

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

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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. 2.3×10^{-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

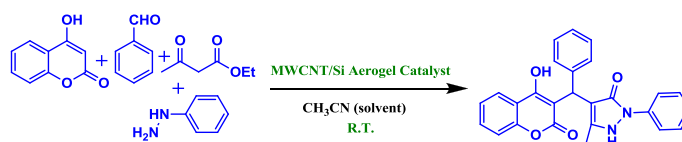
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explored in greening organic chemistry for the design and syntheses of biologically active molecules [1]. Partha P. Ghosh *et al.* [2] reported one such MCR for the combinatorial synthesis of highly functionalized benzylpyrazolyl coumarin scaffolds. 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 2.3×10^{-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, Na_2SiO_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 μm , 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 (2.3×10^{-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 $\text{H}_2\text{O}:\text{Na}_2\text{SiO}_3$ molar ratio and the concentration of MWCNTs were kept constant at 146.67 and 2.3×10^{-3} 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 α 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_2 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 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. ^1H NMR and ^{13}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 (2.3×10^{-3} wt%) incorporated silica aerogel material by ambient pressure drying. Herein, low density (0.056 g/cc), highly porous (97%), large surface area ($645.65 \text{ m}^2/\text{g}$), 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 2θ of around 30.04° and 43.9° 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 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 cc/g and the pore size of 12.46 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 cm^{-1} are due to weak OH stretching and bending vibrations. The IR band near 1065 cm^{-1} is due to O–Si–O asymmetric stretching and bending vibrations. There are additional bands at 2960 cm^{-1} related to C–H and near 844 cm^{-1} related to Si–C. The peak at around 800 cm^{-1} corresponds to Si–O–Si bond. There is a weak peak at around 1630 cm^{-1} corresponding to the C=C stretching of the MWCNTs [26].

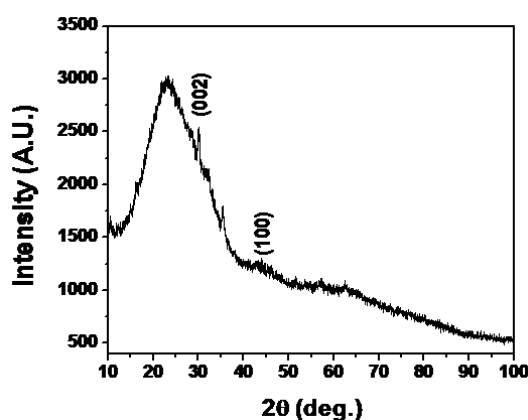


Figure 1. XRD of MWCNT incorporated silica aerogel

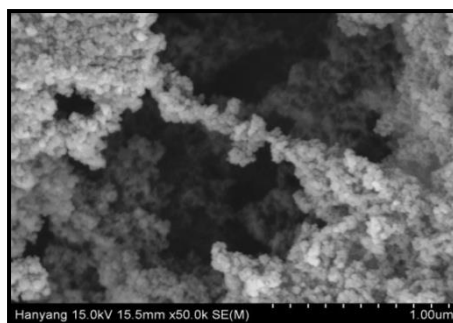


Figure 2. FE-SEM image of MWCNT incorporated silica aerogel

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 ₃ OH	Room Temp. (R.T.)	24 hrs	-
No catalyst	CH ₃ CN	Reflux (82 °C)	4 hrs	-
MWCNT/ Silica Aerogel	CH₃CN	R.T.	40 min	60
No catalyst	CH ₃ OH	R.T.	24 hrs	-
MWCNT/ Silica Aerogel	CH ₃ OH	R.T.	4 hrs	-
MWCNT/ Silica Aerogel	CH ₃ OH	Reflux (65 °C)	4 hrs	25
Ceria onto MWCNT/Silica Aerogel	H₂O	Reflux (100 °C)	15 to 20 min	90 (1 PDT)

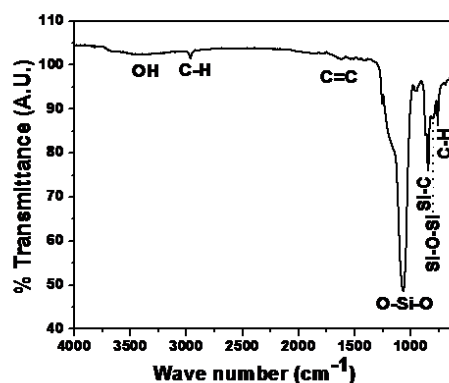
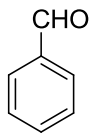
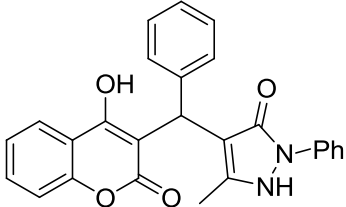


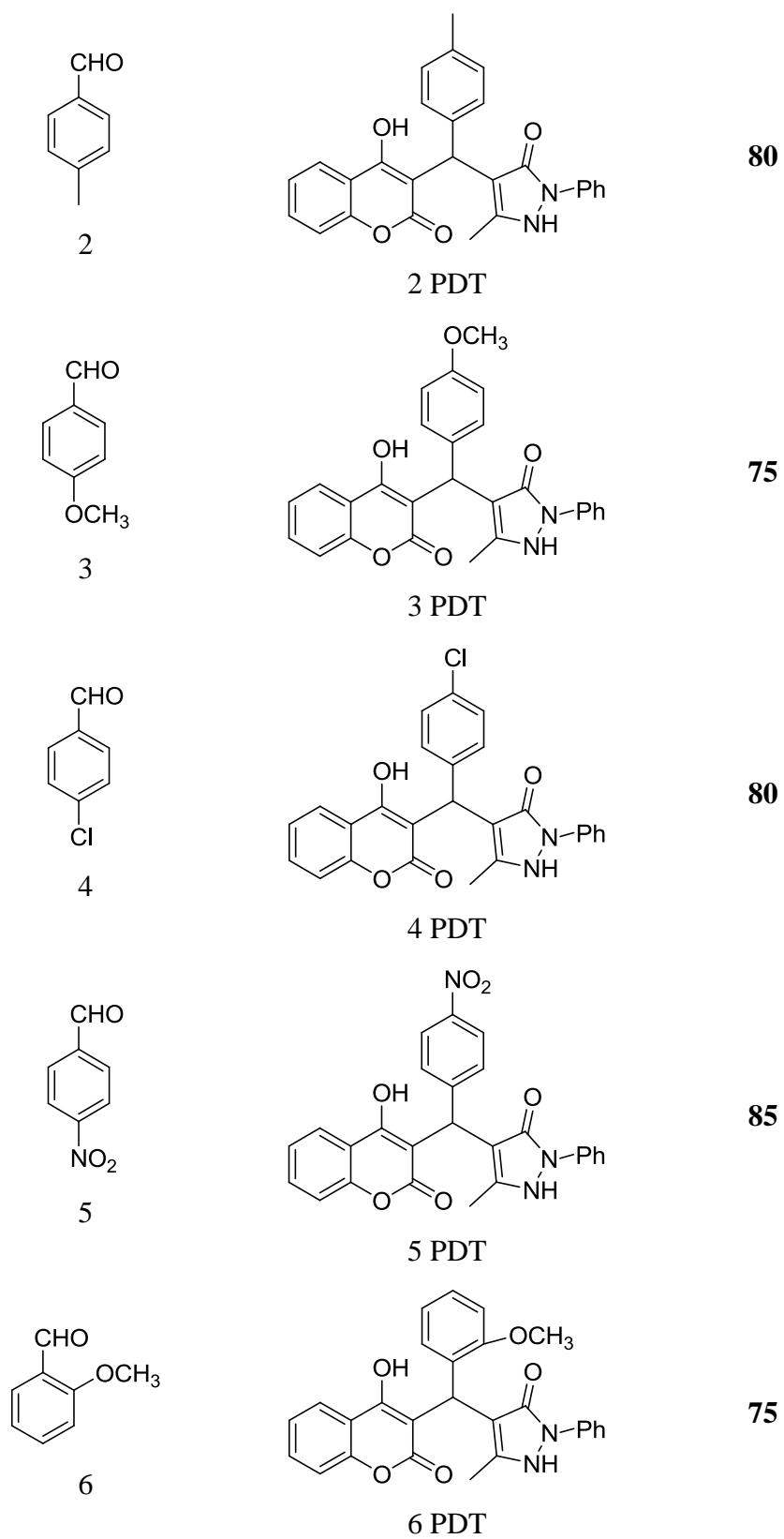
Figure 3. FT-IR spectrum of the MWCNT incorporated silica aerogel

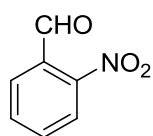
In order to optimize the reaction conditions [29], the use of water as solvent and the use of ceria impregnated MWCNT/Silica aerogel catalyst were examined with changing aromatic aldehydes as the substrates yielding various benzylpyrazolyl coumarin derivatives. (Table 3). It was observed that the formation 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.

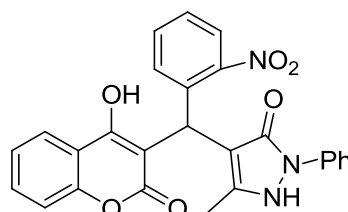
Table 3. Synthesis of various benzylpyrazolyl coumarin derivatives over ceria modified MWCNT/Silica aerogel using different aromatic aldehydes in the MCRs in water at reflux temperature within 15 to 20 minutes^a

Aromatic Aldehydes	Products	Yield (%) ^b
 1	 1 PDT	90



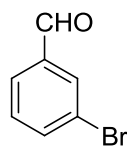


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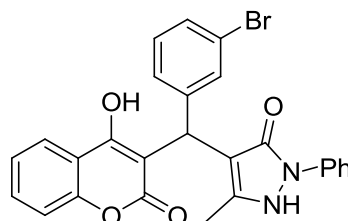


7 PDT

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.

¹H NMR (300 MHz; DMSO-d₆): 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⁻¹. ¹H (300 MHz; DMSO-d₆; 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); ¹³C (75 MHz, DMSO-d₆; 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⁺, 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⁻¹; ¹H (300 MHz; DMSO-d₆): δ 2.69 (s, 3H), 6.15 (s, 1H), 7.26-7.58 (m, 9H), 7.91-8.94 (m, 5H); ¹³C (75 MHz, DMSO-d₆): 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): δ 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): δ 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 2.3×10^{-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.

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