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Synthesis, characterization and evaluation of green catalytic activity of nano Ag–Pt doped silicate

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ABSTRACT

In order to get materials with enhanced adsorption and organic transformation performance, nanosized Ag–Pt nanoparticles loaded SiO_2 was prepared by sol–gel method. This catalyst has been characterized by Fourier transform infrared (FT-IR) spectra, diffuse reflectance spectra (DRS), fluorescence, high-resolution scanning electron microscopy (HR-SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Ag–Pt/SiO_2 catalyst induces the reaction of condensation of indole and aldehyde to give bis(indolyl)methanes in striking lesser time under microwave (MW) irradiation and it has been examined with different substituted benzaldehydes. The coupled product is confirmed by FT-IR, ^1H, ^{13}C NMR and DFT theoretical methods.

1. Introduction

There has been a lot of interest to the development of highly efficient transformations in organic synthesis. There is also a need to find new, efficient and strategically acceptable protocols, which are environmentally benign and lead to the greater structural variations with high yields and simple work-up procedures [1]. Indole and their derivatives are known to posses various pharmacological and biological properties, including antibacterial, cytotoxic, antioxidative and insecticidal activities [2,3]. To abate the environmental pollution of the disposal of the excess acids in the condensation reactions of indole and carbonyl compounds, a number of catalytic systems such as sulfated zirconia [4], naffion-H [5], zeolites [6], Fe pillared clays [7], amberlite [8], amberlyst-15 [9], $HClO_4$–SiO_2 [10], $NaHSO_4{\cdot}iO_2$ [11], Yb-amberlyst XN-1010 [12], zeolites [13], ionic liquids [14], I_2 [15], $LiClO_4$ [16], $CeCl_3{\cdot}7H_2O$ [17,18] and $RuCl_3{\cdot}3H_2O$ [19] have been successfully utilized. Synthesis, characterization and evaluation of catalytic activity of nanobimetallic system such as Au–Ag/SiO_2, Pt–Ni/SiO_2, Au–Cu/SiO_2, Au–Ni/SiO_2, Ag–Ni/SiO_2 of their wide range of industrial and synthetic applications [20–24] and some of the unique physical fabrication methods of metal nanoparticles in polymer or semiconductors has reported [25,26]. The preparation of bis(indolyl)methanes has received renewed interest of researchers for the discovery of improved protocols and still awaits further development of milder and high-yielding processes.

On the other hand, solvent-free organic reactions have been applied as an useful protocol in organic synthesis [27]. Solvent-free conditions often lead to shorter reaction times, increased yields, easier workup, matches with green chemistry protocols, and may enhance the regio- and stereoselectivity of reactions [27]. Although nanobimetal doped catalyst are effectively used for the CO oxidation, hydrogenation of benzene, dehydrogenation of aqueous NH_3BH_3, etc. but catalytic synthesis of bis(indolyl)methanes not yet reported so far. Hence, we report the coupled formation of bis(indolyl)methanes through the reaction of indole with various aldehydes in microwave (MW) condition catalyzed novel Ag–Pt doped silicate catalyst.

2. Experimental

2.1. Preparation of the catalyst

All chemicals were of the highest purity available and were used as received without further purification. Silver nitrate ($AgNO_3$) and chloro platinic acid were used as Ag, Pt source. Nano-SiO_2 was prepared by the hydrolysis of tetraethyl orthosilicate (TEOS, 0.5 mL) well dispersed in the mixture of ethanol (160 mL), deionized water (40 mL) and concentrated ammonia aqueous solution (5.0 mL, 28 wt.%), under stirring for 3 h at ambient temperature. Ag–Pt bimetal colloid was prepared by the reported procedure [28]. Then bimetal Ag–Pt colloid was added into the mixture. After stirring for 24 h at room temperature, the colloidal solution was kept in autoclave at 28 psi for 6 h. The product was filtered, washed with ethanol and water, and then dried. The catalysis was carried out at 120 °C for 3 h, 25 (psi). The solution was taken in a filtering flask with heavy wall and tabulation (250 mL borosil (5340)) with tightly closed glass lid on the top to avoid the any other contamination.

2.2. Instruments

FT-IR spectra were measured using on an Avatar-330 infrared spectrometer in KBr pellet. The DRS of both doped and undoped silicate were recorded in Shimadzu UV 2450 model UV–visible spectrophotometer in the range of 800–200 nm

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equipped with an integrating sphere and using powdered $BaSO_4$ as a reference. The fluorescence spectrum at room temperature was recorded using a Perkin–Elmer LS 55 fluorescence spectrometer. The nanoparticles were dispersed in carbon tetrachloride and excited using light of wavelength 280 nm. SEM (JSM 6700F) was used to observe the particle size and morphology of the samples.

XRD patterns of SiO_2 and Ag–Pt/SiO_2 powder samples were obtained using a model *D*/Max 2550 V with Cu anticathode radiation. The diffractograms were recorded in 2θ range between 10° and 100° in steps of 0.02° with count time of 20 s at each point. The average crystalline sizes were determined according to the Debye–Scherrer equation using the full width half maximum data of each phase.

$$D = 0.9\lambda/B\cos\theta$$

where *D* is the crystal size of the catalyst, λ is the X-ray wavelength (0.154 nm), *B* is the full width half maximum (FWHM) of the peak and θ is the diffraction angle.

To study the morphology of the catalyst, TEM measurements were performed on a TECNAI G2 FEI F12 model TEM instrument operated at an accelerating voltage of 200 eV. For AFM, JSPM-5200 7 M, JEOL model instrument was used. This instrument uses a silicon tip with a radius of 20 mm and a low resonance frequency cantilever that has a manufactures spring, constant at 35–65 nm^{-1}. Scan of 1.8 × 1.8 μm were obtained for each sample. The images were recorded in the non-conduct mode. All recording made in air under ambient condition to produce 2D and 3D image.

Theoretical calculation was performed using Gaussian-03 program package on a personal computer without any constraint on the geometry using LANL2DZ basis set [29]. Microwave irradiations were performed in a LG ECN:MG-395 WA/01, MOD:MG-395 WA model. Proton and carbon NMR spectrum were recorded on a BRUKER AVIII FT-NMR spectrometer operating at 400 MHz for the sample.

2.3. Preparation of bis(indolyl)methanes

Ag–Pt/SiO_2 (50 mg) was added to a mixture of indole (10 mmol, 1.17 g) and benzaldehyde (5.5 mmol, 0.580 g). The reaction mixture was irradiated under microwave oven at 320 W for the appropriate time. The progress of the reaction was monitored by Thin Layer Chromatography (TLC). After completion of reaction, methanol (10 mL) was added to the mixture and filtered off to separate the catalyst. The product was then extracted in ethyl acetate. Evaporation of the solvent under vacuum resulted in crude product. The crude product was further purified by column chromatography on a silica gel (Merck, 60–120 mesh, ethyl acetate/petroleum ether – 1:4).

3. Result and discussion

3.1. Characterization of Ag–Pt/SiO_2 catalyst

3.1.1. FT-IR and DRS analysis

In the FT-IR spectrum of bare SiO_2 and bimetal doped SiO_2 are shown in Fig. 1a and b. The absorption band are assigned 3421 cm^{-1}, corresponding to O–H stretching frequency and broad band at 1108 cm^{-1}, due to Si–O–Si stretching vibration, 952 cm^{-1} of Si–OH stretching vibration, 807 cm^{-1} of Si–O bending vibration and 474 cm^{-1} of Si–O out-of-plane deformation are identified [30,31]. As analyzed, the bands at 1108, 982, 807, 474 cm^{-1} shift to lower wavenumbers due to the doping of Ag–Pt colloid exerts an influence on the structure of SiO_2. The diffuse reflectance spectra (DRS) of bare SiO_2 and Ag–Pt/SiO_2 are shown in Fig. 2. The absorption intensity significantly increased in the visible light range on the metal loaded SiO_2 while bare is not having much absorbance. This may be accounted for the presence of Ag–Pt nanometal particles are having surface plasmon absorbance in the visible region.

3.1.2. Fluorescence analysis

Fig. 3a and b shows the extinction spectra of the bare SiO_2 and Ag–Pt/SiO_2. It can be seen that the Ag–Pt/SiO_2 is having significant photoluminescence intensity (360 nm) when compared to the bare SiO_2 (433 nm). This is because of suppression of recombination of the electron–hole pairs by Ag–Pt metal present in SiO_2. Bimetal has strong interaction with the radiation field in the UV region. This interaction causes the excited conducting electrons to oscillate in a collective manner. Noble metal nanostructures (e.g. Au, Ag) can enhance the fluorescence intensities of Near-infrared fluorescent (NIRF) molecules which exist in their electromagnetic field.

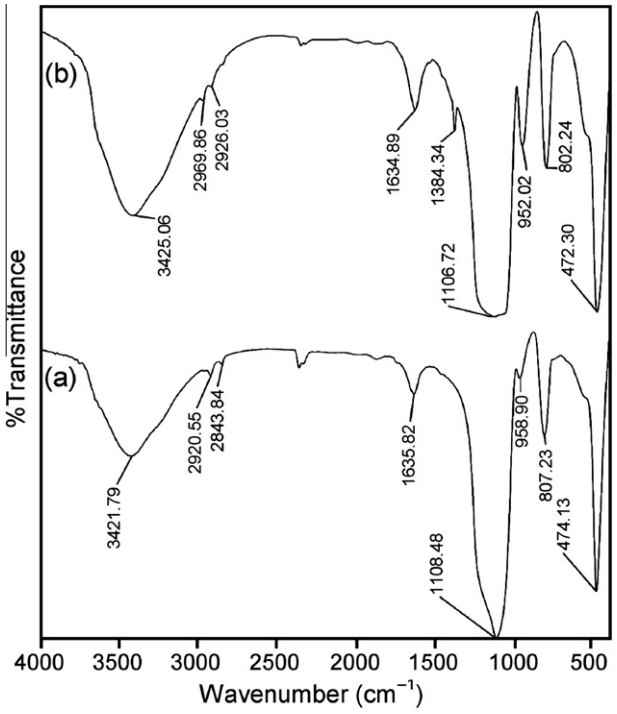

Fig. 1. FT-IR spectra of (a) bare SiO_2 and (b) Ag–Pt/SiO_2.

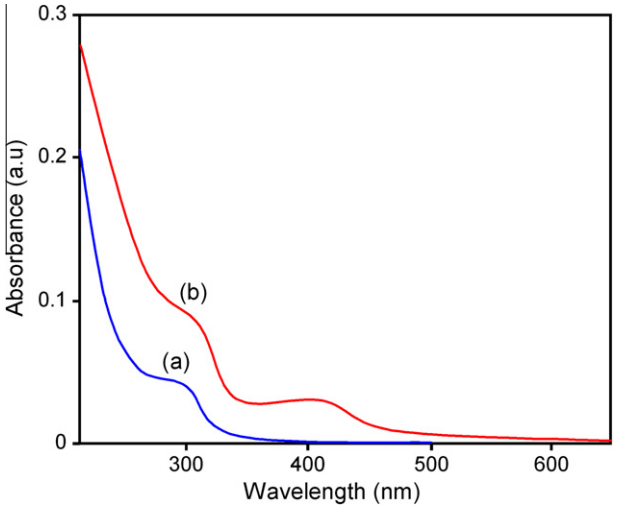

Fig. 2. Diffuse reflectance spectra of (a) bare SiO_2 and (b) Ag–Pt/SiO_2.

This phenomenon is called surface plasmon resonance enhancement [32].

3.1.3. HR-SEM and EDX analysis

The HR-SEM images of the bare SiO_2 and Ag–Pt/SiO_2 are shown in Fig. 4a and b, monodisperse characteristic in particles of range between diameter of 245 and 260 nm and having spherical morphology is inferred in bare SiO_2. When compared with SiO_2, the size of Ag–Pt/SiO_2 was altered. The EDX spectra (Fig. 4c and d) confirm the presence of elements silicon, oxygen in bare and silicon, oxygen, silver, platinum, respectively in the catalyst.

3.1.4. XRD analysis

X-ray diffraction patterns of bare and nanobimetal loaded catalyst are shown in Fig. 5a and b. The peaks observed at 38.1°, 39.7° and 64.5° are the diffractions of the crystalline planes of Ag (1 1 1)