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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<sup>2</sup>/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.

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#### 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<sub>2</sub>SO<sub>4</sub>, HCl, HF, H<sub>3</sub>PO<sub>4</sub>, and CISO<sub>2</sub>OH [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 acidcatalysed liquid-phase reactions is concerned [13]. But the main disadvantages of such HPAs as catalysts lie in their relatively low surface area  $(1-10 \text{ m}^2/\text{g})$  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<sub>2</sub>, 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  $<2 \,\mu$ m fraction before use. The oxide compositions of the clay as determined by weight chemical and flame photometric methods were SiO<sub>2</sub>: 49.42; Al<sub>2</sub>O<sub>3</sub>: 20.02; Fe<sub>2</sub>O<sub>3</sub>: 7.49; MgO: 2.82; CaO: 0.69; LOI: 17.51; others (Na<sub>2</sub>O, K<sub>2</sub>O and TiO<sub>2</sub>) 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<sub>2</sub> vapour adsorption data was obtained for the vapour pressure range  $(p/p_0)$  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  $10 \,^{\circ}$ C min<sup>-1</sup> 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  $1080 \text{ cm}^{-1}$  (P–O in central tetrahedral),  $984 \text{ cm}^{-1}$  (terminal W=O),  $894 \text{ cm}^{-1}$  and  $801 \text{ cm}^{-1}$  (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  $982 \text{ cm}^{-1}$  and  $893 \text{ cm}^{-1}$  and other bands were merged up with the AT-Mont bands (Fig. 1).



Fig. 2. (a) Pore size distribution curves of different samples determined by applying BJH method. (b) N<sub>2</sub> adsorption-desorption isotherms for AT-Mont (15 min) and 30% DTP/AT-Mont (15 min).

#### 3.1.2. Nitrogen adsorption

The surface area and pore volume of AT-Mont (15 min) and different wt% of DTP on AT-Mont (15 min) are given in Table 1. The surface area  $(390 \text{ m}^2/\text{g})$  and total pore volume (0.30 cc/g) of AT-Mont (15 min) decreases as the amount of DTP loading increases. For 30% DTP loading the surface area becomes  $101 \text{ m}^2/\text{g}$  while the total pore volume becomes 0.10 cc/g only. The acid-leaching has fundamentally transformed the layered Montmorillonite into an amorphous silica-like structure. The high surface area of 15 min acid treated clav is related to the removal of some of the aluminum from octahedral sites in the clay. The reduction in surface area and pore volume upon DTP loading may be due to the blockage of pores by DTP molecules. The pore size distribution plot in Fig. 2(a) shows that the average pore sizes of AT-Mont (15 min) and different wt% of DTP on AT-Mont (15 min) fall in the range of 35-50 Å suggesting that pore sizes of the catalysts lie in the mesoporous region, i.e. >20 Å. The adsorption-desorption isotherms of AT-Mont (15 min) and 30% DTP/AT-Mont (15 min) in Fig. 2(b) show that they have the form of Type IV isotherms with the hysteresis loop of type H3, which is a characteristic of a mesoporous solid.

#### 3.1.3. Thermal analysis

The thermal analyses have been carried out on bulk DTP, AT-Mont (15 min) and on 20% DTP/AT-Mont (15 min) samples. The results of these analyses are reported in Fig. 3. The TGA of 12-tungstophosphoric acid shows a weight loss of about 8% up to a temperature of 180 °C, indicating loss of free and adsorbed water. The gradual weight loss of about 3% up to 500 °C corresponds to the mass loss due to the reaction between acidic protons and structural oxygen from phosphotungstic acid, releasing water, followed by decomposition to WO<sub>3</sub> and PO<sub>x</sub> species [31]. The thermal data of AT-Mont (15 min) shows a steady loss of weight of about 17% up to 500 °C; such a loss is attributed to the loss of physisorbed and interlayer water and also due to dehydroxylation caused by the breaking of structural OH-groups of the support [32]. The TGA of supported DTP onto AT-Mont (15 min) shows about 18% weight loss within the temperature range of 80–150 °C due to a loss of

#### Table 1

Surface area and pore volume of different samples.

Catalyst	BET surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)
AT-Mont (15 min)	390	0.30
10% DTP/AT-Mont (15 min)	140	0.15
20% DTP/AT-Mont (15 min)	120	0.12
30% DTP/AT-Mont (15 min)	101	0.10

adsorbed water molecule. A gradual weight loss of about 3% up to 500 °C was also observed, such a result indicates an increase in the thermal stability of DTP on AT-Mont support. This may be due to the formation of intermolecular bondings between the support and heteropoly acid and indicates the presence of chemical interaction between the support and heteropoly acid.

#### 3.1.4. Cation exchange capacity

The cation exchange capacities of different supports were determined and are given in Fig. 4. It is evident that as the time of acid treatment increases, the cation exchange capacity of the support decreases from a value of 95.8 meq/100 g of clay to 6.7 meq/100 g of clay only. This reduction in CEC is due to the destruction of the layered structure of the clay as the time of acid treatment increases.

#### 3.2. Catalytic activity

The esterification of acetic acid with sec-butanol is an electrophilic substitution reaction; it is a relatively slow reaction and needs activation either by higher temperature or by a catalyst to achieve higher conversion.



Fig. 3. Thermal analyses of bulk DTP, AT-Mont (15 min) and 20% DTP/AT-Mont (15 min) samples.



Fig. 4. Cation exchange capacities of different supports.



**Fig. 5.** The effects of different loading of DTP on the esterification of acetic acid with sec-butanol. Reaction conditions: temperature: 100 °C, catalyst amount: 0.3 g, acid: alcohol: 3:1 (mole ratio).

A plausible mechanism that is involved in the esterification of acetic acid with sec-butanol reaction is as follows:



The reaction, following the Eley–Rideal mechanism, takes place between acetic acid and protons chemisorbed on the active sites (Brønsted acid sites) of the catalyst surface, resulting in a stable carbocation. The positive charge on the carbon atom is then attacked by one of the lone pairs on the oxygen of the sec-butanol to form an unstable intermediate. In the final step removal of a water molecule from the intermediate gives the final product, i.e. sec-butyl acetate along with the regeneration of the catalyst.

The conversion and selectivity of different catalysts are given in Figs. 5 and 6. It can be seen from Fig. 5 that, on increasing the loading from 5% DTP to 20% DTP on AT-Mont (15 min), the conversion increases; thereafter, however it decreases on further loading



**Fig. 6.** Effects of different catalysts on esterification of acetic acid with sec-butanol. Reaction conditions: temperature: 100 °C, catalyst amount: 0.3 g, acid: alcohol: 3:1(mole ratio).

to 30% DTP on AT-Mont (15 min). It is interesting to note that the activity of DTP is significantly lower than that of the same amount supported on AT-Mont (15 min) [e.g. esterification reaction with 20% DTP alone, gives about 22% conversion at 100  $^\circ\text{C}$  (not shown in the figure) with a selectivity of about 97%, while 20% DTP/AT-Mont (15 min), shows about 31% conversion (Fig. 5) with a selectivity of about 99.5%] under the same reaction conditions. The enhanced activity may be ascribed to a high dispersion of the DTP on AT-Mont, providing more surface area and active sites than pure HPA. Fig. 6 shows that, with the increase in acid treatment time of the support, the corresponding conversions decrease. This may be due to the decrease of surface area (Table 1) with the increased amount of loading and also due to decrease in CEC of the AT-Mont supports (Fig. 4). In view of the above, all further evaluations were carried out using 20% DTP/AT-Mont (15 min) catalyst. Thus, AT-Mont impregnated with DTP appeared to be a very active catalyst for the liquid-phase esterification of sec-butanol with acetic acid. In the present study, comparative results for the esterification of sec-butanol with acetic acid over some reported typical solid acid catalysts [33–35] are given in Table 2.

Some other factors such as reaction time, mole ratio of acid to alcohol, and catalyst amount also influence the conversion and selectivity of the reaction. The variation of different reaction parameters was studied on 20% DTP/AT-Mont (15 min) catalyst using sec-butyl alcohol and acetic acid. Moreover, control of water content in HPA catalysts is essential for their efficient performance. This can be achieved by thermal pretreatment of the catalysts [36], typically at 130–200 °C. Excess water causes a decrease in the HPA acid strength, and thus lowers its activity. At higher calcination temperature, dehydration/dehydroxylation of the catalyst occurs [37]. Dehydration of the catalyst increases the acid strength but decreases the number of acid sites, which may reduce the overall catalytic activity [15]. Therefore, the catalysts were activated at an optimum temperature, i.e. 120 °C before use.

Table 2

Results of esterification of sec-butanol with acetic acid catalysed by different solid acid catalysts.

Catalyst	Conversion (%)	References
Zirconia <sup>a</sup>	38	[33]
20% STA/Zirconiaª	71	[33]
30% STA/Hydrous Zirconia <sup>b</sup>	57	[34]
Amberlite IR-120 <sup>c</sup>	74	[35]
Crosslinked poly-(4-vinylpyridine)	27	[35]
hydrochloride <sup>c</sup> 20% DTP/AT-Mont.(15 min)	80	Present work

STA: Silicotungstic acid.

Reaction conditions: <sup>a</sup>Time: 4 h, reaction temperature: 98 °C, catalyst amount: 0.025 g, acid: alcohol: 1:16; <sup>b</sup>Catalyst amount: 0.5 g; alcohol: acid 1:2; <sup>c</sup>Time: 1 h, reaction temperature: 80 °C, catalyst amount: 0.125 g, acid: alcohol: 1:2.



**Fig. 7.** The effects of reaction time on the esterification of acetic acid with secbutanol using 20% DTP/AT-Mont (15 min). Reaction conditions: temperature:  $150 \circ C$ (closed system), pressure: 3 atm., catalyst amount: 0.3 g, acid: alcohol: 3:1 (mole ratio).

#### 3.2.1. Influence of reaction time

The influence of reaction time on the acetic acid conversion using 20% DTP/AT-Mont (15 min) as catalyst is given in Fig. 7. A gradual rise in the conversion is seen with increase in duration of the reaction period. Fig. 7 reveals that in 9 h of reaction time, about 79% of conversion was observed, which enhanced to 79.9% at the end of 12 h. The selectivity towards sec-butyl acetate remains almost 100% in all cases.

#### 3.2.2. Influence of reaction temperature

The reaction was carried out at various reaction temperatures, ranging from  $100 \,^{\circ}$ C to  $150 \,^{\circ}$ C at a given acetic acid to sec-butanol ratio of 3:1 for 1 h, 6 h and 9 h. The conversion amount of sec-butyl acetate versus reaction temperature is given in Fig. 8. From the figure it is evident that the conversion of acetic acid increases with the increase in reaction temperature. This suggests that increase in reaction temperature favors the formation of carbonium ion from acetic acid, this ion can reacts with sec-butyl alcohol to produce sec-butyl acetate. The selectivity remains nearly 100%.

#### 3.2.3. Influence of molar ratio of reactants

The effect of the mole ratio of reactants on the esterification of acetic acid with sec-butanol for 1 h and 9 h are shown in Fig. 9. For all mole ratios of acetic acid to sec-butanol, sec-butyl acetate is observed as the main product. With the increase in acetic acid: sec-butanol mole ratio from 1:2 to 3:1, the conversion increases because the increased acid amounts enhance the conversion of secbutanol. With further increase in mole ratio to 4:1, a decrease in conversion was observed. This decrease may be due to leaching of HPA from clay support; this is likely to occur in the course of the reaction because of its higher solubility in a more polar medium. The selectivity towards sec-butyl acetate remained nearly 100% in all cases.



**Fig. 8.** The effects of reaction temperature on the esterification of acetic acid with sec-butanol using 20% DTP/AT-Mont (15 min). Reaction conditions: catalyst amount: 0.3 g, acid: alcohol: 3:1 (mole ratio), pressure: autogeneous.



**Fig. 9.** The effects of mole ratio on the esterification of acetic acid with sec-butanol using 20% DTP/AT-Mont (15 min). Reaction conditions: temperature: 150 °C (closed system), pressure: 3 atm., catalyst amount: 0.3 g.



**Fig. 10.** The effects of catalyst amount on the esterification of acetic acid with secbutanol using 20% DTP/AT-Mont (15 min). Reaction conditions: temperature: 150 °C (closed system), pressure: 3 atm., acid: alcohol: 3:1 (mole ratio).

#### 3.2.4. Influence of catalyst amount

The effects of catalyst amounts on the esterification of acetic acid with sec-butanol for 1 h and 9 h are shown in Fig. 10. With the increase in catalyst amount, the conversion of sec-butyl alcohol increases marginally; this increase may be due to diffusional resistance in catalyst pores [38]. It is well known that reactions on Montmorillonites generally involve adsorption and diffusion of reactants through the pores and interlayers [39]. The diffusion of the reactants to the active sites can become a limiting process in such porous solid acids [5]. The product molecules remain adsorbed within the pores/channels of the catalyst and may restrict diffusion for the fresh reactants. The selectivity, however, towards sec-butyl acetate is nearly 100% in all cases.

#### 3.3. Recyclability of the catalyst

In order to regenerate a catalyst like 20% DTP/AT-Mont (15 min) after 9 h reaction, we separated it by filtration, washed it with conductivity water several times, dried it at 120 °C in an air oven and then used it in the esterification reaction with a fresh reaction mixture. The results obtained are shown in Table 3. A decrease in conversion was observed with its subsequent reuse, i.e. the conver-

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Esterification of acetic acid with sec-butanol using recovered catalyst.

Cycle	Conversion (%)	Selectivity (%)
1st run	79	>99
2nd run	74	>99
3rd run	68	>99

Reaction conditions: temperature: 150 °C (closed system), pressure: 3 atm., acid: Alcohol: 3:1 (mole ratio), reaction time: 9 h.

sion of 79% in the first run decreases to about 74% in the 2nd run and to 68% in the third run. That decrease in catalytic activity is due to the subsequent leaching of DTP (of about 3-5%) from the support into the liquid phase during the catalytic reactions was confirmed by a well-known ascorbic acid test [40]. However, the selectivity remains almost unchanged, i.e. >99.5%.

#### 4. Conclusion

Dodecatungstrophosphoric acid, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O, supported on AT-Mont acts as an efficient stable solid acid catalyst for esterification of acetic acid with sec-butanol. The high catalytic activity is attributed to the high surface area and BrÖnsted acid sites of the catalyst. The highly dispersed DTP on AT-Mont may provide higher active sites for the esterification. In all the esterification reactions the selectivity was nearly 100% while the conversion was about 80% within 12 h of reaction time. The 20% loading of DTP on AT-Mont (15 min) shows the highest efficacy. The catalyst can be regenerated and reused for several runs.

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