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Aluminium and titanium modified mesoporous TUD-1: A bimetal acid catalyst for Biginelli reaction

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ABSTRACT

Using a simple, non-surfactant template triethanolamine (TEA), bimetal (Al^{3+} and Ti^{4+} ions) incorporated mesoporous catalyst AlTiTUD-1 (Si/Al+Ti = 50) was synthesized. The catalyst was characterized by XRD (Low and High angle), N_2 Sorption, FTIR, SEM, TEM, DR UV Visible, and pyridine adsorbed FT-IR techniques. The XRD and N_2 sorption studies confirmed its amorphous, mesoporous nature, which possessed a BET surface area of 590 $m^2 g^{-1}$ and pore diameter of 4.4 nm. The Al^{3+} and Ti^{4+} co-ordination within the TUD-1 was evaluated by DR UV–Vis. Pyridine adsorbed FTIR revealed both Bronsted (B) and Lewis (L) acidity, which is responsible for the catalytic activity. The acid catalyst showed a good catalytic performance in Biginelli type multicomponent coupling reaction for the substituted aldehydes, ethyl acetoacetate and thiourea to yield about 70% in reflux condition.

1. Introduction

Multicomponent reactions have been considered great importance in organic and medicinal chemistry due to the synthetic efficiency and molecular variety in the discovery of new compounds [1]. One of the most useful multicomponent reaction is Biginelli reaction which offers an efficient multifunctionalized 3,4-dihydropyrimidine-2-(1H)-ones ($DHPM_S$) and related heterocyclic compounds [2]. Such heterocyclic compounds exhibited wide scope of important pharmacological activities. Further, the DHPMs scaffolds developed as an integral back bone of several drugs used as calcium channel blockers, antihypertensive, antibiotic and anticancer agents [3,4]. The direct synthesis method of DHPMs is reported by Biginelli in 1893, which involves the one-pot condensation of an aldehyde, β-ketoester, and urea/thio urea under acidic conditions [5]. However, this method suffers from poor yields in the cases of aliphatic and some other substituted aromatic aldehydes. The DHPM derivatives have been synthesized using number of catalysts, such as $InBr_3$, tetrabutylammonium bromide (TBAB), polystyrene-poly(ethylene glycol)-sulfonic acid (PS-PEG-SO3H), and CaF_2 etc., Also, the researchers have been paid more attention for the synthesis with milder and more practical synthesis route. In particular, many catalytic methods were developed to improve the scope and yield of the reaction. Noticeably, most of the catalysed reactions are based on Bronsted/Lewis acidity in the catalyst.

In recent years, the conventional acid catalysts ($TiCl_4$, BF_3, $AlCl_3$, HF, H_2SO_4, etc.) are being replaced by heterogeneous acid catalysts due to the environmental problem, expensive reagents, low product yield, recovery catalyst, and excess usage of catalyst [6,7]. Recently, Titova et al. reported that the single, mixed metal oxides and silica based materials are efficiently utilized as heterogeneous catalysts for the preparative organic chemistry [8]. Mesoporous materials such as MCM-41, MCM-48, SBA-15, TUD-1 and KIT-6 with metal ions (M^{x+}) modified catalysts were synthesized and examined as a solid acid catalyst. Anand et al. have been reported the M^{x+} modified three dimensional, mesoporous TUD-1 type heterogeneous acid catalysts and revealed good catalytic activities for many organic transformations [9–11]. Mainly, Al^{3+} and Ti^{4+} based TUD-1 catalysts showed excellent catalytic activities with good leaching stability [12–15]. Moreover, the incorporated Al^{3+} and Ti^{4+} into TUD-1 were mainly generates Bronsted and Lewis acidity. At the same time, bimetal incorporated TUD-1 catalyst such as Al-Zr-TUD-1, Al-Fe-TUD-1, Co-Cr-TUD-1 and Fe-Ti-TUD-1 also

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exhibited better catalytic activities than monometallic catalyst, due to their synergistic effects [16–19]. Based on these results, in this work, bimetal Al and Ti incorporated mesoporous TUD-1 catalysts synthesis; characterization and the synthesis of DHPMs over the AlTiTUD-1 catalyst are discussed.

2. Materials and methods

2.1. Synthesis of AlTiTUD-1 catalyst

The synthesis of AlTiTUD-1 catalyst was completed by the ageing, drying, hydrothermal treatment and calcining a homogeneous synthesis mixture, which mainly consisting of tetraethyl orthosilicate (TEOS), titanium(IV) n-butoxide, aluminium isopropoxide, triethanolamine (TEA) and tetraethylammonium hydroxide (TEAOH, 35%). The molar ratio composition of 1 SiO_2: 0.01 Al_2O_3: 0.01 TiO_2: 0.5 TEAOH: 1 TEA:11H_2O is followed for the preparation [16,20]. In the typical synthesis, titanium(IV) n-butoxide, aluminium isopropoxide were dissolved in ethanol and added to TEOS. After stirring for few minutes TEA is added in drop wise followed by the addition of TEAOH in water under vigorous stirring for 2 h. Then the clear pale yellow colored gel was aged at room temperature for 12 h and dried at 100 °C for 20 h. It is then hydrothermally treated in Teflon lined autoclave at 180 °C for 6 h. Finally, the organic moieties were removed by calcination, in the presence of air at 600 °C for 5 h with a temperature ramp of 1 °C min^{-1}. The obtained clear white powder mentioned as AlTiTUD-1.

2.2. Catalyst characterizations

The powder X-ray diffraction patterns (XRD) were recorded on a Rigaku instrument with CuKα (λ = 1.54 Å) in the 2θ range of 0.5–4° (low angle) and 10–80° (high angle). Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 porosimeter. Chemical compositions were analyzed by ICP - OES using a Perkin Elmer OES optima 5300 DV spectrometer. Fourier – Transform infrared spectroscopy (FT-IR) was carried out on a FTIR - Bruker (Tensor) instrument measured in the range of 4000 to 400 cm^{-1} at 4 cm^{-1} resolution. DR UV–Visible spectrum was recorded by a Thermo scientific (Evolution 600) spectrometer with $BaSO_4$ as reference. The morphology was studied using scanning electron microscope (SEM) imaging FEI Quanta FEG 200 microscope. Also, transmission electron microscope (TEM) was examined with HRTEM JEOL 3010 with UHR pole piece and accelerating voltage of 300 kV. Pyridine adsorbed FT-IR measurement carried out in the FTIR - Bruker (Tensor) instrument by following the previous report [21].

2.3. Biginelli reaction over AlTiTUD-1

In typical reaction condition, a solution of benzaldehyde (2 mmol), ethyl acetoacetic ester (2 mmol), and thiourea (3 mmol) were transferred into 50 ml round bottom flask, which contains pre-dried AlTiTUD-1 (100 mg) catalyst and acetonitrile (5 ml) solvent. The solution mixture was heated at 80 °C under reflux condition for 6 h. The progress of the reactions was monitored by thin-layer chromatography (TLC). After completion of the reaction, the mixture was poured into crushed ice with stirring. The obtained crude product was filtered and washed with 95% hot ethanol. Finally, the catalyst was filtered and the obtained product was recrystallized with hot ethanol to give pure DHPMs. The compounds were confirmed by the mp, FTIR and NMR (^1H and ^{13}C) spectrometry.

3. Results and Discussion

3.1. Characterization of catalyst

The powder XRD pattern of AlTiTUD-1 is displayed in Fig. 1. The mesoporous nature of the synthesized material was determined by a low angle XRD peak between 0.5 and 2° 2θ (Fig. 1 a), that are typically observed for TUD-1 type materials [11,15,17,20]. Further, an amorphous nature of the silica is confirmed from a wide hump 2θ at 10–40° in the wide angle XRD (Fig. 1 b) [15,17]. However, there is no peaks were noticed for crystalline TiO_2 and Al_2O_3 which indicating that the homogeneous dispersion of Ti^{4+} and Al^{3+} into the framework of TUD-1 or finely dispersed TiO_2 and Al_2O_3 particles.

The N_2 sorption studies of AlTiTUD-1 catalyst (Fig. 2) exhibited type IV adsorption isotherm with a sharp inflection at a relative pressure (P/Po) = 0.4–0.9. Further, the catalyst displayed a H2 type hysteresis loop, due to the disordered interconnected porous nature [10,11,17,21]. The surface area of 590 m^2/g, pore volume of 0.7 cm^3/g and average pore size of 4.4 nm measured by BET and BJH methods. Furthermore, ICP – OES method displayed a Si/(Al+Ti) atomic ratio of 58, which is nearly same as that in the synthesis gel indicating that major portion of metal ions were incorporated into the TUD-1 silica. The DR UV Visible spectrum (Fig. 3) of AlTiTUD-1 displayed an intense peak centered at around 214 nm. The observed

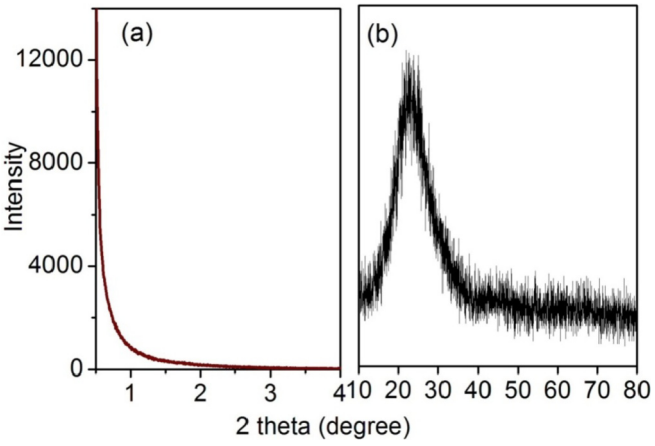

Fig. 1. (a) Low angle and (b) wide angle XRD patterns of AlTiTUD-1.

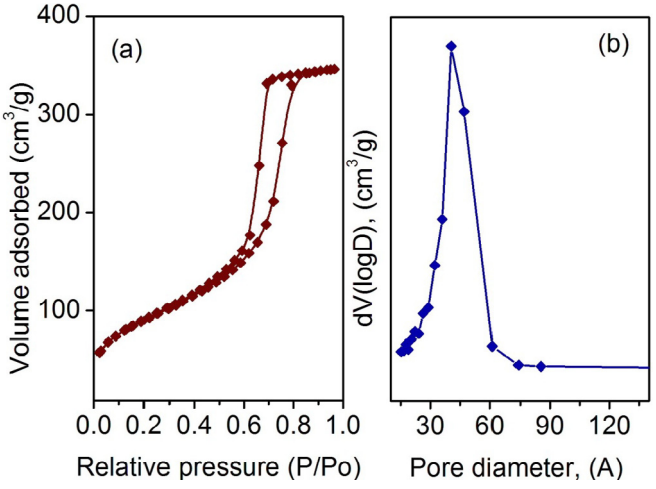

Fig. 2. (a) N_2 sorption isotherms, and (b) Pore size distributions of AlTiTUD-1.