Polyaniline/SiO₂ Catalyzed One-pot Synthesis of Tetrahydrobenzo[b]pyran Derivatives

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Received 20 August 2010, revised 27 October, accepted 19 November 2010.

ABSTRACT
Polyaniline/SiO₂ is an efficient catalyst for the synthesis of tetrahydrobenzo[b]pyran derivatives from a one-pot, three component, condensation of aldehydes, malononitrile and dimedone at room temperature. This protocol has several advantages such as high yield, a simple work up procedure, low toxicity and easy recovery and reusability of the catalytic material. The catalyst has been readily prepared and characterized by means of thermal analysis (TG-DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR).

KEYWORDS
Chemical oxidative method, Polyaniline/SiO₂ tetrahydrobenzo[b]pyran.

1. Introduction
In recent years there have been extensive studies in the use of conducting polyanilines because of their wide range of electrical, electrochemical and optical properties, as well as their good stability.1-4 Polyaniline is commonly synthesized by oxidizing aniline monomers using electrochemical or chemical methods.5-7 Polyaniline-supported catalysts often display good environmental, thermal and chemical stability as well as interesting electrical and optical properties, facile redox and pH-switching behavior.8 Polyaniline and polyaniline-supported metal oxides have been extensively used as solid acid or redox catalysts for various organic transformations such as oxidation, dehydrogenation, condensation, Michael, Suzuki–Miyaura cross-coupling and esterification reactions.9-16

The 4H-pyran group is a constituent of a series of natural products and its derivatives represent a major class of heterocycles.17,18 These compounds continue to attract attention in chemistry due to their useful biological and pharmacological properties such as anticoagulant, spasmolytic, diuretic and anticancer properties.19 It has also been reported that some benzopyran derivatives possess photochemical activities.20 Realizing the importance of these compounds, various methods for the synthesis of tetrahydro-4H-benzopyran derivatives have been developed. The conventional synthesis of tetrahydrobenzo[b]pyrans involves the condensation of aldehydes with malononitrile and dimedone under reflux in acetic acid.21 Recently, several alternative methods towards tetrahydrobenzo[b]pyrans have been reported, including the use of 1,1,3,3,N,N,N,N-tetramethylguanidinium trifluoroacetate (TMGT) as an ionic liquid,22 diammonium hydrogen phosphate (DAHP),23 molecular iodine,24 N,N,N,N-diethylmethylbenzyl ammonium bromide (HDMBAB).25 Additionally, electrochemical reactions,26 microwave heating in the solid state27 and cerium (III) chloride have been utilized to synthesize the tetrahydrobenzo[b]pyran motif.28 However, several of these methods are plagued by one or more drawbacks such as long reaction times, the use of volatile solvents, low yields and harsh reaction conditions employed. It is therefore desirable to develop an improved route for the synthesis of tetrahydrobenzo[b]pyran under mild reaction conditions.

In continuation of our interest towards the development of new heterogeneous catalyst for the synthesis of bioactive heterocycles,29-34 herein, we report an efficient protocol for the synthesis of tetrahydrobenzo[b]pyran derivatives over polyaniline/SiO₂ by way of a one pot condensation of aldehydes, malononitrile and dimedone.

2. Results and Discussion
The synthesis of tetrahydrobenzo[b]pyran derivatives by way of the condensation of aldehydes, malononitrile and dimedone as catalyzed by polyaniline/SiO₂ is shown in (Scheme 1). The polyaniline/SiO₂ catalyst was prepared by using a chemical oxidative method. The details of the synthesis and characterization of this material are described in the experimental section of this paper. In order to this paper was the utilization of a model reaction, based on Scheme 1, for the development of a stable catalyst system which would perform the desired reaction under optimized conditions, such as the weight percentage of catalyst on the support and the amount of catalyst and type of solvent utilized.

The stability of the prepared catalyst was tested in different solvents (methanol, acetone, acetonitrile and ethanol) to determine the stability of the material in these solvents. This was done by spectrophotometric analysis in which the extent of degradation of the catalyst was monitored by the change in optical density of the solution (catalysts solutions were monitored after 15 days at room temperature). The results are summarized in Table 1 and shows that the catalyst had the best stability in ethanol with the lowest optical density after the time period measures. Hence, in order to get the optimum reaction condition, the reactions of 4-chlorobenzaldehyde, malononitrile and dimedone using ethanol as a solvent at room temperature was considered as a standard model reaction.

To examine the effect of the catalyst composition on the activity, various amounts of polyaniline supported SiO₂ were used and the results are summarized in Table 2. Pure silica exhibits poor catalytic activity in terms of reaction time and yield of the products. Pure polyaniline however, gave a good yield of
the product but only after increased reaction time. In terms of the optimized amount of catalyst we observed that 10 wt % polyaniline/SiO₂ was sufficient and gave an excellent yield of the desired product in a short reaction time. However, an increase in the amount of polyaniline utilized in the SiO₂ support (from 10% to 20 and 30 %) resulted in lower yields of the product and longer reaction time were required for the completion of the reaction.

However, it is important to note that in the absence of catalyst, formation of the desired product was not observed (Table 3, entry 3a). To investigate the effect of the amount of catalyst (10 wt % of polyaniline/SiO₂) used, the standard model reaction was carried out using different amounts of catalyst, ranging from 0.05 to 0.2 g (Table 3, entry 3b–e). It was observed that 0.1 g of catalyst was sufficient to complete the reaction efficiently (Table 3, entry 3c).

To explore the scope and generality of the present method, a variety of different substituted aromatic aldehydes possessing electron rich and electron deficient groups, as well as heterocyclic aldehydes, were tested and afforded the desired products in excellent yields (91–93 %). Of additional importance was that the reactions were completed within 60–70 min in ethanol at room temperature (Table 4).

Of significance in catalytic transformations is the possible recovery and reusability of the catalyst as this is important from an industrial and an economic point of view. After a reaction the catalyst was thus separated by filtration, washed with n-hexane and dried at 80 °C for 1 h before the next catalytic run. Reusability of the catalyst was investigated for three times and it was found to retain almost consistent activity (Table 4, entry 4b).

In order to show the merits of polyaniline/SiO₂ over other catalysts reported in the literature, results with the polyaniline/SiO₂ catalyst were compared with other catalysts utilized for the synthesis of a tetrahydrobenzo[b]pyran. From Table 5 it can be seen that polyaniline/SiO₂ appears to promote the reaction more effectively than a number of other catalysts, particularly in terms of the time required to complete the reaction.

3. Conclusion

In summary, an efficient catalytic system has been utilized for the synthesis of tetrahydrobenzo[b]pyran derivatives from a one-pot three component condensation of aldehydes, malononitrile and dimedone at room temperature. The present method offers significant advantages such as non-toxic, non-corrosive and simple reaction conditions. In addition, simply recovery and reusability of the catalyst makes the reaction successful under environmental benign conditions.

4. Experimental

All chemicals were purchased either from Merck or Fluka and used without further purification. Melting points were taken in
an open capillary and are uncorrected. TG-DTA was performed using PYRIS 1 Thermogravimetric analysis. IR spectra were recorded on JASCO-FT-IR/4100, Japan, in KBr disc. Thin-layer chromatography was performed on Merck pre-coated silica gel 60-F254 plates. 1H NMR spectra were recorded on an 300 MHz FT-NMR spectrometer in CDCl3 as a solvent and chemical shifts values are recorded δ (ppm) relative to tetramethylsilane (Me4Si) as an internal standard. The X-ray diffraction (XRD) patterns were recorded on Bruker 8D advance X-ray diffractometer using monochromator Cu-Kα radiation in which wavelength λ = 1.5405 Å. Conventional scanning electron microscopy (SEM) images were obtained on JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA.

4.1. Preparation of Pure Silica

Silica samples were synthesized by using a sol-gel process requiring the addition of tetraethyl ortho-silicate (TEOS) (16 mL) was in aqueous ammonia (60 mL). The resulting reaction mixture was then stirred continuously for 1 h to obtain uniform silica spheres. The resulting silica material was next retrieved by centrifugation, washed with distilled water and dried at 110 °C for overnight. Finally, the resulting material was calcined at 500 °C for 5 h under air atmosphere to produce solid porous silica materials.

4.2. Preparation of Polyaniline/SiO2 Catalyst

The series of polyaniline/SiO2 catalytic materials with varying aniline (10, 20, 30 wt %) and SiO2 were prepared by chemical oxidative method. In a typical procedure, 10 wt % polyaniline/SiO2 catalyst was synthesized by slowly mixing a solution of aniline (0.3 mL) in distilled water (30.8 mL) with concentrated sulphuric acid (0.61 mL) at 5–10 °C. The resultant mixture was successively treated with aqueous potassium persulphate (16 mmol) and solid porous silica (2.68 g). The mixture was then kept at 5 °C and stirring continued for 5–6 h resulting in a precipitate that was obtained by filtration. This precipitate was next washed with distilled water and acetone. The product, polyaniline/SiO2 salt, was then dried in an oven at 70 °C for 3 h. Similarly, 20 and 30 wt% polyaniline/SiO2 catalysts were prepared in the same manner.

4.3. General Procedure for the Synthesis of Tetrahydrobenzo[b]pyran 4(a–h)

A mixture of aldehydes (1 mmol), malononitrile (1 mmol) and catalytic amount of polyaniline/SiO2 (0.1 g) in ethanol (15 mL) was stirred for 5–10 min before been treated with dimedone (1 mmol) and stirring continued at 60–70 °C. The progress of the reaction was monitored by TLC (petroleum ether: ethyl acetate = 7:3 as eluent). After completion of the reaction, the mixture was heated to solubilize the products and the catalyst removed by filtration. The filtrate was concentrated under reduced pressure, and the crude product obtained was recrystallized from ethanol to afford pure products 4(a–h).

4.3.1 Spectroscopic Data of 2-Amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile (4g)25

IR (KBr, ν max): 3307, 2964, 2191, 1677, 1443, 769 cm −1. 1H NMR (300 MHz, CDCl3) δ: 1.11 (s, 3H), 1.21 (s, 3H), 2.20 (s, 2H), 2.45 (s, 2H), 3.70 (s, 2H, NH ), 4.63 (s, 1H), 7.11–7.12 (m, 2H, Ar-H), 7.19–7.26 (m, 1H, Ar-H), 7.30–7.33 (dd, 1H, Ar-H).
temperature (140 °C) for the removal of water from the polymer materials. The second weight loss was observed at 200 °C and corresponds to the degradation and decomposition of the polymer back bone. However, complete decomposition occurs between 350 °C for the polyaniline chain as shown in Fig. 1(a). Fig. 1(b) shows the thermal decomposition of polyaniline supported on SiO₂. From this it can be seen that the thermal stability of polyaniline/SiO₂ materials has noticeably improved, which may be due to the strong interaction between polyaniline and SiO₂.

4.5 XRD Analysis
Figure 2(a–c) shows the XRD pattern of the synthesized materials. Figure 2(a) shows a broad peak at 2θ (21.98°) corresponding to the amorphous nature of silica.35 Figure 2(b) shows the broad peak at 2θ (25.13°) which are characteristic of the polyaniline.36 Finally, Fig. 2(c) indicates a broad peak at 2θ (22.18°) for 10 wt % polyaniline/SiO₂; the peak was slightly shifted due to the addition of polyaniline into the mesoporous silica.

4.6 SEM Analysis
Figure 3(a–c) shows the surface morphology of the synthesized materials. Figure 3(a) shows good agglomeration of the particles of mesoporous silica which are spherical in shape, while a fibrous or globular morphology was observed in Fig. 3(b) which is the characteristic of polyaniline.37 Figure 3(c) shows some porosity – this may be due to the insertion of 10 wt % polyaniline on the surface of SiO₂. Finally, from the SEM micrograph it can be concluded that, the polyaniline addition clearly shows alteration in morphology, which helps to generate the porous materials and that the porosity may increase the catalytic activity of the material.

4.7 FT-IR Analysis
Figure 4(a–c) shows the FT-IR spectra of the synthesized materials. Figure 4(a) shows a peak at 3477 cm⁻¹ which is due to the Si-OH stretching vibration, 1627 cm⁻¹ for the Si-OH bending mode, 1080 cm⁻¹ for Si-O stretching vibration and 815 cm⁻¹ due to the Si-O-Si bending vibration mode. Figure 4(b–c) shows the FT-IR spectra of the pure polyaniline and 10 wt % polyaniline/SiO₂, respectively. The characteristic peaks of the polyaniline at
Figure 4 FT-IR spectra of (a) SiO₂ (b) polyaniline (c) 10 wt % polyaniline/SiO₂.

3389 and 3371 cm⁻¹ is attributed to N–H stretching, 1572 and 1509 cm⁻¹ due to C=C stretching mode of the quinoid rings, 1489 and 1454 cm⁻¹ due to C=C stretching vibration of benzenoid rings, 1323 and 1309 cm⁻¹ for C–N stretching vibration, 1138 cm⁻¹ for N=Q=N, where Q represents the quinoid rings, peaks at 825 and 808 cm⁻¹ due to aromatic C–H bending mode of 1,4-disubstituted benzene ring. Figure 4(c) shows a peak at 1084 cm⁻¹ due to the presence of silica.

Acknowledgements
The authors are grateful to the Head of the Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India, for providing the laboratory facility.

References