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Silicotungstic acid nanoparticles dispersed in the micropores of Cr-pillared clay as efficient heterogeneous catalyst for the solvent free synthesis of 1,4-dihydropyridines

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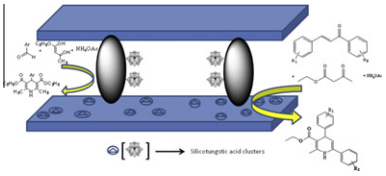
HIGHLIGHTS

- Cr-P clay served as efficient support for dispersion of silicotungstic acid.
- IR and UV–Vis study illustrates the structural integrity of the STA particles.
- The interlayer spacing of Cr-P was retained after incorporation of STA particles.
- The particle size of the supported STA is in the range of 15–25 nm.
- The STA/Cr-P material highly efficient catalyst for synthesis of 1,4-dihydropyridines.

GRAPHICAL ABSTRACT



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ABSTRACT

Chromium pillared clay (Cr-P) is prepared by intercalating chromium oligomeric clusters into the interlayer of the montmorillonite clay. The Cr-oligomeric clusters are prepared by the partial base hydrolysis of chromium nitrate solution. Cr-P clay served as efficient support for dispersion of silicotungstic acid (STA). The STA particles are dispersed in the micropores of Cr-P clay by wet impregnation method. The synthesized materials are characterized by XRD, FTIR, UV–Vis, sorptometric, TGA, SEM and TEM techniques. XRD study indicates an expansion in the interlayer space as a result of Cr-polycations pillaring. The interlayer spacing is found to be retained after incorporation of STA particles. IR and UV–Vis study illustrates the structural integrity of the STA particles in the micropores of the pillared clay. N_2 adsorption/desorption shows that the synthesized materials are microporous in nature exhibiting Type I sorption isotherm. The catalytic activity of the STA/Cr-P materials is evaluated for the synthesis of 1,4-dihydropyridines (DHPs) by multicomponent reaction of aldehydes/chalcones, ethylacetoacetate and ammonium acetate. Structurally diverse DHPs are prepared by using different aryl aldehydes and chalcones as starting materials. The STA/Cr-P materials are found to be highly efficient for the multicomponent reaction generating a variety of DHPs with high yield and purity under microwave irradiation and solvent free conditions.

1. Introduction

Dihydropyridines (DHPs) and their derivatives are an important class of bioactive molecules which have been extensively investigated for their application as anticonvulsant, antidiabetic, antianxiety, antidepressive, antitumor, and anti-inflammatory agents [1–3]. DHPs are also useful compounds for synthesis of neuroprotectants and treatment of Alzheimer's disease due to their cerebral anti-ischemic properties [2]. The 1,4-dihydropyridines are generally synthesized by Hanztsch method which involves one-pot condensation of β-keto esters, aromatic aldehyde and

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ammonia under reflux condition in alcoholic media [1,2]. In the past few years, there have been significant efforts to modify this classical method by employing various acidic/basic catalysts to improve the yield and purity of the synthesized products. Hanztsch process has been modified by using different catalysts such as TMSCl–NaI, ionic-liquids, $InCl_3$, ceric ammonium nitrate (CAN), Na- and Cs-exchanged carbons, and metal triflates [4–8]. However, most of the catalytic protocol reported so far uses homogeneous catalysts, Lewis acidic salts or supported reagents which suffer from the drawback of leaching, separation, recovery and handling of the catalyst. A stable heterogeneous catalytic system which is recyclable and provide good yield of the product is highly desirable.

Heteropoly acids (HPAs) are a class of polyoxometallates with tunable acidic and redox properties [9]. From catalysis point of view, Keggin type HPAs are widely studied because of their higher structural stability, Brønsted acidity, oxidation potential and resistance to deactivation by hydrolysis [10–13]. Silicotungstic acid (STA) is an important member of the Keggin type HPA family which shows promising catalytic activity for selective nitration and liquid phase bromination of phenol, synthesis of 1-methyl-2-(hetero) aryl benzimidazoles, dehydration of glycerol, esterification and veratrole acylation reaction [14–18]. The partially Cs- and Rb-doped $H_4SiW_{12}O_{40}$ materials show enhanced surface area, improved acidity and catalytic activity for dehydration of glycerol to acrolein and biodiesel production [19,20]. Although there are many studies available on the catalytic properties of STA, very few of these studies deal with organic reactions involving the synthesis of biologically important molecules.

Pillared clays, prepared by intercalation of the inorganic cationic nanoclusters into the clay interlayer, are a class of microporous materials with high surface area and acidic property [21–23]. In the past few years, these materials have been increasingly used as catalysts and support for a variety of biologically important and industrially significant organic transformations [21–29]. Clay pillared with Zr-polycations has been used for the synthesis of dihydropyrimidinones under-solvent free conditions [28]. Sulphated tin oxide (STO) particles supported on Al-pillared clay have been used as catalyst for the synthesis of dihydropyrimidones, coumarins and thiochromans [29]. Among several pillared clay reported in literature, Cr-pillared clay is one of the extensively studied pillared clay system which show promising catalytic activity for hydrocracking of liquid fuels, CO oxidation and thiophene hydrodesulphurization [30,31]. In order to improve the catalytic properties as well as to evaluate the applicability of the Cr-pillared clay based materials in organic synthesis, in the present investigation, we have dispersed silicotungsitc acid nanoparticles in the micropores of the Cr-pillared clay (STA/Cr-P) and studied their catalytic activity for the synthesis of synthesis of 1,4-dihydropyridines under solvent free conditions.

2. Experimental

2.1. Preparation of Cr-pillared clay

Na-montmorillonite, $(Na_{0.35}K_{0.01}Ca_{0.02})\ (Si_{3.89}Al_{0.11})^{tet}(Al_{1.60}Fe_{0.08}Mg_{0.32})^{oct}O_{10}(OH)_2{\cdot}nH_2O$ (Kunipia-F) was used for the preparation of Cr-pillared clay. The cation exchange capacity of the clay was 120 mequiv (100 g clay)$^{-1}$. The clay was used as such without any further purification. Chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$) and sodium carbonate (Na_2CO_3) were procured from S.D. fine chemicals India Ltd. The Cr-pillaring solution was prepared by partial base hydrolysis of $Cr(NO_3)_3{\cdot}9H_2O$ solution using sodium carbonate as base to obtain OH/Cr molar ratio of 2.0 [32,33]. The resulting solution was aged at 90 °C for 24 h before using in the pillaring process. In a typical pillaring procedure, 2 g of the montmorillonite clay was dispersed in 200 ml of deionised water to form 1.0 wt.% clay slurry. The slurry was stirred at room temperature for 2 h and sonicated for 15 min for better dispersion of the clay platelets. The pillaring solution was then added drop wise (50 ml/h) to the clay slurry under continuous stirring to obtain Cr/montmorillonite ratio 20 mmol/g. The mixture was kept at constant stirring for 24 h at room temperature, filtered, washed with deionised water (6 times with 200 ml portions), centrifuged and dried in hot air oven and calcined at 500 °C for 1 h.

2.2. Preparation of STA/Cr-P material

Cr-pillared clay was used as carrier for catalytically active silicotungstic acid. The silicotungstic acid was obtained from Lobachemie Pvt. Ltd., India. The 10 wt.% STA/Cr-P catalyst was prepared by wet impregnation method. Required amount of STA was dissolved in 50 ml of water and to the solution 2.0 g of chromia pillared clay was added. The resulting aqueous suspension was stirred for 3 h at room temperature. The temperature was then raised to 90 °C and was heated continuously under stirring to remove the excess water. The resulting material was dried in air at 120 °C followed by calcination at 250 °C for 1 h to obtain the STA/Cr-P material.

2.3. Characterization method

The XRD patterns of the pillared clay samples were obtained using a Siemens D-500 diffractometer using Ni filtered Cu $K\alpha_1$ radiation (λ = 1.5405 Å) in the 2θ range of 3–20° with a scan speed of 2° per min. Thermogravimetric analysis of the air dried clay samples was performed using Shimadzu TGA7 apparatus by heating the sample at the rate of 10 °C min^{-1} from RT to 800 °C in nitrogen atmosphere. The FTIR spectra of the pillared clay samples (as KBr pellets) were recorded in transmittance mode using a Perkin–Elmer infrared spectrometer with a resolution of 4 cm^{-1}, in the range of 400–4000 cm^{-1}. The specific surface area of the samples was determined by BET method using N_2 adsorption/desorption at 77 K on a Quantachrome autosorb gas sorption system from Quantachrome corporation. The samples were degassed at 120 °C for 12 h prior to the sorptometric studies. The UV–Vis spectra of the pillared clays were recorded using Shimadzu spectrometer model-2450 with $BaSO_4$ coated integration sphere. Scanning electron micrograph (SEM) of the pillared clay samples were recorded using JEOL JSM-6480 LV microscope (acceleration voltage 15 kV). The sample powder was deposited on a carbon tape before mounting on a sample holder. Transmission electron micrograph (TEM) of the STA/Cr-P sample was recorded using PHILIPS CM 200 equipment using carbon coated copper grids. Reactions were monitored by thin layer chromatography on 0.2 mm silica gel F-254 plates. Melting points were measured on a Micro Scientific works apparatus and are uncorrected. ^{1}H NMR spectra were recorded with Bruker 400 MHz NMR spectrometer using TMS as internal standard.

2.4. Catalytic studies for synthesis of 1,4-dihydropyridines

A mixture of benzaldehyde (1 mmol), ethylacetoacetate (2 mmol), NH_4OAc (1 mmol) and 0.1 g of STA/Cr-P in a 20 ml beaker was exposed to microwave radiation for the required amount of time. The reaction mixture was irradiated at 900 W for the specified time with an intermittent cooling interval of 60 s after every 60 s of microwave irradiation. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was transferred to 10 mL of ethyl acetate, stirred for 15 min, filtered and the reaction product was recovered from the ethyl acetate solution and recrystallized. The used catalyst was