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Heteropoly acid supported modified Montmorillonite clay: An effective catalyst for the esterification of acetic acid with sec-butanol

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ABSTRACT

Esterifications of acetic acid with sec-butanol catalysed by supported dodecatungstophosphoric acid, $H_3PW_{12}O_{40}$ (DTP) on acid modified Montmorillonite clay (AT-Mont) matrix have been carried out. A series of catalysts having 5%, 10%, 20% and 30% loading of DTP on different AT-Mont (15 min to 4 h) were synthesized and evaluated as catalysts; 20% DTP loaded on acid activated (15 min) clay showed the highest catalytic activity with about 80% conversion, having nearly 100% selectivity towards sec-butyl acetate. The high catalytic activity may be due to a high dispersion of the DTP on AT-Mont, providing more surface area (120 m^2/g) and active sites than pure HPA. The variation of different reaction parameters, such as reaction temperature, reaction time, mole ratio of acid and alcohol and catalyst amount, on the conversion of acetic acid were studied. The samples were characterized by surface area, cation exchange capacity (CEC) measurements, TGA-DTA and FTIR spectroscopy.

1. Introduction

Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used as plasticizers, solvents, perfumery, and flavor chemicals, and also as precursors for a gamut of pharmaceuticals, agrochemicals and other fine chemicals [1]. Compared to primary alcohols, esterification of a secondary alcohol is much more difficult to achieve. The steric effect of these substrates and the lower nucleophilicity of the oxygen atom hinders the formation of the corresponding ester [2]. Conversions are also limited by slow reaction rates and reversible reactions. Conventional homogenous catalysts widely used in industries for esterification include H_2SO_4, HCl, HF, H_3PO_4, and $ClSO_2OH$ [3,4]. They suffer, however, from several drawbacks, such as their corrosive nature, the existence of side reactions and the fact that the catalyst cannot be easily separated from the reaction mixture [5]. Due to stringent and growing environmental regulations, the chemical industry needs the development of more ecocompatible synthetic methodologies [6]. The use of heterogeneous acid catalysts offers an alternative and has received a lot of attention in the past years [5]. The heterogeneous catalysts reported in the literature for esterification reactions include ion exchange resin [7], H-ZSM–5 [8], zeolites-Y [9], niobic acid [10], and sulphated oxides [11]. However, the systematic study of esterification of sec-butanol with acetic acid using the above mentioned solid acid catalysts is not yet adequate. Heteropoly acids (HPAs) have been widely used in numerous acid-catalysed reactions due to their strong Bronsted acidity [3,12]. Dodecatungstophosphoric acid (DTP) is the most stable among all HPAs and is commonly used for acid catalysis, since it possesses the highest Bronsted acidity [13,14]. In homogeneous liquid-phase catalysis, the advantages of the HPAs are more distinctive due to their low volatility, low corrosiveness, high acidity, activity and flexibility. These acids have fairly high thermal stabilities and are stable up to 300–350 °C [15–17]. Depending on the reaction conditions, it has been found that the activity/mole proton of HPA is higher by a factor of 3–100 times than sulphuric acid as far as its reactivity in Bronsted acid-catalysed liquid-phase reactions is concerned [13]. But the main disadvantages of such HPAs as catalysts lie in their relatively low surface area (1–10 m^2/g) and in separation problems from reaction mixture [4]. HPAs on suitable supports are expected to overcome the above mentioned problems. A number of porous supports with high surface areas, such as silica, ZrO_2, active carbon, SBA-15, and zeolite etc. [18–23], have been used for supporting HPAs. Acid modified clay minerals can also be used as an efficient supports [24] because they exhibit higher surface area, pore volume, pore diameter and higher surface acidity [25] which results in its improved adsorption and catalytic properties. In particular, the acid treated clay catalysts have received considerable attention in different organic syntheses as a catalyst or as a support because

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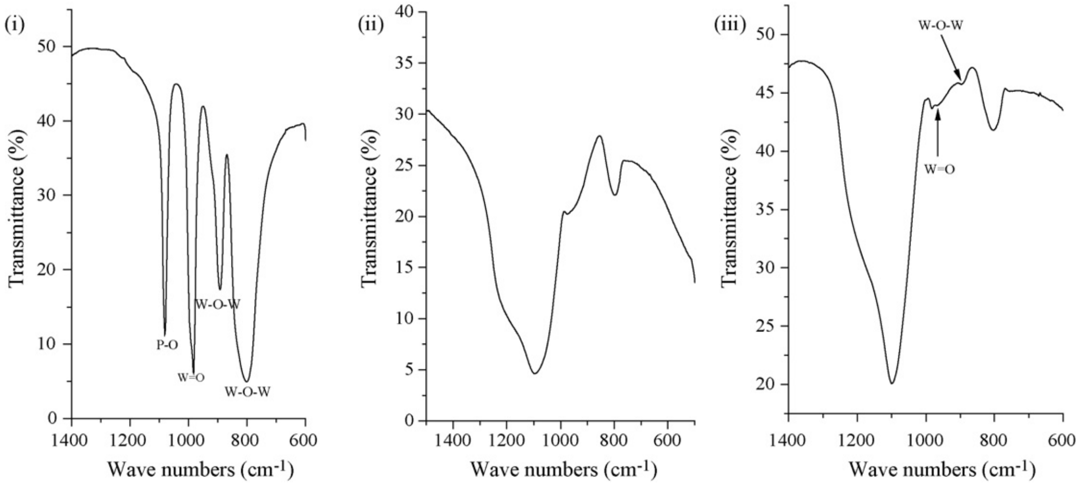

Fig. 1. FTIR spectra of (i) pure DTP, (ii) AT-Mont (15 min) and (iii) 20 wt% DTP/AT-Mont (15 min).

of their environmental compatibility, low cost and operational simplicity. Using clay catalysts, one can conduct environmentally benign green chemistry both at industrial level and on laboratory scale. The acid strength of HPA supported on some of the materials mentioned above is lower than that of bulk HPA, due to the interaction of HPA with surface functional groups of supports. In cases of composite material, there is an influence of support on the acidity function of HPA and vice versa [26]. Acid treated Montmorillonite exhibits comparatively strong acid sites [27]. Therefore, fine and uniform dispersion of DTP on large surface area mesoporous AT-Mont supports will increase the overall acidity and catalytic activity. In the present study, we report that HPA-like DTP is supported on acid modified Montmorillonite clay; it is also evaluated as solid acid catalyst for the esterification of sec-butanol with acetic acid.

2. Experimental

2.1. Support preparation

Natural Montmorillonite clay (procured from Gujarat, India) that contains silica sand, iron oxide, etc. as impurities was purified by a standard sedimentation method [28] to collect the <2 μm fraction before use. The oxide compositions of the clay as determined by weight chemical and flame photometric methods were SiO_2: 49.42; Al_2O_3: 20.02; Fe_2O_3: 7.49; MgO: 2.82; CaO: 0.69; LOI: 17.51; others (Na_2O, K_2O and TiO_2) 2.05%.

The purified clay (1 g) was refluxed with 4 M HCl acid (100 ml) for various time intervals (15 min, 1 h, 2 h and 4 h). The slurry was cooled, filtered and washed thoroughly with water and then was dried in an air oven at 393 K for 12 h [25,29]. The clay samples thus prepared are designated as AT-Mont (time).

2.2. Catalyst preparation

A series of catalysts having 5%, 10%, 20% and 30% loading of DTP (Aldrich, 99.9%) on different AT-Mont (time) samples were synthesized. DTP was supported on AT-Mont by means of incipient wetness impregnation method [12]. A known amount of DTP was dissolved in water and the hot support (dried at 120 °C for 6 h in an oven) was added to the solution. The slurry was shaken for 15 min at room temperature, washed with water and dried in the oven at 373 K for 12 h. The samples are designated as wt% DTP/AT-Mont (time).

2.3. Characterization techniques

Primary Keggin structures of bulk as well as supported HPA catalysts were compared by FTIR analysis. FTIR studies were conducted by using a PerkinElmer system 2000 FTIR spectrometer.

Specific surface area and pore volume were measured by using Autosorb1 (Quantachrome, USA). Specific surface areas were determined by using the Brunner–Emmett–Teller (BET) method. N_2 vapour adsorption data was obtained for the vapour pressure range (p/p_o) of 0.03–0.3. Prior to adsorption, samples were degassed at 200 °C for about 1.5 h.

The TG–DTA measurements of the samples were done with a thermal analyzer (TA Instruments, Model STD 2960, simultaneous DTA-TGA) with about 10 mg of sample in a platinum crucible at a heating rate of 10 °C min^{-1} in an air atmosphere.

Cation exchange capacities of different supports were determined by using standard techniques [30].

2.4. Esterification reactions

Into a pressure autoclave were taken 0.3 g of freshly activated catalyst (dried at 120 °C for 2 h in an oven), 0.15 mol of acetic acid (Merck, 99.8%), 0.05 mol of sec-butanol (Merck, 98%). The autoclave temperature was then slowly raised to 100–150 °C (autogeneous pressure 1–3 atm.) and maintained at the desired temperature during the specified reaction periods (1–12 h). The reaction products were collected from the autoclave and analyzed by GC (Chemito GC, Model 8510, FID). The catalyst was then washed with water and activated for the next experiments.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. FTIR

Bulk DTP shows the characteristic IR bands at 1080 cm^{-1} (P–O in central tetrahedral), 984 cm^{-1} (terminal W=O), 894 cm^{-1} and 801 cm^{-1} (W–O–W) associated with the asymmetric vibrations of the Keggin polyanion. After the materials were supported on AT-Mont, some of the characteristic Keggin bands were observed at 982 cm^{-1} and 893 cm^{-1} and other bands were merged up with the AT-Mont bands (Fig. 1).