–O asymmetric stretching and bending vibrations. There are additional bands at  $2960 \text{ cm}^{-1}$  related to C–H and near  $844 \text{ cm}^{-1}$  related to Si–C. The peak at around  $800 \text{ cm}^{-1}$  corresponds to Si–O–Si bond. There is a weak peak at around  $1630 \text{ cm}^{-1}$  corresponding to the C=C stretching of the MWCNTs [26].



**Figure 1.** XRD of MWCNT incorporated silica aerogel



**Figure 2.** FE-SEM image of MWCNT incorporated silica aerogel

### **MWCNTs incorporated silica aerogel catalyzed multicomponent reaction**

The MWCNTs incorporated silica aerogel catalyzed four-component reaction of phenyl hydrazine (1.0 mmol), ethyl acetoacetate (1.0 mmol), benzaldehyde (1.0 mmol) and 4-hydroxycoumarin (1.0 mmol) in the presence of acetonitrile affording around 60% yield of the desired product within 40 minutes. After completion of reaction, the catalyst was immediately filtered out for its reusability and cold water was added to the reaction mixture (for easy and appropriate work-up). The organic product was re-crystallized using ethanol and then characterized (P.S.: Spectroscopic characterization data below and also the Figure 1 in Supporting Information).

Acetonitrile is found to be the suitable solvent for carrying out this MCR at room temperature (R.T.); however, the same reaction did not proceed in the presence of methanol at room temperature (Scheme 1 and Table 2). This might be due to the inhibition of active sites of the composite because of methanol adsorption. The surface might be releasing methanol as we go on increasing the reaction temperature to the boiling temperature of the methanol and so the reaction proceeded under refluxing (methanol). The authors

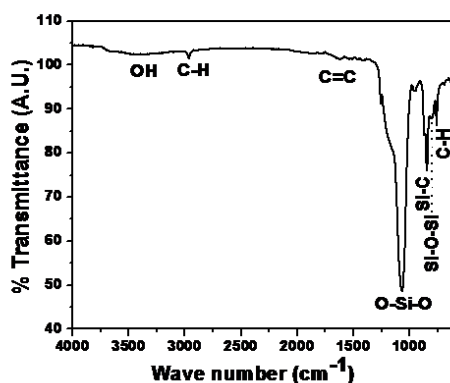
herein mainly highlight only one reference [2] for the synthesis of benzylpyrazolyl coumarin; meanwhile few more papers have also been published by the research group of Banerjee [27-28]. Factually, these reported methods [2, 27-28] look more efficient than the present report, but in view of interesting catalytic application of this MWCNT reinforced silica aerogel, our researches presented here in this manuscript promises to open new gate for heterogeneous catalysis and chemistry. The heterogeneous catalyst under study is easily recovered and reused, and the methodology offers the scope to understand the individual and or co-operative effects of defects or accessible catalytic sites present with the MWCNT/silica aerogel composite. Active sites for the MCR on this catalytic material could have been generated by dehydroxylation of surface isolated hydroxyl groups or the strained siloxane bridge. Though there seems no direct evidence of carbocatalysis as such, there is no metal impurity (in MWCNTs) responsible for this catalytic application. To the best of our knowledge, no such work on multicomponent reactions over an aerogel based catalyst prepared by ambient pressure drying has been reported yet.

**Table 1.** Elemental analysis

Element	Weight%	Atomic%
C K	40.51	50.87
O K	42.36	39.93
Si K	17.12	9.19
Total	100.00	

**Table 2.** Catalytic performance data

Catalyst	Solvent	Temp. (°C)	Time	Yield (%)
No catalyst	CH <sub>3</sub> OH	Room Temp. (R.T.)	24 hrs	-
No catalyst	CH <sub>3</sub> CN	Reflux (82 °C)	4 hrs	-
<b>MWCNT/ Silica Aerogel</b>	<b>CH<sub>3</sub>CN</b>	<b>R.T.</b>	<b>40 min</b>	<b>60</b>
No catalyst	CH <sub>3</sub> OH	R.T.	24 hrs	-
MWCNT/ Silica Aerogel	CH <sub>3</sub> OH	R.T.	4 hrs	-
MWCNT/ Silica Aerogel	CH <sub>3</sub> OH	Reflux (65 °C)	4 hrs	25
Ceria onto MWCNT/Silica Aerogel	<b>H<sub>2</sub>O</b>	Reflux (100 °C)	15 to 20 min	90 (1 PDT)

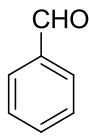
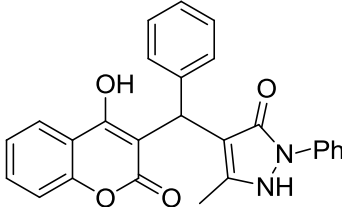


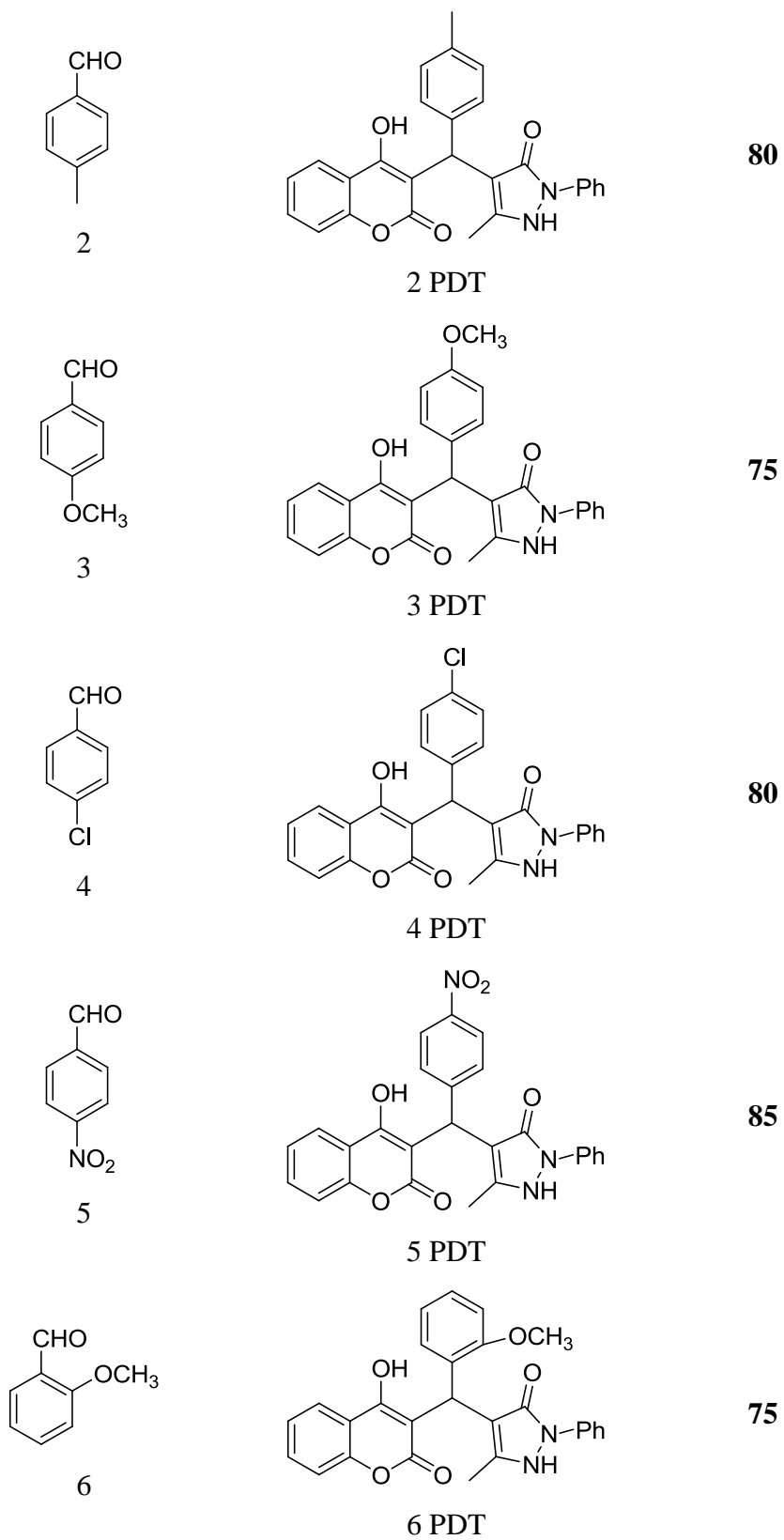
**Figure 3.** FT-IR spectrum of the MWCNT incorporated silica aerogel

In order to optimize the reaction conditions [29], the use of water as solvent and the use of ceria impregnated MWCNT/Silica aerogel catalyst were examined with changing aromatic aldehydes as the substrates yielding various benzylpyrazolyl coumarin derivatives. (Table 3). It was observed that the formation of product is selectively favored with stirring in water upto its reflux temperature within a very short time allowing easy separation of product. Off late, one of our colleagues tried using ceric ammonium nitrate as a catalyst for synthesizing benzylpyrazolyl coumarin

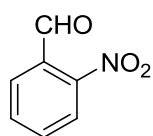
[30]. Herein, we impregnated a catalytic amount of ceria onto the existing aerogel composite to achieve very rapid and high percent yields of various compounds containing benzylpyrazolyl coumarin moiety. This selective and energy-saving methodology minimizes chemical wastage and allows easy isolation of product in water. No leaching of metal impurities observed within reaction time of 15 minutes. The products 1 PDT to 5 PDT are reported in the past [31] but the products namely 6 PDT to 8 PDT are novel and are being reported for the first time here.

**Table 3.** Synthesis of various benzylpyrazolyl coumarin derivatives over ceria modified MWCNT/Silica aerogel using different aromatic aldehydes in the MCRs in water at reflux temperature within 15 to 20 minutes <sup>a</sup>

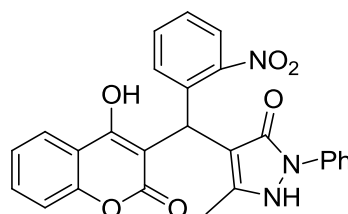
Aromatic Aldehydes	Products	Yield (%) <sup>b</sup>
 1	 1 PDT	90





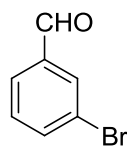


7

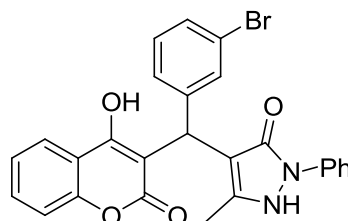


7 PDT

80



8



8 PDT

80

aReaction conditions: 2.0 mmol of 4-hydroxy coumarin, 1.0 mmol of benzaldehyde, 1.0 mmol of ethylacetoacetate, 1.0 mmol of phenyl hydrazine; b Isolated yield.

#### Characterization of the organic product 1 PDT

Name: 4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(phenyl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-one. Melting Point: 233-234 °C, White solid.

<sup>1</sup>H NMR (300 MHz; DMSO-d<sub>6</sub>): methyl group attached to pyrazolone ring at 2.38 (s, 3H); CH proton (methyl group) at 5.75 (s, 1H); fourteen aromatic protons at 7.16-7.29 (m, 8H), at 7.41-7.51 (m, 2H), at 7.67-7.70 (m, 2H), at 7.79-7.82 (d, *J*=7.8 Hz, 2H); a broad signal at 12.11 (bs, 1H) of NH proton from pyrazolone moiety.

The characterization data of this product (1 PDT) is also shown in the Supporting Information and the characterization data for some of the other useful products is placed below.

**Characterisation of the MCR products 6 PDT, 7 PDT and 8 PDT:**  
**4-((4-Hydroxy-2-oxo-2H-chromen-3-yl)(2-methoxyphenyl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-one (6 PDT)**

Melting Point: 205-207 °C. White solid. IR (Neat): 3081, 1654, 1610, 1556, 1500, 1179, 1037, 754 cm<sup>-1</sup>. <sup>1</sup>H (300 MHz; DMSO-d<sub>6</sub>; Me4Si): δ 2.34 (s, 3H), 3.68 (s, 3H), 5.64 (s, 1H), 6.65-6.68 (d, *J*=8.7 Hz, 2H), 7.03-7.19 (m, 5H), 7.31-7.41 (m, 3H), 7.57-7.59 (d, *J*=8.1 Hz, 2H), 7.73-7.75 (d, *J*=7.8 Hz, 1H); <sup>13</sup>C (75 MHz, DMSO-d<sub>6</sub>; Me4Si): δ 9.6, 32.3, 54.0, 105.7, 106.2, 112.5, 114.7, 117.5, 119.7, 122.4, 123.1, 125.4, 126.9, 128.0, 130.2, 130.4, 134.6, 146.0, 151.3, 156.8, 162.9, 164.1; Mass Spectrum EI *m/z* (rel. abundance %): 455 (M<sup>+</sup>, 40).

**4-((4-Hydroxy-2-oxo-2H-chromen-3-yl)(2-nitrophenyl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-one (7 PDT)**

Melting Point: 240-242 °C. Pale yellow solid. IR (Neat): 3073, 1649, 1608, 1560, 1525, 1178, 1039, 748 cm<sup>-1</sup>; <sup>1</sup>H (300 MHz; DMSO-d<sub>6</sub>): δ 2.69 (s, 3H), 6.15 (s, 1H), 7.26-7.58 (m, 9H), 7.91-8.94 (m, 5H); <sup>13</sup>C (75 MHz, DMSO-d<sub>6</sub>): δ 12.34, 35.22, 103.61, 115.48, 118.61, 120.65, 120.79, 121.71, 122.19,

123.66, 124.68, 126.97, 127.12, 127.79, 128.96, 131.17, 131.27, 132.30, 135.81, 138.79, 142.76, 147.84, 151.78, 164.56, 165.98, 166.72; Mass Spectrum EI m/z (rel. abundance %): 470 ( $M^{+1}$ , 40).

**4-((3-bromophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-one (8 PDT)**

Melting Point: 224-226 °C; White solid; IR (Neat): 3078, 1655, 1613, 1570, 1490, 1187, 1099, 756  $cm^{-1}$ ;  $^1H$  (300 MHz; DMSO- $d_6$ ):  $\delta$  2.37(s, 3H), 5.69 (s, 1H), 7.13-7.27 (m, 8H), 7.35-7.50 (m, 3H), 7.60-7.91 (m, 3H) ;  $^{13}C$  (75 MHz, DMSO- $d_6$ ):  $\delta$  10.48, 34.02, 105.81, 106.72, 115.51, 118.07, 120.25, 121.50, 123.33, 124.27, 126.38, 127.87, 128.62, 129.46, 129.87, 130.92, 131.83, 135.1, 138.1, 146.6, 151.9, 162.2, 163.6, 164.3; Mass Spectrum EI m/z (rel. abundance %): 459 ( $M^{+1}$ , 100).

During the course of this paper preparation, we successfully employed the MWCNT/silica aerogel composite to catalyze the classical methodology for synthesis of tetraketone from benzaldehyde and 5,5-dimethylcyclohexane-1,3-dione (dimedone) at room temperature stirring within 30 minutes in acetonitrile solvent.

The reaction protocol affords 100% conversion and 100% selectivity to the product. In another methodology, 2 moles of 4-hydroxy coumarin reacted with one mole of benzaldehyde in acetonitrile solvent to yield the biscoumarin.

**Conclusion**

In conclusion, the  $2.3 \times 10^{-3}$  wt% MWCNTs are successfully incorporated into the sol-gel processing of sodium silicate precursor to prepare the MWCNT/Silica aerogel composite. The ambient pressure dried aerogel

composite was appropriately characterized. This metal-free nanocomposite was found to be active towards the synthesis of benzylpyrazolyl coumarin via a four-component reaction of 4-hydroxy coumarin, benzaldehyde, phenyl hydrazine, and ethyl acetoacetate at room temperature. The catalyst was easily recovered and reused without any loss in activity. In a successful attempt to optimize the reaction conditions, the impregnation of catalytic amount of ceria on MWCNT/Silica aerogel was examined with MCRs selectively yielding various benzylpyrazolyl coumarin derivatives in quick time and in refluxing water - the benign or ideal green chemistry solvent.

**Acknowledgements**

Isak Rajjak Shaikh - the lead author or writer of this draft is thankful to Dr. N.N Maldar (Prof. & Vice-Chancellor, Solapur University), Dr. P.K Zubaidha (Prof. & Host Lab Supervisor, SRTMU) and Dr. S.S Makone (Prof. & Director - School of Chemical Sciences, SRTMU) for providing him the laboratory facilities. Uzma K.H Bangi is very grateful to Department of Science and Technology for Young Scientist Fellowship under fast-track scheme. The synthesis of aerogel catalyst was supported by a major research project on 'aerogels' (Grant No. SB/FTP/PS-030/2014). ). The lead author is grateful to his Father for bearing expenses of Ph.D. study at SRTMU.

**References**

- [1] R.C. Cioc, E. Ruijter, R.V.A. Orru, *Green Chem.*, **2014**, *16*, 2958-2975.
- [2] P. Pratim; G. Pal, S. Paul, A.R. Das, *Green Chem.*, **2012**, *14*, 2691-2698.
- [3] S.S. Kistler, *Nature*, **1931**, *127*, 741.

- [4] B. Gawel, K. Gawel, G. Oye, *Materials* (Basel), **2010**, *3*, 2815-2833.
- [5] M.L.N. Perdigoto, R.C. Martins, N. Rocha, M.J. Quina, L. Gando-Ferreira, R. Patricio, L. Duraes, *J. Colloids Int. Sci.*, **2012**, *380*, 134–140.
- [6] G. M. Pajonk, *Cata. Today*, **1999**, *52*, 3-13.
- [7] L.S. Ling, H. Hamdan, *J. Non-Crystalline Solids*, **2008**, *354*, 3939–3943.
- [8] B. Zhang, J. Zhang, X. Sang, C. Liu, T. Luo, L. Peng, B. Han, X. Tan, X. Ma, D. Wang, N. Zhao, *Scientific Reports*, **2016**, *6*, Article number: 25830. DOI: 10.1038/srep25830.
- [9] M.A. Reicher, E. Ortelli, A. Baiker, *Appl. Catal. B: Environ.*, **1999**, *23*, 187-203.
- [10] C.A. Müller, M. Maciejewski, T. Mallat, A. Baiker, *J. Catal.*, **1999**, *184*, 280-293.
- [11] C.A. Müller, M. Schneider, T. Mallat, A. Baiker, *Appl. Catal. A: General*, **2001**, *201*, 253-261.
- [12] S. Hu, R.J. Willey, B. Notari, *J. Catal.*, **2003**, *220*, 240-248.
- [13] M. Spiro, *Catal. Today*, **1990**, *7*, 167-178.
- [14] L.R. Radovic, F. Rodriguez-Reinoso, *Carbon Materials in Catalysis, In Chemistry and Physics of Carbon; Thrower, P. A. (Eds.); New York: Marcel Dekker, USA, pp. 243-358, Vol. 25, 1997.*
- [15] S. Iijima, *Nature*, **1991**, *354*, 56 - 58.
- [16] S. Iijima, T. Ichihashi, *Nature*, **1993**, *363*, 603 - 605.
- [17] J.M. Schnorr, T.M. Swager, *Chem. Mater.*, **2011**, *23*, 646-657.
- [18] R.P. Rocha, Olívia S.G.P. Soares, J.L. Figueiredo, M.F.R. Pereira, *J. Carbon Res.*, **2016**, *2*(3), 17.
- [19] Q. Zhang, J.-Q. Huang, W.-Z. Qian, Y.-Y. Zhang, F. Wei, *Small*, **2013**, *9*, 1237-1265.
- [20] T. Altalhi, M. Ginic-Markovic, N. Han, S. Clarke, D. Losic, *Membranes*, **2011**, *1*, 37-47.
- [21] H. Bargozin, L. Amirkhani, J.S. Moghaddas, M.M. Ahadian, *Transaction F: Nanotechnology*, **2010**, *17*, 122-132.
- [22] J. Huang, H. Liu, S. Chen, C. Ding, *J. Env. Chem. Eng.*, **2016**, *4*, 3274-3282.
- [23] Uzma K.H. Bangi, M.S. Kavale, S-S Baek, H-H Park, *J. Sol-Gel Sci. Technol.*, **2012**, *62*, 201-207.
- [24] U.K.H. Bangi, C-S Park, S-S Baek, H-H Park, *Ceramics Int.*, **2012**, *38*, 6883–6888.
- [25] I. Stamatina, A. Morozan, A. Dumitru, V. Ciupina, G. Prodan, J. Niewolski, H. Figiel, *Physica E*, **2007**, *37*, 44-48.
- [26] O. Eren, N. Ucar, A. Onen, N. Kizildag, I. Karacan, *J. Composite Mater.*, **2016**, *50*, 2073-2086.
- [27] A. Saha, S. Payra, S.K. Verma, M. Mandal, S. Thareja, S. Banerjee, *RSC Advances*, **2015**, *5*, 100978-100983.
- [28] A. Saha, S. Payra, S. Banerjee, *Green Chem.*, **2015**, *17*, 2859-2866.
- [29] I.R. Shaikh, U.K.H. Bangi, P.R. Shaikh, *Songklanakar J. Sci. & Tech.*, Article in press, Manuscript ID SJST-2017-0145.R1, <http://rdo.psu.ac.th/sjstweb/ArticleInPre ss.php>.
- [30] B.B. Totawar (Supervisor: P. K. Zubaidha), *Ph.D. thesis*, SRT Marathwada University, Nanded, India, **2017**.
- [31] P.P. Ghosh, A.R. Das, *Tet. Lett.*, **2012**, *53*, 3140-3143.