

# Heteropoly acid intercalated Zn/Al HTlc as efficient catalyst for esterification of acetic acid using *n*-butanol

J. Das, K.M. Parida\*

Regional Research Laboratory (CSIR), Bhubaneswar 751 013, Orissa, India

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## Abstract

Heteropoly acids (molybdophosphoric acid and tungstophosphoric acid) of different wt.% (5–20 wt.%) were intercalated in Zn–Al hydrotalcite-like-compounds by indirect intercalation via terephthalate route and the materials were characterized by PXRD, FTIR, BET, acid sites, etc. PXRD reveals intercalation of MPA and TPA species, which is further corroborated by the presence of these Keggin ions by FTIR. The catalytic activity of the prepared catalysts was tested for the liquid phase esterification of acetic acid using *n*-butanol under autogenous condition. The effect of various reaction parameters such as molar ratio of the reactants, temperature, time and catalyst dose, etc. on the conversion of acetic acid was studied and the findings are discussed. The 15 wt.% MPA intercalated sample shows highest conversion (84.15%) with 100% selectivity for *n*-butyl acetate.

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**Keywords:** Hydrotalcite-like-compounds; Heteropoly acid; Esterification; Acetic acid; *n*-Butanol

## 1. Introduction

The drive to develop environmentally benign processes has led to a considerable increase in research activities both in academic and industrial section for the development of solid acid catalysts. Though homogeneous catalysts (mineral acids) are widely used in industrial processes from economic considerations, ecological factors favour the use of heterogeneous catalysts. Use of mineral acids suffers from several inherent disadvantages due to the fact that they are highly corrosive and need to be neutralized at the end of the reaction or pose difficulties in separation from the reaction products which is very tedious in industrial processes. Therefore, heterogeneous catalysts can be considered as a viable alternative to their homogeneous counterparts as they can be easily recovered from the reaction mixture and the catalyst can be regenerated. A variety of materials have been used as solid acid catalysts such as clays,

H-ZSM-5, zeolites, mesoporous Al-MCM-41, sulphated metal oxides, etc. [1–5].

Of late, heteropoly acids (HPAs) have attracted considerable attention for both homogeneous and heterogeneous catalysis [6–11]. But the disadvantages with the HPAs are their low surface area and thermal stability [12,13]. Improvement in the thermal stability and surface area can be brought about by supporting the HPAs with different supports [14,15]. Supported HPAs [14] have been proved to be almost comparable, in terms of efficiency, to a series of acid catalysed reactions in liquid phase [16].

Esterification of acetic acid with *n*-butanol assumes commercial significance in view of the importance of the product *n*-butyl acetate, which finds vital application in the manufacture of artificial perfume, leather, photographic films, lacquer, plastic and safety glass. Not much work has been reported on the heteropoly acid intercalated hydrotalcite-like-compounds (HTlcs) towards esterification reaction.

The present paper deals with the synthesis and characterization of molybdophosphoric and tungstophosphoric acid intercalated Zn/Al HTlcs and the evaluation of their catalytic activity towards the esterification of acetic acid with *n*-butanol.

\* Corresponding author at: Colloids & Materials Chemistry Cell, Regional Research Laboratory (CSIR), Bhubaneswar 751 013, Orissa, India.

Tel.: +91 674 2581 636/38/39x425; fax: +91 674 2581 637.

E-mail addresses: [kmparida@yahoo.com](mailto:kmparida@yahoo.com), [kmparida@rrlbhu.res.in](mailto:kmparida@rrlbhu.res.in) (K.M. Parida).

## 2. Experimental

### 2.1. Materials preparation

#### 2.1.1. Zinc aluminium hydrotalcite-like-compound (ZAH)

Zn–Al hydrotalcite like compound with a Zn:Al molar ratio of 2:1 was prepared by co-precipitation (at constant pH) method [17]. In this method two solutions: one containing mixed metal nitrates of Zn(II) and Al(III) of desired concentrations and another containing NaOH (0.65 mol) were added (at 50 ml/h) simultaneously to a 1 l reaction vessel containing 100 ml of deionised water at 308 K under constant stirring. An inert atmosphere was maintained throughout the addition by bubbling N<sub>2</sub> gas. The pH of the solution was around 9.8. Then it was filtered, washed thoroughly with hot deionised water till neutral pH and dried at 383 K for further studies.

#### 2.1.2. Zinc-aluminium HTlc-terephthalate (ZAH-TA)

ZAH-TA was prepared by taking 12.5428 g (0.0755 mol) of terephthalic acid in stoichiometric amount of alkali (NaOH) in a closed container. The desired amount of mixed metal solution of Zn(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> were taken in a separating funnel and added drop wise to the solution containing terephthalic acid in NaOH with vigorous stirring. After complete addition it was aged for 18 h at 338 K. Then the slurry was filtered, washed with hot distilled water and dried at 383 K for intercalation with molybdophosphoric acid (MPA) and tungstophosphoric acid (TPA).

#### 2.1.3. Molybdophosphoric acid (MPA)

Approximately 20 g of ammonium heptamolybdate was dissolved in dilute orthophosphoric acid. It was further acidified with concentrated HCl till complete formation of yellow precipitate. Then it was filtered and washed with acetone to get the yellow crystals [18].

#### 2.1.4. Tungstophosphoric acid (TPA)

Tungstophosphoric acid (TPA) was prepared following reported method [18]. To 160 ml of deionised water, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (100 g) and Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O (50 g) were added and the mixture was refluxed at 353 K for around 2–3 h. This was followed by drop-wise addition of 24% HCl (150 ml) at 353 K and the solution was concentrated to a volume of 100 ml. The residual solution was shaken vigorously with ether and concentrated HCl. The adduct formed with ether, which settled down at the bottom, was separated from the aqueous phase. The white crystals of TPA were dried at room temperature.

#### 2.1.5. Sodium form of MPA and TPA

The heteropoly acids prepared above was dissolved in water followed by the drop-wise addition of Na<sub>2</sub>CO<sub>3</sub> solution till complete neutralization. Then the whole solution was evaporated to dryness at 383 K.

#### 2.1.6. MPA and TPA intercalated ZAH-TA

The ZAH-terephthalate (0.5 g) was taken in a closed reaction vessel with required amount of sodium form of heteropoly acids

in aqueous solution. Intercalation was done with (5–20 wt.%) of sodium form of MPA and TPA. Then the pH of the solution was adjusted in the range 4.5–5 using 0.2 M HNO<sub>3</sub> [19]. Then it was filtered, washed with deionised water and dried at 383 K for characterization and catalytic activity study.

### 2.2. Textural characterization

The XRD pattern of the powdered samples were recorded by a semiautomatic X-ray diffractometer (Model-PW 3710) with auto-divergent slit using Cu K $\alpha$  radiation at a scanning speed of 2°/min operated at 35 kV and 20 mA. The XRD data were matched with standard JCPDS data files. For the determination of crystallite size, the 003 reflection was scanned at a scan speed of 0.5°/min. The average crystallite size (*L*) of the particles was determined by X-ray diffraction line broadening technique using Scherrer equation:

$$L = \frac{0.94\lambda}{b \cos \theta} \quad (1)$$

where  $\lambda$  is the wavelength of the X-ray used (1.5406 Å), *b* the relative peak broadening, calculated as  $b^2 = b_{\text{exp}}^2 - b_{\text{ref}}^2$ , where *b*<sub>exp</sub> and *b*<sub>ref</sub> are half-widths at maxima observed on a given sample and a reference material which is ideally crystalline, respectively. FT-IR spectra were taken using a Nicolet FT-IR instrument (Model: Magna 550) with KBr phase in the range 400–4000 cm<sup>-1</sup> by KBr pelletization technique. About 4–5 mg of the sample was ground with 200 mg of KBr (spectroscopic grade) and then made pellets using hydraulic press. The specific surface area of the samples was determined by the N<sub>2</sub> adsorption/desorption method at liquid N<sub>2</sub> temperature (77 K) using Quantasorb (Quantachrome, USA). Prior to the surface area measurements, samples were degassed at 383 K in vacuum.

### 2.3. Acidity measurements

Acid sites have been determined based on the principles of irreversible adsorption of organic bases depending on their p*K*<sub>a</sub> values. Irreversible adsorption means that the adsorption experiments are carried out for a predetermined period of time (1 h), which is sufficient enough for the organic bases to form a monolayer of adsorption on the surface of the acid sites available on the catalyst. In the present work surface acidity was determined by spectrophotometric method by the irreversible adsorption of pyridine (p*K*<sub>a</sub> = 5.3) and 2,6-dimethyl pyridine (p*K*<sub>a</sub> = 6.9), which measures strong acid sites [20] and Bronsted acid sites [21], respectively.

### 2.4. Catalytic activity

The esterification reaction was carried out taking 0.025 g of the samples (dried at 110 °C for 6 h in an oven), 2 mmol of acetic acid (Merck, 99.8%), 32 mmol *n*-butanol (Merck, 98.0%) and 0.2 mmol of *n*-heptane (Merck 99.0%) as an internal standard in a 100 ml round bottom flask equipped with a reflux condenser. The contents were then refluxed gently at 371 K. Then the reaction mixture was filtered and the products were analyzed by

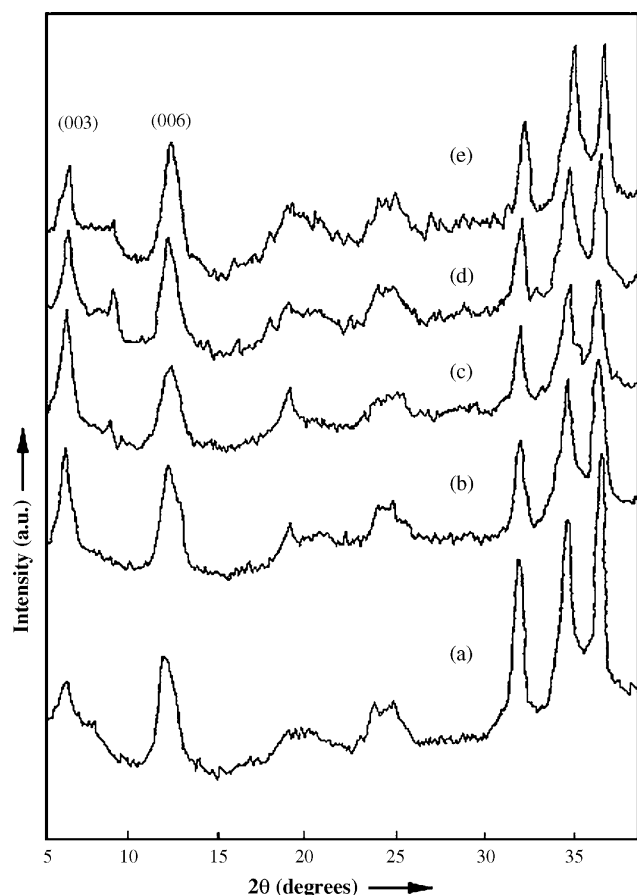


Fig. 1. PXRD pattern of (a) ZAH-TA; (b) ZAH-TA-TPA, 5 wt.%; (c) ZAH-TA-TPA, 10 wt.%; (d) ZAH-TA-TPA, 15 wt.%; (e) ZAH-TA-TPA, 20 wt.%.

Shimadzu gas chromatograph (GC-17A) using capillary column (ZB WAX).

### 3. Results and discussion

#### 3.1. Textural characterization

The XRD pattern of 383 K dried Zn/Al HTlc (ZAH) sample showed sharp and symmetric peaks at lower  $2\theta$  values, which

Table 1  
Crystallite size, surface area basal spacing and acid sites of various samples

Catalysts <sup>a</sup>	Crystallite size (Å)	Surface area (m <sup>2</sup> /g)	Basal spacing (Å)	Acid sites (μmol/g)	
				PY	2,6-DMPY
ZAH	134.45	45.7	7.65	27.2	17.2
ZAH-TA	67.4	80	13.9	29.2	18.7
ZAH-TA-MPA (5 wt.%)	93.8	75	14.1	32.0	20.4
ZAH-TA-MPA (10 wt.%)	79.0	86	14.0	35.7	22.9
ZAH-TA-MPA (15 wt.%)	71.3	89	14.2	37.1	24.0
ZAH-TA-MPA (20 wt.%)	64.0	74	14.1	33.5	23.6
ZAH-TA-TPA (5 wt.%)	67.1	71	14.0	31.9	19.7
ZAH-TA-TPA (10 wt.%)	61.5	78	14.1	36.4	21.5
ZAH-TA-TPA (15 wt.%)	63.0	86	14.3	39.1	23.1
ZAH-TA-TPA (20 wt.%)	69.2	66	14.2	33.0	22.8

<sup>a</sup> Zinc aluminium hydroxalcalite-like compound (ZAH); terephthalic acid intercalated ZAH (ZAH-TA); molybdophosphoric acid intercalated ZAH-TA (ZAH-TA-MPA); tungstophosphoric acid intercalated ZAH-TA (ZAH-TA-TPA).

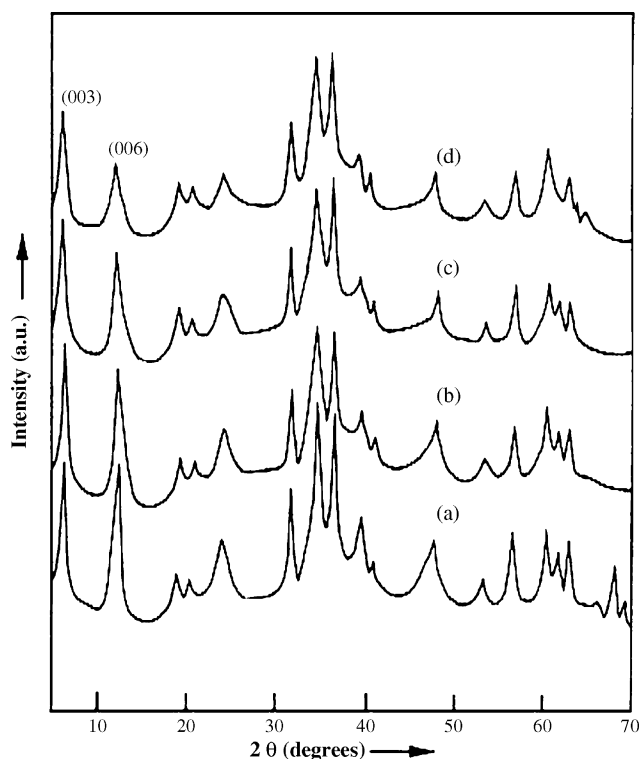


Fig. 2. PXRD pattern of (a) ZAH-TA-MPA, 5 wt.%; (b) ZAH-TA-MPA, 10 wt.%; (c) ZAH-TA-MPA, 15 wt.%; (d) ZAH-TA-MPA, 20 wt.%.

are characteristic of layered compounds (pattern not shown) [22]. The (003) reflection corresponding to a basal spacing of 7.65 Å in case of ZAH was increased to 13.9 Å (ZAH-TA) when terephthalic acid was used as the intercalating agent. This confirms the exchange of smaller anions in the interlamellar space of ZAH sample by terephthalate anions Fig. 1(a). Upon intercalation of different (5–20) wt.% of TPA by the indirect route, the basal spacing increased from 7.65 to 14.0–14.3 Å (Fig. 1(b–d)). Similarly, upon intercalation of MPA (5–20) wt.%, an increase in the basal spacing to 14.0–14.2 Å was observed (Fig. 2). Table 1 presents the basal spacing ( $d$  values) of various intercalated samples. The increase in basal spacing could be due to the insertion of the bigger anion (terephthalate ion)

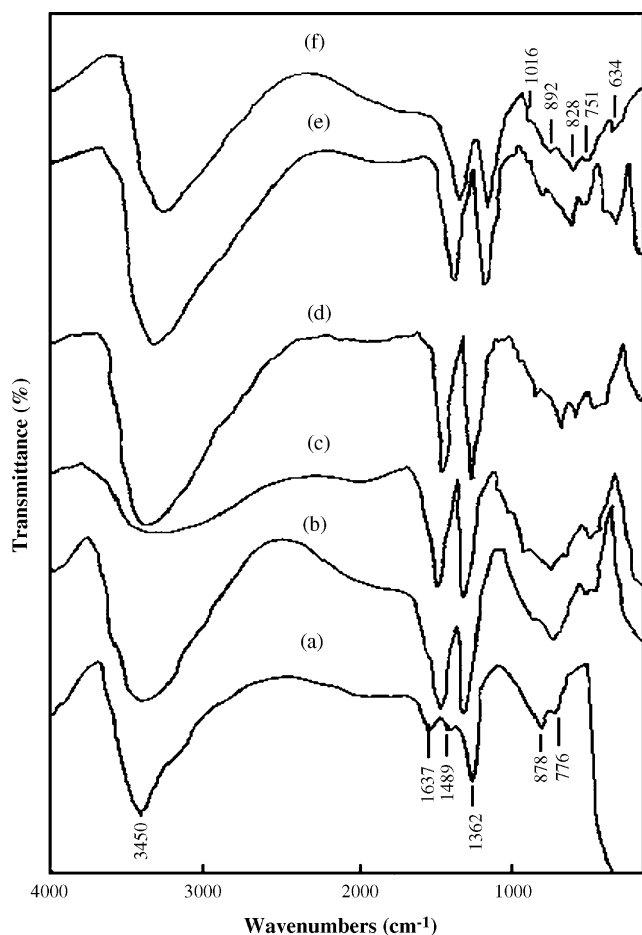


Fig. 3. FT-IR spectra of (a) ZAH; (b) ZAH-TA; (c) ZAH-TA-TPA, 5 wt.%; (d) ZAH-TA-TPA, 10 wt.%; (e) ZAH-TA-TPA, 15 wt.%; (f) ZAH-TA-TPA, 20 wt.%.

by replacement of the smaller anions, which helps in propping up the interlayer space thereby facilitating the incorporation of the guest heteropolyanions [19]. A small but broad reflection around 11–11.5 Å ( $d$ -value) has been marked for intercalation with heteropolyanions above 10 wt.%. This could be ascribed to the partially hydrolyzed salts of TPA [23].

Fig. 3 shows the FT-IR spectra with characteristic vibrations in ZAH, ZAH-TA and ZAH-TA-TPA intercalated samples. A broad and very intense absorption band between 3600 and 3200  $\text{cm}^{-1}$  was observed in case of all the samples. This band is associated with the –OH stretching vibrations in the metal hydroxide layers and interlayer water [24]. Strong absorption bands at 1637 and 1362  $\text{cm}^{-1}$  may be attributed to the deformation mode of water and nitrate anions, respectively [25]. The band between 700 and 400  $\text{cm}^{-1}$  could be due to the superposition of the characteristic metal-oxygen stretching modes in ZAH. The evidence for the retention of Keggin POMs present in the gallery region, generally show characteristic vibrations in the range 700–1100  $\text{cm}^{-1}$ . The TPA Keggin anion showed absorption bands at 1067, 1021, 992, 893, 822 and 771  $\text{cm}^{-1}$  [26]. Upon intercalation with different wt.% of TPA in ZAH, the Keggin bands were observed at 1016, 892, 828 and 751  $\text{cm}^{-1}$  and no considerable change in the peak position is observed.

This indicates the retention of Keggin anions in the interlayer space of ZAH. As for MPA intercalated samples, the Keggin bands were observed at 1026, 964, 827 and 754  $\text{cm}^{-1}$  (figure not shown) [27].

The surface area of the neat, terephthalate and various wt.% of TPA and MPA intercalated samples are presented in Table 1. ZAH-TA sample possesses higher surface area as well as basal spacing than that of neat ZAH. Upon intercalation with MPA and TPA, the surface area of the samples increases. It is observed that for ZAH-TA-MPA samples, the surface area increases from 75 to 89  $\text{m}^2/\text{g}$  with increase in wt.% of MPA from 5 to 15 wt.% and then decreases to 74  $\text{m}^2/\text{g}$  with increase in wt.% to 20 wt.%. Similarly for ZAH-TA-TPA samples, the surface area increases from 71 to 86  $\text{m}^2/\text{g}$  with increase in wt.% of TPA from 5 to 15 wt.% and then decreases to 66  $\text{m}^2/\text{g}$  with increase in weight percentage to 20 wt.%.

From Table 1 it is also observed that ZAH-TA samples possess lower crystallite size than that of ZAH. After intercalation with heteropoly acids (TPA and MPA), the crystallite size of the samples decreases. With increase in different wt.% of MPA (from 5 to 20 wt.%), the crystallite size of the samples gradually decreases from 93.8 to 64 Å. But with increase in different wt.% of TPA (from 5 to 20 wt.%), the crystallite size decreases up to 10 wt.% (61.5 Å) and then increases.

The acid sites of the catalysts were presented in Table 1. The number of Bronsted acid sites increases with increase in MPA and TPA loading up to 15 wt.% and thereafter decreases. It was found that among all the samples, 15 wt.% ZAH-TA-MPA sample possesses highest number of Bronsted acid sites (24.0  $\mu\text{mol}/\text{g}$ ).

### 3.2. Esterification of acetic acid

The conversion, selectivity and rate constants of different wt.% (5–20 wt.%) of TPA, MPA intercalated Zn–Al HTlcs are presented in Table 2. From the table it is observed that when the esterification is carried out in the absence of the catalyst a conversion of 31% was obtained. On employing Zn–Al HTlc (ZAH) as catalyst 56% conversion could be achieved. But when the reaction is carried out with heteropolyoxometalate intercalated samples, a considerable increase in the conversion is observed.

Table 2

Catalytic activity of various heteropolyoxometalate intercalated Zn–Al HTlcs towards esterification of acetic acid with *n*-butanol

Catalysts	Conversion (%)	Selectivity (%)	Rate constant ( $\text{s}^{-1}$ )
Without catalyst	30.76	100	$2.6 \times 10^{-5}$
ZAH	56.24	100	$5.7 \times 10^{-5}$
ZAH-TA-MPA5	67.43	100	$7.8 \times 10^{-5}$
ZAH-TA-MPA10	76.64	100	$10.1 \times 10^{-5}$
ZAH-TA-MPA15	84.15	100	$12.6 \times 10^{-5}$
ZAH-TA-MPA20	79.46	100	$11.0 \times 10^{-5}$
ZAH-TA-TPA5	64.87	100	$7.3 \times 10^{-5}$
ZAH-TA-TPA10	71.49	100	$8.7 \times 10^{-5}$
ZAH-TA-TPA15	77.23	100	$10.3 \times 10^{-5}$
ZAH-TA-TPA20	74.86	100	$9.9 \times 10^{-5}$

In case of both the series of samples, i.e. MPA, TPA intercalated samples the conversion increases from 5 to 15 wt.% and thereafter decreases with further increase in the wt.% to 20. On increasing the wt.% of MPA intercalation from 5 to 15 wt.% an increase in the conversion from 67.4 to 84.15% was observed. In case of TPA, the conversion increases from 64.9 to 77.2% with increase in wt.% from 5 to 15 wt.% and then decreases to 73.9% with further increase up to 20 wt.%. This may be ascribed to the increase in the Bronsted sites and surface area with the increase in the percentage of intercalating agents. In all cases selectivity was found to be 100%. Among all the intercalated samples, the 15 wt.% MPA intercalated Zn–Al HTlc (ZAH-TA-MPA15) shows a maximum conversion of 84.2% at 4 h reaction time and 373 K reaction temperature, respectively. This may be due to the presence of maximum number of Bronsted acid sites as well as highest surface area.

Though considerable conversion of acetic acid takes place in both the MPA and TPA intercalated samples, 15 wt.% MPA intercalated sample shows highest conversion with 100% selectivity. The said sample was taken for studying the effect of various reaction parameters such as molar ratio of the reactants, temperature, time and catalyst dose, etc.

### 3.2.1. Effect of molar ratio of acetic acid to *n*-butanol

The effect of molar ratio of acetic acid to *n*-butanol on the esterification of acetic acid at a fixed catalyst amount (0.025 g), temperature (373 K) and reaction time (4 h) has been presented in Fig. 4. From the figure it is observed that the percentage of conversion of acetic acid decreases from 83.8 to 58.6% with the increase in the molar ratio of acid:alcohol from 1:10 to 1:20. In all the feed ratios the selectivity was found to be 100%. The decrease in the conversion may be explained on the basis of the fact that the increase in alcohol concentration hinders the esterification reaction by blocking the active sites on the catalyst surface or the prevention of nucleophilic attack by shielding protonated alcohol due to its own excess. Similar observations have

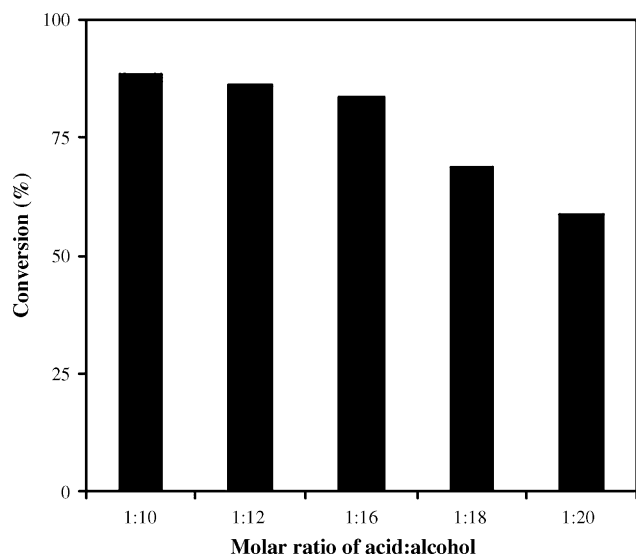


Fig. 4. Effect of molar ratio of acetic acid to *n*-butanol on the esterification of acetic acid with *n*-butanol over 15 wt.% MPA intercalated Zn–Al HTlc.

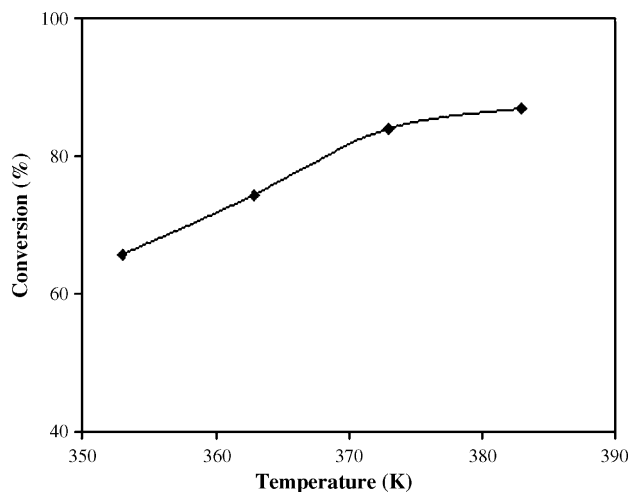


Fig. 5. Effect of reaction temperature on the esterification of acetic acid with *n*-butanol over 15 wt.% MPA intercalated Zn–Al HTlc.

been made by others [28,29]. This also confirms the Eley–Rideal mechanism with chemisorption of alcohol on the Bronsted acid sites.

### 3.2.2. Effect of reaction temperature

Fig. 5 depicts the effect of reaction temperature (353–383 K) on the esterification of acetic acid with molar ratio of acid:alcohol at 1:16, catalyst amount 0.025 g and reaction time 4 h. It has been observed from the figure that the conversion of acetic acid increases from 65.7 to 83.9% with increase in the reaction temperature from 353 to 383 K. This suggests that the increase in reaction temperature favours the formation of carbonium ion for nucleophilic reaction with acetic acid after adsorption on Bronsted acid sites leading to the formation of ester (*n*-butyl acetate).

### 3.2.3. Effect of reaction time

The effect of reaction time on the conversion of acetic acid with molar ratio of acid:alcohol at 1:16, catalyst amount 0.025 g, temperature 373 K is shown in Fig. 6. It has been observed from

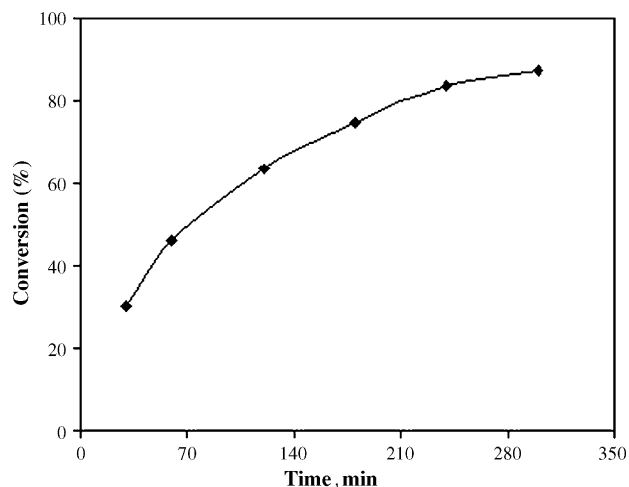


Fig. 6. Effect of reaction time on the esterification of acetic acid with *n*-butanol over 15 wt.% MPA intercalated Zn–Al HTlc.

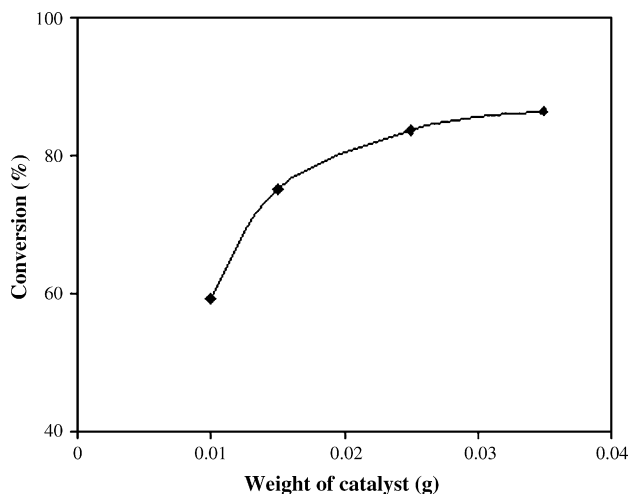


Fig. 7. Effect of catalyst amount on the esterification of acetic acid with *n*-butanol over 15 wt.% MPA intercalated Zn–Al HTlc.

the figure that with the increase in reaction time from 0.5 to 4 h, there has been a significant increase in the conversion of acetic acid from 30.2 to 83.8%. Increase in the reaction time beyond 4 h seems to have marginal effect up to 5 h. This suggests that optimum conversion of acetic acid to *n*-butyl acetate takes place at 4 h reaction time.

#### 3.2.4. Effect of catalyst amount

Fig. 7 represents the effect of catalyst amount (g) on the esterification of acetic acid while keeping the molar ratio of acid:alcohol at 1:16, temperature 383 K and reaction time 4 h. From the figure it is observed that with the increase in the catalyst amount from 0.01 to 0.025 g, the conversion increases linearly from 59.2 to 83.8% and thereafter remains almost constant. This may be due to the increase in the number of active sites with the increase in the catalyst amount.

#### 4. Possible reaction mechanism

The esterification of acetic acid with *n*-butanol is an electrophilic substitution reaction. As the reaction is relatively slow, in order to have a reasonable conversion, it is required to employ either higher temperature or catalyst dose. With increase in catalyst amount in the esterification of acetic acid, the conversion increases (Fig. 7). This suggests that the transfer of reactants from the liquid phase to the catalyst phase is not a rate limiting step, implying that the rate is independent of the catalyst mass [29]. Fig. 8 depicts the plot of  $-\ln(1 - \text{conversion})$  versus reaction time for the reactions carried out at 373 K. This plot shows a near linear character. This suggests a first-order dependence of the rate of the reaction on acetic acid concentration.

The reaction of acetic acid with *n*-butanol proceeds according to a rate equation, which is first order with respect to acetic acid and zeroth order with respect to *n*-butanol [30,31]. In general esterification reaction is a Bronsted acid catalysed reaction. The first step in this reaction involves the formation of carbonium ion due to the chemisorption of *n*-butanol on the catalyst surface following the Eley–Rideal mechanism. The carbonium ion, thus,

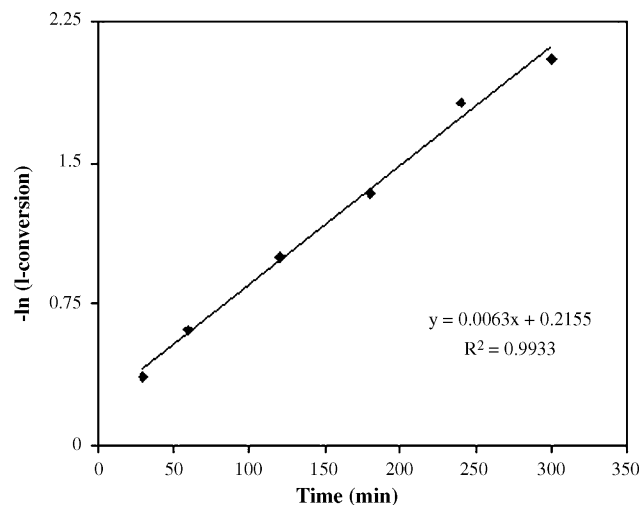
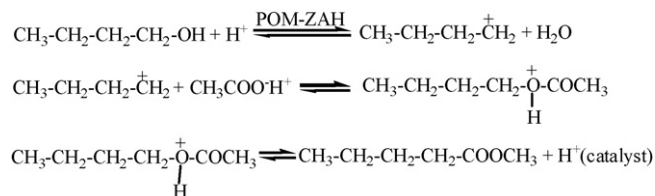


Fig. 8. Plot of  $-\ln(1 - \text{conversion})$  vs. reaction time for the esterification of acetic acid over 15 wt.% MPA intercalated Zn–Al HTlc.

formed is stable and attacks the nucleophilic center of acetic acid, leading to the formation of an unstable intermediate which in the final step releases a proton, thus, regenerating the catalyst and formation of the ester, i.e. *n*-butyl acetate. The role of an acid catalyst here is to facilitate the formation of the carbocation, and to help remove  $\text{OH}^-$  from *n*-butanol [32]. The mechanism involved in the above reaction may be represented as follows:



#### 5. Conclusions

Intercalation of HPAs with Keggin structure in Zn/Al HTlcs can be successfully made by indirect intercalation following terephthalate route as confirmed from PXRD and FT-IR. Intercalation leads to an increase in basal spacing, surface area and acid sites. Of the two series of intercalated samples, MPA intercalated samples show better catalytic activity compared to their TPA counterparts for conversion to *n*-butyl acetate in general and 15 wt.% MPA intercalated sample shows highest catalytic activity (84.15%) with 100% selectivity in particular. This may be ascribed to the highest surface area and maximum number of Bronsted acid sites of the catalyst sample.

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