



Synthesis of phenylacetates using aluminium-exchanged montmorillonite clay catalyst

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Abstract

Esterification of phenylacetic acid with phenol, cresols, nitrophenols and resorcinol has been carried out in the presence of montmorillonite clay exchanged with H⁺-ions, Al³⁺-ions and polyhydroxy oligomer cations of Al. Na⁺-montmorillonite (raw clay) was inactive, H⁺- and Al³⁺-montmorillonites, dried at 100 °C, showed 52 and 67% conversions to ester, respectively, upon refluxing the phenylacetic acid (20 mmol) and p-cresol (40 mmol) for 6 h. While Al³⁺-montmorillonite dried at 200 °C showed a conversion of 36% the same catalyst when dried at 400 °C showed no conversion. Montmorillonite exchanged with aluminium polyhydroxy oligomers dried at 100 °C and calcined at 500 °C to get pillared clay (d001=17.5 Å) failed to bring about the esterification. Effect of concentration of reactants, amount of catalyst and the reaction time on the yield of p-cresyl phenylacetate has been investigated. The esterification of phenylacetic acid with phenol and substituted phenols like m-cresol, o-cresol, p-nitro phenol and o-nitro phenol showed reduced yield due to steric factors. The activity of the clay catalyst after regeneration has also been studied.

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1. Introduction

Conventional Brønsted acids such as H₂SO₄, HF and HCl have many drawbacks when used as catalysts. These include harmful and high corrosive nature, difficulty in handling and work up procedure and their disposal. In order to overcome these drawbacks, several environmentally benign heterogeneous solid acid catalysts such as zeolites [1], metal oxides [2] and clays [3] are in usage. In particular, the clay catalysts have received considerable attention in different organic syntheses because of their environmental compatibility, low cost, high selectivity, reusability and operational simplicity. Among smectite clays, montmorillonite, in natural and exchanged forms, possesses both Lewis and Brønsted

acidity that enables it to function as an efficient catalyst in organic transformations with excellent product-, regio- and stereo-selectivity [4]. Smectite clays and their derivatives show catalytic activity in esterification reaction of alkenes and carboxylic acids [5]. Aluminium-exchanged montmorillonite clays have been found to be very effective acid catalysts for reactions such as dimerisation of ethylene oxide to dioxygen heterocycles [6], for α,ω-dicarboxylic acids to cyclic anhydrides [7] and ether synthesis [8].

Organic esters are very important class of chemicals having applications in the production of cosmetics, perfumes, flavors, pharmaceuticals, plasticizers, solvents and intermediates. Varieties of heterogeneous catalysts have been developed to synthesize industrially important esters. Zeolites in different forms have been studied in esterification reactions such as reactions between simple alcohols and carboxylic acids [9], amyl alcohol and acetic acid [10] and oleic acid and oleyl alcohol in the formation of jojoba oil analog [11].

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Filtrol-24, Amberlyst-15, sulfated zirconia and heteropolyacids have been used as catalysts in the synthesis of phenethyl acetate and cyclohexyl acetate [12]. Lipase has also been used as a catalyst in the synthesis of esters of cresols, but here the reaction times are very high [13]. However, to our knowledge no systematic study has been reported on the synthesis of the esters of phenylacetic acid using montmorillonite clay catalyst.

In the present work an attempt is made to investigate the esterification reaction of phenylacetic acid with different substituted phenols using Al^{3+} -montmorillonite. The *p*-cresyl phenylacetates have many industrial applications in perfumes such as lily, narcissus, hyacinth, and jasmine and in floral soaps [14].

2. Experimental

2.1. Clay materials

The clay mineral used in this work is a smectite rich white montmorillonite GK-129 (Na-GK, provided by Ceramic Technological Institute, Bangalore, India). The clay fraction containing less than $2\ \mu\text{m}$ was used for the study. The composition of the white montmorillonite was found by XRF to be 67.2% SiO_2 , 15.2% Al_2O_3 , 1.9% Fe_2O_3 , 3.2% MgO , 1.92% CaO , 2.58% Na_2O , 0.09% K_2O and LOI 7.91% with cation exchange capacity of 0.8 mequiv./g clay.

2.2. Catalyst preparation and characterisation

The montmorillonite clay was subjected to exchange by stirring overnight, 5 g of clay sample separately with 0.5 M (200 mL) solutions of aluminium chloride (pH 3.5) and hydrochloric acid (pH 0.88), to get Al^{3+} and H^+ -montmorillonite clay catalysts. The clay was then centrifuged and washed with distilled water repeatedly until the washings showed negative test for chloride ions. The clay sample was then dried at $100\ ^\circ\text{C}$ for 2 h and ground to pass through a mesh size 100. The exchangeable Al^{3+} was estimated following the procedure adopted by Selvaraj et al. [15] and was found to be equivalent to cation exchange capacity. The preparative procedure for pillared clay is described elsewhere [15]. The catalyst was activated at $100\ ^\circ\text{C}$ for 30 min prior to the study of its catalytic activity.

The XRD patterns of the clay samples were recorded on Siemens D5005 diffractometer using $\text{Cu K}\alpha$ radiation source between 2θ values 3° and 45° . Thermal analysis of clay samples was carried out using Polymer Laboratory make STA 1500 thermogravimetric analyzer between the temperature range of 30 – $750\ ^\circ\text{C}$ at heating rate of $15\ ^\circ\text{C min}^{-1}$. BET surface area of clay samples were determined by nitrogen adsorption–desorption method at liquid nitrogen temperature using a Quantachrome NOVA 1000 surface area analyzer. Prior to the analysis, the clay samples were degassed for 2 h at $100\ ^\circ\text{C}$.

2.3. Catalytic study

The liquid phase esterification reaction of phenylacetic acid with phenol and substituted phenols was carried out in 100 mL round-bottom flask fitted with Dean-Stark trap for water removal and a reflux condenser. Test reactions were conducted by refluxing 20 mmol of phenylacetic acid, 40 mmol of *p*-cresol and 2 g of different catalysts using 30 mL of toluene as a solvent for different time intervals (Table 1). After the reaction, the catalyst was separated by filtration. The filtrate was washed with 5% sodium hydroxide solution in a separating funnel to remove unreacted starting compounds. The organic layer was dried over anhydrous sodium sulphate and the solvent was distilled off under reduced pressure. The product was extracted with diethyl ether and checked by TLC and melting point and characterised using IR (Nicolet AVATAR 320 FT-IR) and $^1\text{H NMR}$ (Bruker-AMX 400) spectra. The effect of reaction time, mole ratio of reactants and amount of catalyst on yield of the ester was also investigated. Further, esterification of phenylacetic acid was carried out with *m*- and *o*-cresols, resorcinol, phenol and *p*- and *o*-nitro phenols.

2.4. Catalyst regeneration

The clay was separated from the reaction mixture by filtration, dried to evaporate the organic solvent and washed two times with distilled water. The resulting clay was dried at $100\ ^\circ\text{C}$ for 1 h, ground to a fine powder and used again to study its activity for the esterification reaction.

3. Results and discussion

3.1. Characterization of material

Fig. 1 shows the XRD patterns of montmorillonite exchanged with both simple aluminium cations and polyhydroxy oligomer cations of aluminium. The raw montmorillonite clay shows basal spacing equal to $14.7\ \text{\AA}$ (Fig. 1a)

Table 1
Effect of different catalysts on esterification of phenylacetic acid with *p*-cresol

Entry	Catalyst	Calcination temperature ($^\circ\text{C}$)	Reaction time (h)	Ester yield ^a (%)
1	Na^+ -montmorillonite (raw clay)	100	16	Nil
2	H^+ -montmorillonite	100	12	52
3	Al^{3+} -montmorillonite	100	6	67
		200	12	36
		400	12	Nil
4	Al-pillared montmorillonite	100	12	Nil

Concentration of phenylacetic acid: 20 mmol; concentration of *p*-cresol: 40 mmol; catalyst amount: 2 g.

^a Isolated yields.

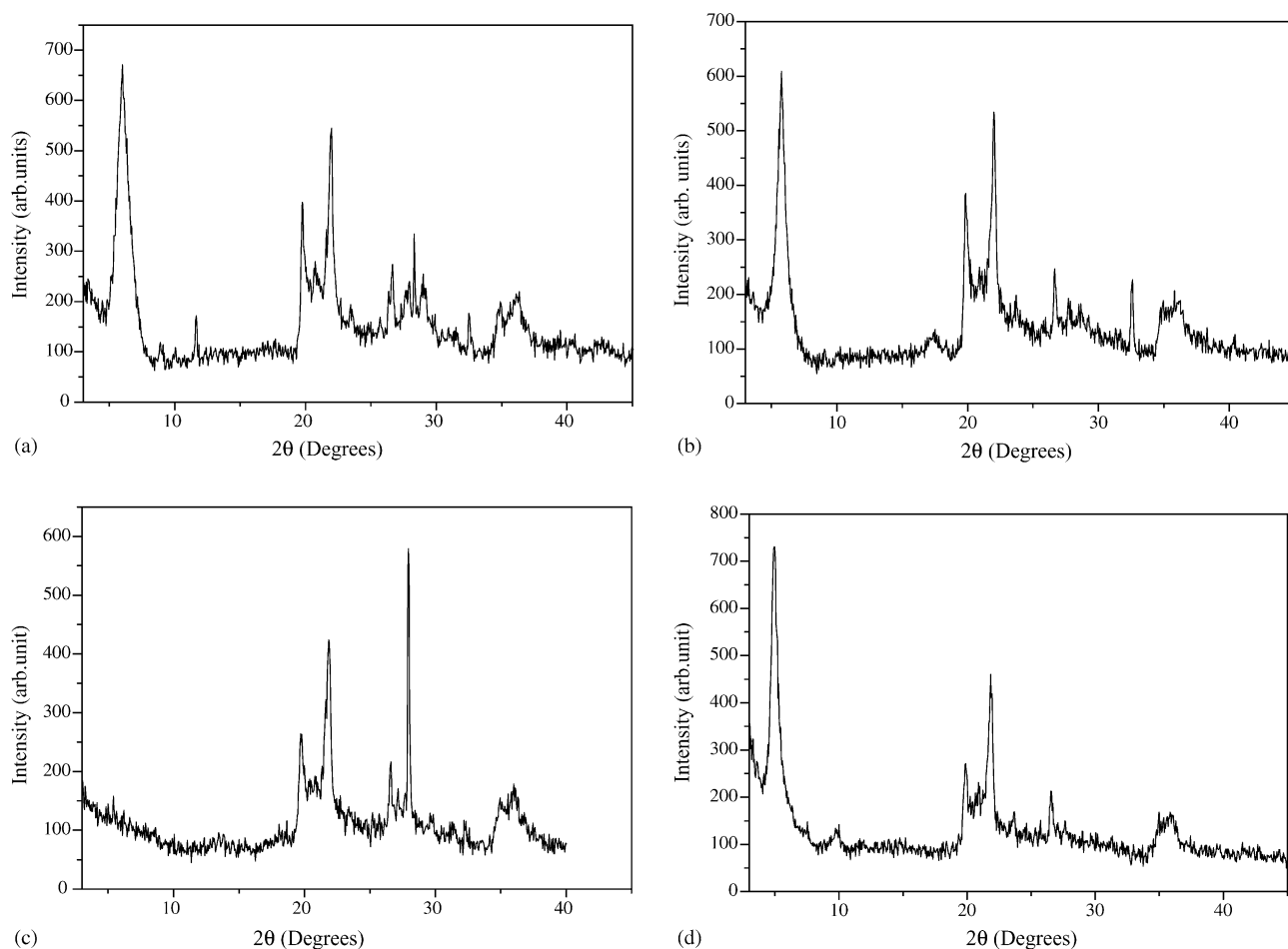


Fig. 1. XRD patterns of (a) raw montmorillonite, (b) Al^{3+} -montmorillonite dried at $200\text{ }^{\circ}\text{C}$, (c) Al^{3+} -montmorillonite dried at $400\text{ }^{\circ}\text{C}$, (d) aluminium pillared clay calcined at $500\text{ }^{\circ}\text{C}$.

and the Al^{3+} -montmorillonite dried at 100 and $200\text{ }^{\circ}\text{C}$ showed a similar XRD pattern with basal spacing equal to 15.5 \AA (Fig. 1b). The variation in basal spacing of Al^{3+} -montmorillonite is due to replacement of cations such as Na^{+} in interlayer of clay by aqua ions of aluminium. The same Al^{3+} -montmorillonite calcined at $400\text{ }^{\circ}\text{C}$ (Fig. 1c) showed a collapse of c -axis characteristic of smectites. Montmorillonite clay pillared with aluminium hydroxy oligomers (Fig. 1d) showed characteristic intense peak, corresponding to a basal spacing of 17.5 \AA .

TGA plots for montmorillonite exchanged with both simple and polyhydroxy oligomer cations of aluminium are presented in Fig. 2. The TGA plot of Al^{3+} -montmorillonite (Fig. 2a) shows maximum weight loss below $200\text{ }^{\circ}\text{C}$ and reasonable loss between 200 and $400\text{ }^{\circ}\text{C}$ and the weight remained almost constant on further thermal treatment. Montmorillonite clay exchanged with polyhydroxy oligomer cations of aluminium (Fig. 2b) shows gradual weight loss till $650\text{ }^{\circ}\text{C}$ and the weight remained almost constant on further thermal treatment. Similar observations have been made by Occelli et al. [16]. The TGA observation shows that the

hydrated water molecule is loosely coordinated in Al^{3+} -montmorillonite and strongly coordinated in pillared material.

Fig. 3 shows the adsorption–desorption curves of nitrogen gas at liquid nitrogen temperature for aluminium pillared clay catalyst. The hysteresis loop shown by pillared clay belongs to H3 type under the IUPAC classification indicating slit shaped pores [17]. The surface area of pillared clay catalyst was found to be $201\text{ m}^2\text{ g}^{-1}$.

3.2. Effect of different catalysts on esterification

Table 1 gives the effect of different catalysts on the esterification of phenylacetic acid with p -cresol (1:2) using 2 g of each catalyst. Raw montmorillonite in the Na^{+} -form failed to catalyse the esterification reaction even after refluxing for 16 h . This may be due to low electronegativity of Na^{+} -ions to polarize the water molecules to donate proton. H^{+} -montmorillonite is observed to be active showing a yield of 52% after refluxing for 12 h . Al^{3+} -montmorillonite dried at $100\text{ }^{\circ}\text{C}$ showed a yield of 67% after refluxing for 6 h whereas

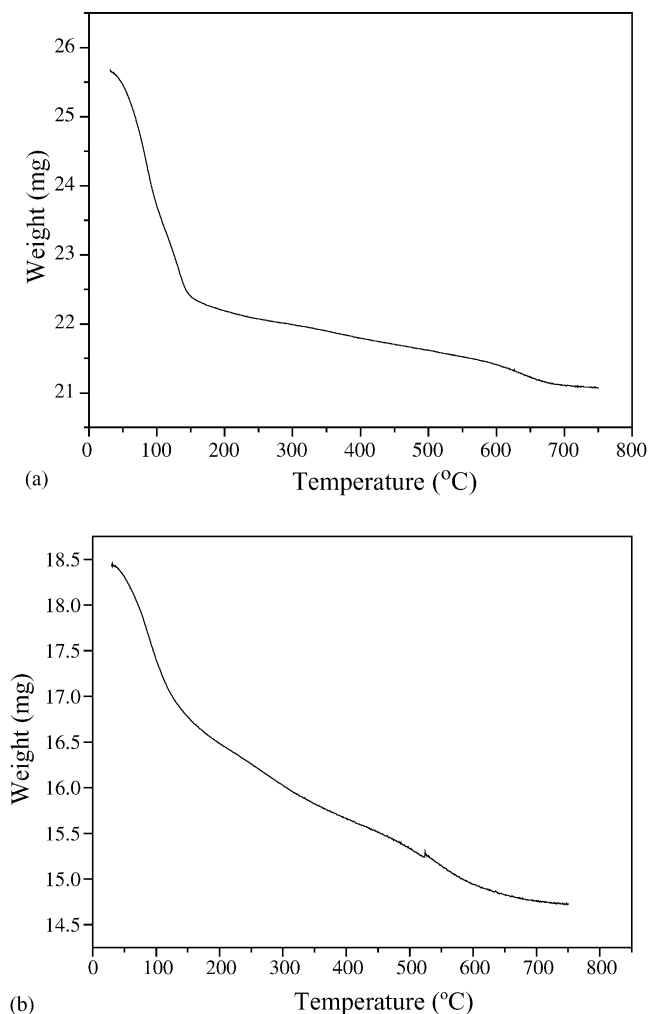


Fig. 2. Thermogravimetric patterns of air dried (a) Al³⁺-montmorillonite and (b) aluminium pillared montmorillonite.

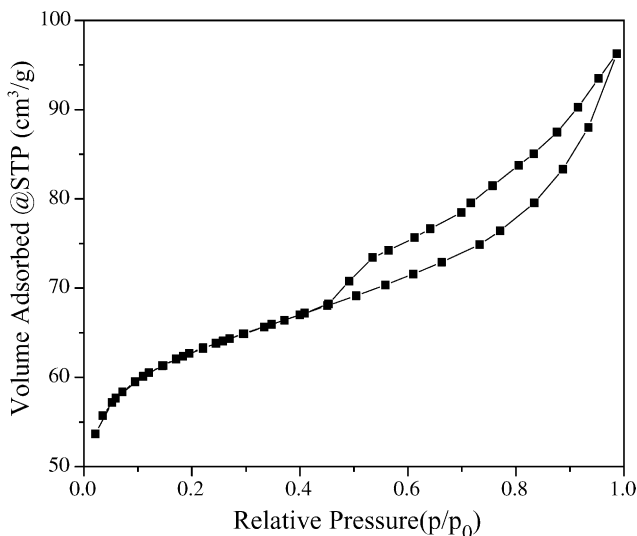


Fig. 3. Nitrogen adsorption-desorption curves of pillared clay catalyst.

the same clay dried at 200 °C showed a reduced yield of 36% and a negligible yield when calcined at 400 °C even after refluxing for 12 h. The activity of Al³⁺-montmorillonite is due to the presence of highly electronegative and polar Al³⁺-ions, which generates Brønsted acidity [18]. Montmorillonite pillared with aluminium hydroxy oligomers dried at 100 °C and the same clay calcined at 500 °C to form oxide pillars did not show any activity even after refluxing for 12 h.

The mechanism of esterification is shown in Scheme 1. Esterification reaction between carboxylic acid and alcohol is catalysed by Brønsted acids through the formation of conjugated acid ion i.e., oxonium ion (2) as given in Scheme 1. Addition of alcohol to the oxonium ion forms an intermediate adduct (3) which on loss of proton and water leads to formation of ester (4). The Brønsted acid site required for esterification is available from the dissociation of water molecule coordinated to the interlamellar metal ion (Scheme 2). Al³⁺-montmorillonite possesses hydration sphere that provides strong Brønsted acid site by dissociation of water molecule (Scheme 2) at the interlayer [19]. The loss of hydration sphere on calcining at 200 and 400 °C (Scheme 3) makes the clay ineffective. Hence it is not surprising that Al³⁺-montmorillonite loses its ability to catalyse esterification after removal of water on drying at high temperature (Table 1). The inactivity of clays exchanged with aluminium hydroxy oligomers dried at 100 °C for esterification reaction may be due to nonavailability of proton dissociated from the strongly coordinated hydration sphere. Also the failure of the calcined pillared clay to catalyse the esterification may be attributed to the conversion of Brønsted acid sites in to Lewis ones [16].

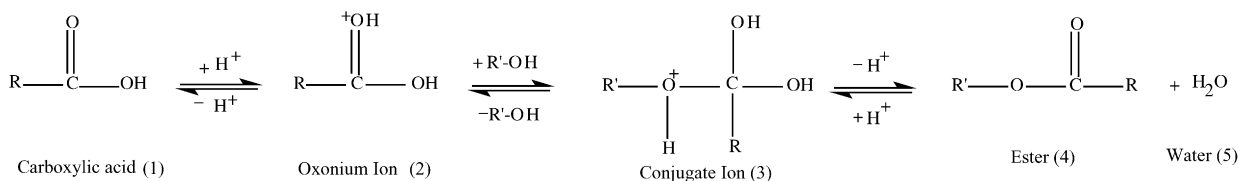
3.3. Effect of molar ratio on esterification

Table 2 gives the effect of molar ratio of phenylacetic acid to *p*-cresol on yield of the ester. The ratio of concentration of phenylacetic acid to *p*-cresol was varied between 20 and 80 mmol to get 1:1, 1:2, 1:3, 1:4, 4:1, 3:1 and 2:1 molar ratios, respectively. The reactions were carried out for 6 h in the presence of 2 g of Al³⁺-montmorillonite catalyst. The yield of the ester increased with increase in the concentration of *p*-cresol and reached a maximum of 74% when phenylacetic acid to *p*-cresol ratio was 1:4. Similarly the yield of the ester increased with increase in the concentration of phenylacetic

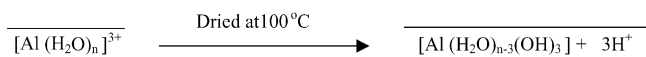
Table 2
Effect of molar ratio of phenylacetic acid to *p*-cresol on ester yield

Entry	Molar ratio (phenylacetic acid: <i>p</i> -cresol)	Ester yield (%)
1	1:1	64
2	1:2	67
3	1:3	72
4	1:4	74
5	4:1	77
6	3:1	77
7	2:1	75

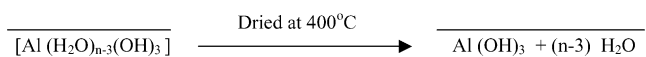
Reaction time: 6 h; catalyst amount: 2 g; concentration of phenylacetic acid: 20–80 mmol; concentration of *p*-cresol: 20–80 mmol; catalyst used: Al³⁺-montmorillonite.



Scheme 1.



Scheme 2.



Scheme 3.

acid and reached a maximum of 77% when phenylacetic acid to *p*-cresol ratio was 3:1. However the slight increase in the yield of ester with increase in the concentration of phenylacetic acid or *p*-cresol can be attributed to shifting of equilibrium towards ester formation. The higher yield of the ester at higher concentrations of phenylacetic acid shows that the acid has more influence on the reaction.

3.4. Effect of catalyst amount on esterification

Fig. 4 gives the effect of varying the amount of Al^{3+} -montmorillonite catalyst on the yield of ester. The amount of Al^{3+} -montmorillonite catalyst was increased from 0.5 to 3 g. It was observed that the yield of ester increased with increase in catalyst amount and was maximum when 2.5 g of the catalyst was used. The increase in the yield of the ester with the

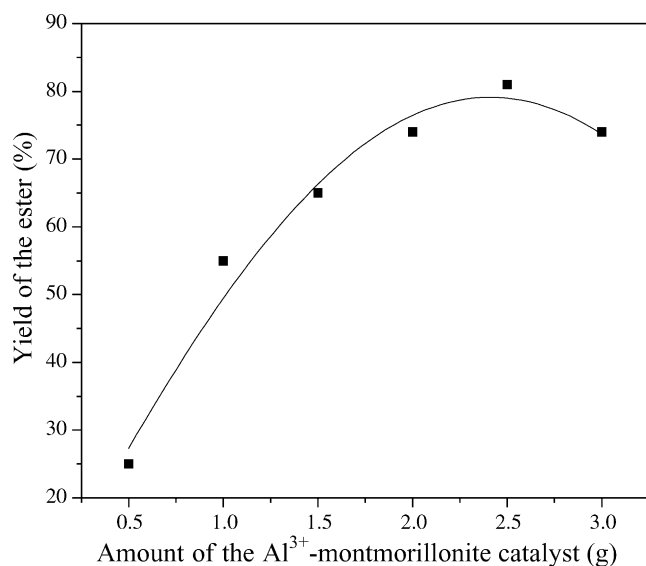


Fig. 4. Effect of catalyst amount on yield of the ester. Concentration of phenylacetic acid: 20 mmol; concentration of *p*-cresol: 80 mmol; reaction time: 6 h; catalyst used: Al^{3+} -montmorillonite.

catalyst amount is apparently due to increase in the acid sites available for esterification reaction. The yield of the ester was found to decrease with further increase in the catalyst amount from 2.5 to 3 g. This is attributed to the increase in adsorption of desired product on the excess active sites perhaps resulting in the formation of unwanted byproducts.

3.5. Effect of reaction time on esterification

Fig. 5 gives the effect of reaction time on the ester yield for 20 mmol of phenylacetic acid, 80 mmol of *p*-cresol and 2 g of Al^{3+} -montmorillonite. The yield of the ester increased with increase in reaction time from 2 to 12 h and there was no considerable increase in the yield of the ester when the reaction time was 18 h. The reaction was found to follow second order rate equation (Table 3).

$$\text{Rate} = 8.14 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$\times [\text{phenylacetic acid}][\textit{p}\text{-cresol}]$$

3.6. Esterification of phenylacetic acid with different substituted phenols

Table 4 gives the esterification of phenylacetic acid with various substituted phenols using 2 g of clay catalyst. Among

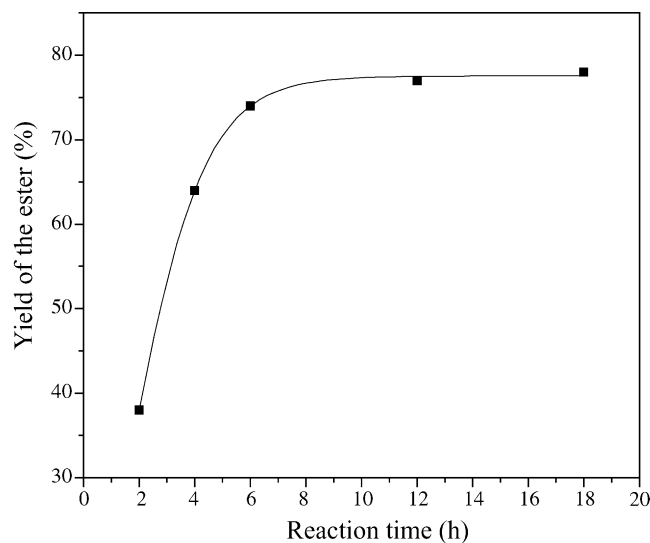


Fig. 5. Effect of reaction time on yield of the ester. Concentration of phenylacetic acid: 20 mmol; concentration of *p*-cresol: 80 mmol; catalyst amount: 2 g; catalyst used: Al^{3+} -montmorillonite.

Table 3
Effect of reaction time on ester yield

Entry	Reaction time (h)	Ester yield (%)	Rate constant, k ($\times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$)
1	2	38	8.84
2	4	64	9.89
3	6	74	8.92
4	12	77	4.90
5	18	80	–

Concentration of phenylacetic acid: 20 mmol; concentration of *p*-cresol: 80 mmol; catalyst amount: 2 g. Catalyst used: Al^{3+} -montmorillonite.

Table 4
Reaction of phenylacetic acid with various substituted phenols on Al^{3+} -montmorillonite

Entry	Substituted phenol	Ester yield (%)
1	<i>p</i> -Cresol	77
2	<i>m</i> -Cresol	66
3	Phenol	62
4	<i>p</i> -Nitro phenol	08
5	<i>o</i> -Cresol	05
6	<i>o</i> -Nitro phenol	Nil
7	Resorcinol	Nil

Concentration of phenylacetic acid: 20 mmol; concentration of substituted phenol: 80 mmol; reaction time: 6 h; catalyst amount: 2 g; catalyst used: Al^{3+} -montmorillonite.

the cresols, *p*-cresol showed the highest yield whereas the *ortho* isomer showed negligible conversion possibly due to steric factors. Looking at the results of esterification with nitrophenols, it is clear that the nitro group has negative effect on the rate of reaction because, its electron withdrawing property reduces the nucleophilic character of phenol. It is not clear why resorcinol does not undergo esterification. However, it is quite likely that it gets protonated and hence rendered less nucleophilic.

The activity of regenerated clay catalyst was also investigated after washing the spent catalyst with distilled water and drying it at 100 °C. The yield of the ester per unit weight of the regenerated catalyst was found to be nearly the same as that obtained using fresh catalyst. The results remained essentially unchanged even after regenerating the clay catalyst five times.

4. Conclusion

Al^{3+} -montmorillonite is found to be active in bringing about the synthesis of phenylacetates, which have applications in the perfume industry. Interlamellar water attached to aluminium ions provides strong Brønsted acid sites to catalyse the esterification. This is clearly demonstrated by the fact that the catalyst loses its activity upon dehydration,

which converts the Brønsted acid sites to Lewis ones and supports the mechanism proposed. The method suggested here is superior to the conventional procedures that make use of concentrated H_2SO_4 in respect of selectivity, as well as the ecofriendly and reusable nature of the catalyst. The results indicate that less acidic phenols with no substituent in the *ortho* position give good yields. Mere washing of the spent catalyst with distilled water regenerates the acid sites required for esterification.

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