Esterification of succinic anhydride to di-(*p*-cresyl) succinate over M^{n+}-montmorillonite clay catalysts

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Abstract

Esterification of succinic anhydride to di-(*p*-cresyl) succinate over heterogeneous acid clay catalysts is reported. Montmorillonite clay samples exchanged with different cations were prepared and catalytic activity of the resulting materials was investigated in the synthesis of di-(*p*-cresyl) succinate esters. Among the exchanged clay catalysts, Al^{3+} and H^+-mont were found to be more active for the esterification of succinic anhydride with *p*-cresol. The activity of M^{n+}-mont was found to be directly related to the charge to radius ratio of M^{n+}-ions. The influence of molar ratio of reactants, reaction time, and catalyst amount on the esterification reaction was investigated. The esterification was found to follow the second order rate kinetics and the kinetic parameters such as rate constant (k), equilibrium constant (K) and Gibbs free energy (ΔG°) for the reaction have been determined. The activity of Al^{3+}-mont clay catalyst for the esterification of succinic anhydride with phenol, *m*-cresol, *o*-cresol, *p*-nitrophenol and resorcinol have been studied. Regeneration and reusability of the clay catalyst has also been investigated.
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1. Introduction

Organic esters are an important class of chemicals having applications in various preparations such as cosmetics, perfumes, flavors, pharmaceuticals, and plasticizers. Esters of cresol, especially, are more useful in food industry as flavor compounds as they possess a combination of sweet, floral and fruity odour [1]. Conc H_2SO_4, dry HCl gas and *p*-toluene sulphonic acid are commonly used as catalysts to catalyze esterification reactions [2]. The use of such catalysts, however, have some drawbacks that include corrosion, loss of catalyst, environmental problems and formation of unwanted side products along with the desired one reducing the yield of the latter.

Efforts have therefore been made to develop eco-friendly heterogeneous catalysts for synthesis of industrially important esters. Zeolites have been reported as active catalysts in the esterification of salicylic acid with dimethyl carbonate [3] and Amberlyst-15, a cation exchanged resin, catalyses esterification of acrylic acid with butanol [4]. Sulphated-ZrO_2 [5], aluminophosphates and silicoaluminophosphate molecular sieves [6] have been reported to be active in catalyzing the esterification of phthalic anhydride with 2-ethylhexanol. Recently it has been reported that lipase enzyme can catalyze the esterification of different carboxylic acids with *p*-cresol and *m*-cresol [7].

The clay catalysts, in particular, have received considerable attention in different organic syntheses because of their environmental compatibility, low cost, high selectivity, reusability and operational simplicity [8]. Among smectite clays, montmorillonites, both in natural and exchanged forms, possess both Lewis and Brønsted acidities, which

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enable them to function as efficient catalysts in organic transformations. Montmorillonite clay exchanged with metal ions (M^{n+}-mont) are efficient catalysts in many organic transformations such as Diels-Alder reaction [9,10], polymerization [11], benzylation of aromatics [12], etherification [13,14], and acetalization reactions [15].

Fe^{3+}-K-10 montmorillonite is reported to be an effective catalyst in bringing out the esterification of carboxylic acids with alcohols [16] and also in synthesis of amides from carboxylic acids [17]. In the present study we are reporting the preparation of different cation exchanged montmorillonite catalysts for the esterification of succinic anhydride (SA) with p-cresol (p-C) to give di-(p-cresyl) succinate ester and the factors that influence the activity of the catalyst.

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 enriched clay containing less than 2 μm fraction was used for exchange. The composition of the white montmorillonite was found by XRF to be 67.26% SiO_2, 13.42% Al_2O_3, 1.87% Fe_2O_3, 3.2% MgO, 2.72% Na_2O, 1.27% K_2O, 1.55% CaO, 0.09% TiO_2, 0.02% MnO, 0.07% BaO, 0.03% P_2O_5, 0.89% S, and 5.04% ignition loss. The cation exchange capacity (CEC) value was found to be 0.8 meq/g of clay.

The montmorillonite K-10 was procured from Sigma Aldrich and other chemicals and solvents were purchased from SD Fine Chemicals.

2.2. Catalyst preparation

The cation exchanged clay catalysts were prepared by adopting the standard procedure given in literature [18]. The method involves stirring of 5 g montmorillonite clay sample with 200 mL of 0.5 M salt solution containing the respective cation for 24 h. Table 1 gives the source of cation and pH of the salt solutions used to prepare cation exchanged clays. The clay was then centrifuged and washed with distilled water repeatedly until the washings showed negative test for anions. The clay sample was then dried at 373 K for 3 h and

Table 1
Preparative conditions for cation exchanged clay (M^{n+}-mont) catalysts

Cation	Cation source (exchanging salt)	pH of exchanging solution[a]
Al^{3+}	AlCl$_3$ (anhydrous)	2.55
Cr^{3+}	CrCl$_3$·6H$_2$O	1.99
Fe^{3+}	FeCl$_3$·6H$_2$O	1.03
Zn^{2+}	ZnCl$_2$ (anhydrous)	5.35
Mn^{2+}	MnCl$_2$·4H$_2$O	5.16
Ni^{2+}	NiCl$_2$·6H$_2$O	4.94
Cu^{2+}	CuSO$_4$·6H$_2$O	3.44
H$^+$	HCl (aqueous)	0.88

[a] Concentration of exchanging solution is 0.5 M.

subsequently ground to a fine powder. Clay catalysts were activated at 373 K for 30 min prior to the activity test.

2.3. Methods

XRD patterns of the clay samples were recorded on a Siemens D5005 diffractometer using Cu Kα radiation and a Ni filter. Basal spacings were calculated by making use of $d_{0\,0\,1}$ values. Specific surface area of clay samples was determined by the BET method at liquid nitrogen temperature using a Quantachrome NOVA 1000 surface area analyzer. Prior to the surface area analysis the clay samples were degassed for 2 h at 373 K. The total acidity of the samples was evaluated by the n-butylamine back titration method [19]. The exchangeable cations of the clay catalysts were determined according to the standard methods available [20] after extracting with dilute hydrochloric acid. The metal content of Al^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Mn^{2+} was found to be 0.74, 0.78, 0.75, 0.79, and 0.76 meq/g, respectively, which is almost equivalent to cation exchange capacity (CEC) of the parent montmorillonite. However, it was observed that in the case of Fe^{3+}-mont the amount of iron is more than the CEC.

2.4. Catalytic study

The liquid phase esterification reaction of succinic anhydride with p-cresol (Scheme 1) was carried out in a 100 mL round-bottomed flask fitted with a Dean-Stark trap for water removal and a reflux condenser. The flask was charged with succinic anhydride (5 mmol), p-cresol (15 mmol), 0.5 g of clay catalyst and 35 mL of toluene. The reaction mixture was refluxed for 8 h, then cooled and filtered to separate clay catalyst and washed with solvent (2 × 5 mL). The fil-
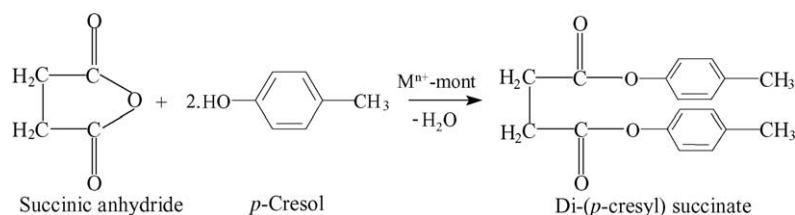
Scheme 1. Esterification of succinic anhydride with p-cresol over M^{n+}-mont catalyst.
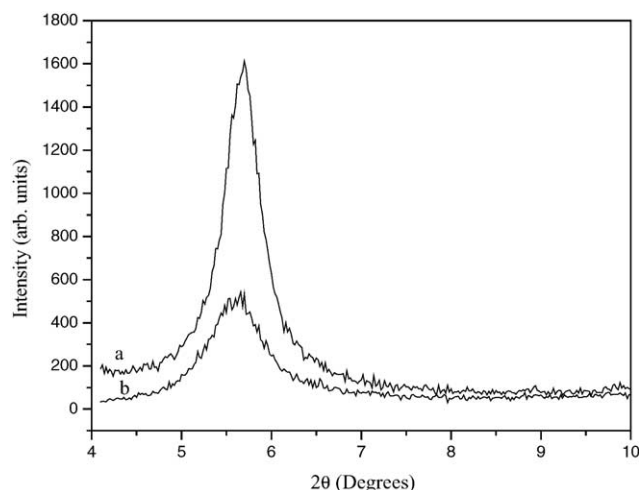
Fig. 1. X-ray diffraction patterns of Al^{3+}-mont catalyst: (a) before esterification, (b) after esterification.

trate was washed with 5% sodium hydroxide (4 × 15 mL) to remove unreacted starting compounds. The organic layer was washed with water (2 × 15 mL), saturated brine (1 × 15 mL) and dried over anhydrous sodium sulphate and finally the solvent was distilled off under reduced pressure. The product was extracted with diethyl ether and was identified by its melting point, and IR, ^1H NMR and ^{13}C NMR spectral analyses. Esterification of succinic anhydride was also carried out with phenol, m-cresol, o-cresol, o-nitrophenol, resorcinol and salicylic acid.

2.5. Regeneration of the catalyst

The clay catalyst was separated from the reaction mixture by filtration or centrifugation, and washed with toluene twice. After the evaporation of toluene, the clay was washed two times with distilled water and was dried at 373 K for 1 h, ground to a fine powder and reused to study its activity for the

esterification reaction. Fig. 1 shows X-ray diffraction patterns of Al^{3+}-mont before and after conducting the esterification (Fig. 1a and b). The patterns show no change in the basal spacing (15.2 Å) of Al^{3+}-mont after conducting the reaction. Apparently, the constituents in the reaction mixture are not able to swell and gain entry into the interlamellar region.

3. Results and discussions

3.1. Esterification of succinic anhydride with p-cresol

Activity for the esterification of succinic anhydride with p-cresol and some characteristics of M^{n+}-mont clay catalysts such as the charge to radius ratio of cation, basal spacing, total acidity and specific surface area are given in Table 2. No correlation was found among specific surface area, basal spacing and total acidity with the esterification activity of the catalysts. However, the activity of the M^{n+}-mont catalysts was found to be linearly related to the charge to radius ratio of M^{n+}-ion exchanged into the montmorillonite clay (Fig. 2). The interlayer acidity of cation exchanged clays increases with increase in the charge to radius ratio of the exchanged cation due to increase in polarization of the water molecules in the primary coordination sphere [21]. Acidity determined by n-butylamine back titration, however, gives total acidity although the esterification reactions are known to be catalyzed by Brønsted acid sites.

The reactions conducted either in the absence of catalyst or in the presence of unexchanged montmorillonite failed to give the ester. Activities of cation exchanged clays were also compared with the results obtained with p-toluenesulphonic acid and montmorillonite K-10, a commercially available acid clay catalyst. The results indicate that montmorillonite K-10 is less effective, as the ester formed is only 10% whereas, p-toluenesulphonic acid shows a good catalytic activity with 78% yield of the ester. Among the M^{n+}-mont clay catalysts,

Table 2
Characteristics and activity of (M^{n+}-mont) catalysts

Catalyst	Charge to radius ratio[a]	Basal spacing (Å)	Total acidity (mmol/g)	Surface area (m²/g)	Activity[b] (% yield[c])
Na^+-mont (raw clay)	1.05	14.7	0.16	37.8	Nil
Al^{3+}-mont	6.00	15.2	0.78	28.0	75
Fe^{3+}-mont	5.00	15.5	0.78	31.0	19
Cr^{3+}-mont	4.69	15.8	0.79	26.7	65
Ni^{2+}-mont	2.89	14.7	0.70	28.0	37
Zn^{2+}-mont	2.70	15.0	0.79	27.7	28
Mn^{2+}-mont	2.50	15.2	0.74	25.3	28
Cu^{2+}-mont	–	13.8	0.75	25.0	42
H^+-mont	–	15.1	0.70	33.3	71
Montmorillonite K-10	–	–	–	254.6	10
p-Toluenesulphonic acid[d]	–	–	–	–	78
Blank (without catalyst)	–	–	–	–	Nil

[a] Ionic radii (Å) values in Pauling's scale.
[b] Reaction conditions: p-cresol:succinic anhydride, 3:1 mol/mol; amount of catalyst, 0.5 g; reaction time, 8 h; solvent, toluene.
[c] Isolated yields.
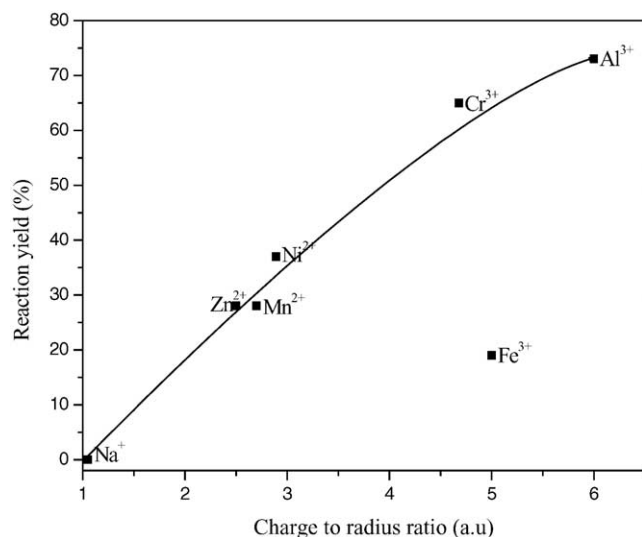[d] In the presence of 0.5 g of p-toluenesulphonic acid.

Fig. 2. Esterification of succinic anhydride with *p*-cresol. Effect of charge to radius ratio of metal cation on esterification activity: *p*-cresol:succinic anhydride, 3:1 mol/mol; catalyst amount, 0.5 g; solvent, toluene; reaction time, 8 h.

Al^{3+}-mont is the most effective catalyst for the esterification with a maximum yield of 75%, which is comparable to the yield from the reaction conducted with *p*-toluenesulphonic acid. The activity of Al^{3+}-mont is attributed to highly polar cation (charge to radius ratio = 6) introduced between the clay layers. The Al^{3+}-mont catalyst dried at 673 K when used in esterification of phenylacetic acid with *p*-cresol failed to give the ester but the same catalyst dried at 273 K yielded the ester [22]. Al^{3+}- and Fe^{3+}-exchanged clay provide Brønsted acid sites whereas Cr^{3+}-exchanged clay provides both Brønsted and Lewis acid sites [23]. Cr^{3+}-mont with reduced Brønsted acid sites was found to be effective only to the extent of 65% ester yield. The low activity of Fe^{3+}-mont, although having a high charge to radius ratio, may be due to the leaching of interlayer Fe^{3+}-ions possibly through Fe^{3+}-cresol complex formation. Fe^{3+} is known to form complex with cresols and this would make the phenolic OH group not available for nucleophilic attack on the anhydride. A reddish brown precipitate of ferric hydroxide was observed when the mixture after the reaction was treated with NaOH indicating the leaching out of ions. Formation of such metal hydroxide precipitates was not observed with other M^{n+}-mont catalysts. This was further confirmed by esterifications conducted without cresols, in the presence of Fe^{3+}-mont as catalyst, which went almost to completion; esterification of succinic anhydride (5 mmol) with *n*-butyl alcohol (15 mmol) in the presence of 0.5 g each of Fe^{3+}-mont and Al^{3+}-mont in 8 h proceeded to give respectively 81 and 96% yield of di-(*n*-butyl) succinate. The montmorillonite exchanged with dipositive metal ions showed reduced yield of the ester in the range of 28–42%. This is attributed to the small charge to radius ratio of the dipositive ions compared to tripositive ions. The montmorillonite exchanged with H^+-ions, apparently due to the presence of strong Brønsted acid sites, gave 71% yield of the ester.

Esterification reaction is known to be catalyzed by Brønsted acid sites. In the case of M^{n+}-mont catalysts the active sites responsible for the esterification are interlayer aqua complexes exposed at the edge sites as given below. Thus Brønsted acidity is generated

$$[M(H_2O)_n]^{m+} \rightleftharpoons [M(H_2O)_{n-1}(OH)]^{(m-1)+} + H^+$$
$$\text{edge site}$$
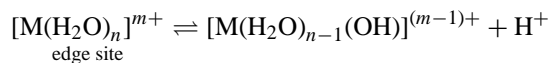
during the reaction from metal aqua complexes. The proton donating ability of M^{n+}-mont apparently depends on the charge to radius ratio of M^{n+}-ion present as aqua complexes in the interlayer space of montmorillonite.

The mechanism of esterification of succinic anhydride (Scheme 2) over M^{n+}-mont should be similar to the conventional mechanism involving the formation of protonated anhydride by using proton donated by the M^{n+}-mont catalyst, followed by the nucleophilic attack of phenolic group.

### 3.2. Effect of molar ratio of reactants on esterification

A set of reactions were conducted by increasing the ratio of *p*-cresol (*p*-C) to succinic anhydride (SA) with molar ratios ranging from 2:1 to 4:1 in toluene solvent with 0.5 g of Al^{3+}-mont as catalyst for 8 h. The results show that the yield of the ester increases with increase in the molar ratio of reactants. The increase in the yield with increase in the molar ratio is attributed to the shifting of equilibrium towards the ester formation. The results also indicate that the optimum molar ratio for the esterification is 3*p*-C:1SA.

3.3. Effect of reaction period on esterification

The effect of reaction time was studied for the esterification of succinic anhydride with *p*-cresol (1:3 mol/mol) in the presence of 0.5 g of Al^{3+}-mont as catalyst and toluene as solvent. The results are presented in Fig. 3, which indicate that the yield of the ester increases with increase in reaction time from 2 to 14 h. There is no considerable increase in the ester yield when the reaction time was beyond 10 h. The reaction was found to follow the second order kinetics with an average rate constant (k) of $1.99 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$; equilibrium constant ($K$) estimated from the maximum yield is $0.34 \times 10^3 \text{ mol}^{-1}$ and standard free energy change ($\Delta G°$) is $-1.86 \times 10^4 \text{ J mol}^{-1}$.

3.4. Effect of catalyst amount on esterification

A set of reactions has been carried out by varying catalyst amount from 0.1 to 0.8 g, keeping all other conditions such as solvent, reaction time and *p*-cresol/succinic anhydride molar ratio constant at 3:1. The results are represented in Fig. 4, which shows the increase the ester yield with increase in the catalyst amount, reaching a maximum of 75% for 0.5 g. Further increase in catalyst amount, beyond 0.5 g,

$$\left[M(H_2O)_n\right]^{m+} \rightleftharpoons \left\{\left[M(H_2O)_{n-1}(OH)\right]^{(m-1)+} + H^+\right\} \longleftrightarrow M^*\text{-}H^+$$
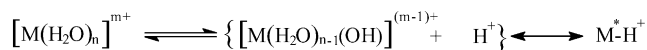
M*-indicates hydrated metal cations of montmorillonite
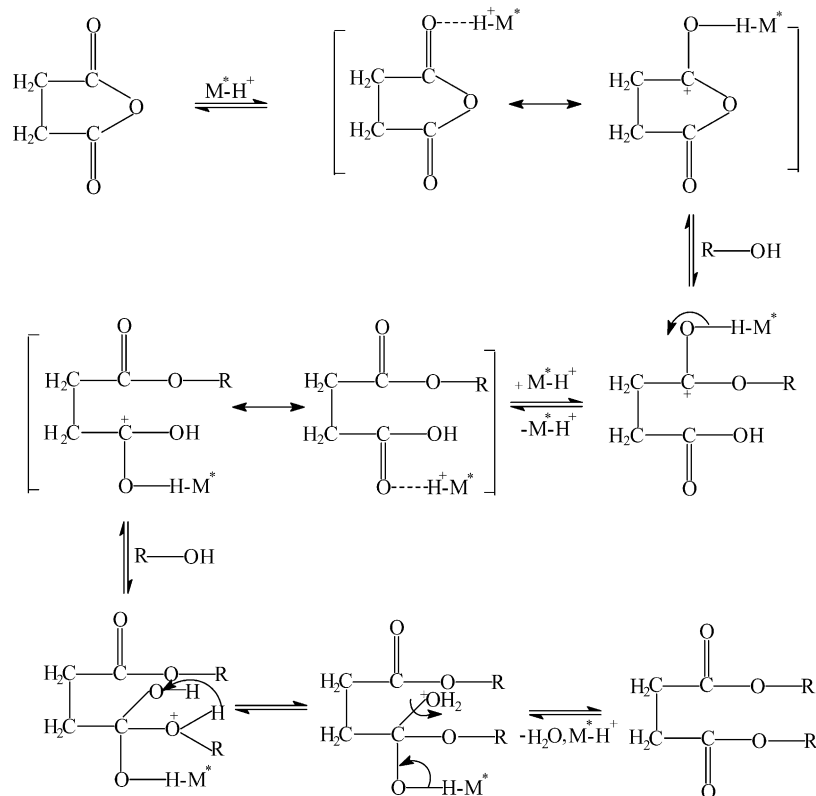
R= phenol, *p*-cresol, or *m*-cresol

Scheme 2. Probable mechanism for the esterification of succinic anhydride with *p*-cresol over M^{n+}-mont catalyst.
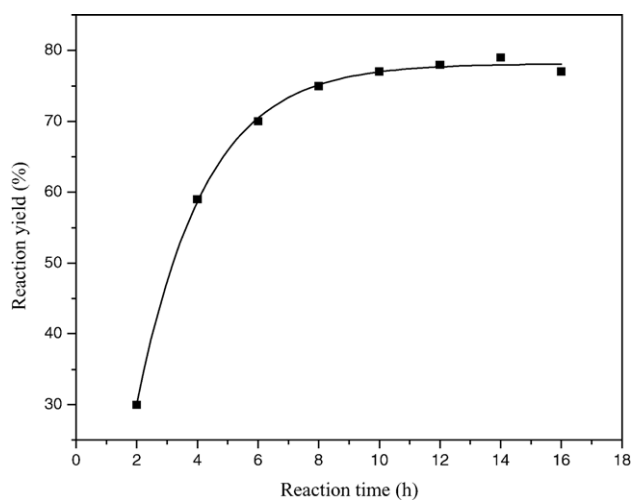

Fig. 3. Esterification of succinic anhydride with *p*-cresol. Effect of reaction time on yield of the ester: *p*-cresol:succinic anhydride, 3:1 mol/mol; catalyst amount, 0.5 g; catalyst used, Al^{3+}-mont; solvent, toluene; reaction time, 2–18 h.
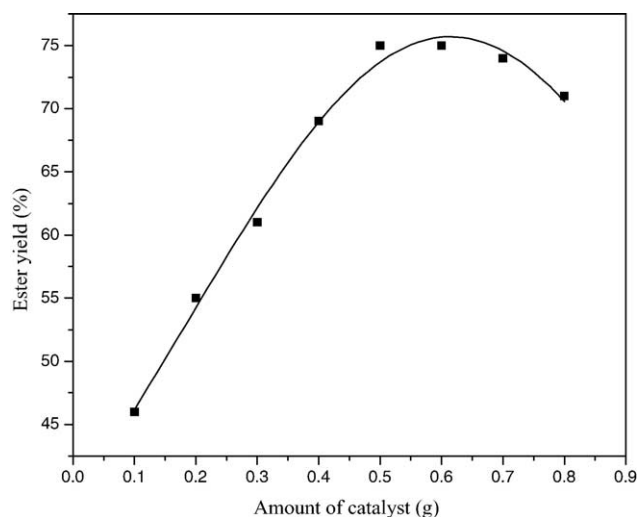
Fig. 4. Esterification of succinic anhydride with *p*-cresol. Effect of catalyst amount on yield of the ester: *p*-cresol:succinic anhydride, 3:1 mol/mol; reaction time, 8 h; catalyst used, Al^{3+}-mont; solvent, toluene; catalyst amount, 0.1–0.8 g.

Table 3
Esterification of succinic anhydride with substituted phenols[a]

Entry	Substituted phenol	Yield[b] (%)
1	Phenol	47
2	*p*-Cresol	75
3	*m*-Cresol	58
4	*o*-Cresol	Nil
5	*p*-Nitrophenol	Nil
6	Resorcinol	Nil
7	Salicylic acid	Nil

[a] Reaction conditions: substituted phenol:succinic anhydride, 3:1 mol/mol; catalyst used, Al^{3+}-mont; amount of catalyst, 0.5 g; reaction time, 8 h; solvent, toluene.

[b] Isolated yields.

decreased the yield of the ester, although the reason is not clear.

3.5. Esterification of succinic anhydride with different substituted phenols

Table 3 gives the results of esterification of succinic anhydride with different substituted phenols such as phenol, *m*-cresol, *o*-cresol, *p*-nitrophenol, resorcinol, and salicylic acid. Among the cresols, *p*-cresol showed the highest yield, *m*-cresol showed a reduced conversion and 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. Resorcinol and salicylic acid form chelated complexes with metal ions in such a way that the protonation of succinic anhydride is possibly hindered.

3.6. Activity of regenerated Al^{3+}-mont catalyst

The activity of regenerated Al^{3+}-mont catalyst was also investigated after washing the spent catalyst with distilled water, and drying at 373 K. The yield of the di-(*p*-cresyl) succinate 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 Al^{3+}-mont catalyst four times.

4. Conclusions

Montmorillonite clay exchanged with different cations (M^{n+}-mont; $M^{n+} = Al^{3+}$, Cr^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} and H^+) catalyses esterification of succinic anhydride with *p*-cresol to yield di-(*p*-cresyl) succinate. The results indicate no correlation between surface areas, d-spacing and total acidity of catalysts with the esterification activity. Among the M^{n+}-mont clay catalysts studied Al^{3+}-mont is the most active towards formation of di-(*p*-cresyl) succinate, which is

nearly equal to the activity of commercially available catalysts used in this study. The yields of the ester increased with increase in the *p*-cresol/succinic anhydride molar ratio. A catalyst amount of 0.5 g of Al^{3+}-mont, a molar ratio of *p*-cresol to succinic anhydride of 3:1, toluene solvent, and 8 h of reaction time are found to be optimal for the formation of di-(*p*-cresyl) succinate. Esterification of succinic anhydride with *n*-butanol in the presence of Al^{3+}-mont went almost to completion. Esterification of succinic anhydride with different substituted phenols such as *o*-cresol, *o*-nitrophenol and resorcinol did not yield the ester and this might be due to steric, electronic and chelation factors. The catalyst can be reused after regenerating by simple washing with water and drying at 373 K. Other advantages of this method include operational simplicity, mild reaction conditions, selectivity for ester, and the eco-friendly and reusable character of the catalyst. This technique can be commercially exploited for preparation of other important esters.

References

[1] G.A. Bardock, Fenaroli's Handbook of Flavour Ingredients, vol. 11, 3rd ed., CRC press, 1994.
[2] Vogel's Textbook of Practical Organic Chemistry, 4th ed., ELBS, 1987, p. 501.
[3] S.R. Kirumakki, N. Nagaraju, K.V.V.S.B.R. Murthy, S. Narayanan, Appl. Catal. A: Gen. 226 (2002) 175.
[4] O. Darge, F.C. Thyrion, J. Chem. Tech. Biotechnol. 58 (1993) 351.
[5] T.S. Thorat, V.M. Yadav, G.D. Yadav, Appl. Catal. A 90 (2) (1992) 73.
[6] Z.H. Zhao, J. Mol. Catal. A: Chem. 168 (2001) 147.
[7] C.V. Suresh Kumar, N.G. Karanth, S. Divakar, Ind. J. Chem. 41B (2002) 1068.
[8] A. Cornelis, P. Laszlo, Synlet (1994) 155.
[9] P. Laszlo, J. Lucchette, Tetra. Lett. 25 (1984) 1567.
[10] J.M. Adams, T.V. Clapp, Clays Clay Miner. 34 (1986) 287.
[11] M.M. Mortland, Soil Sci. Soc. Am. J. 40 (1976) 367.
[12] T. Cresi, S. Bekassy, F. Figueras, S. Rizner, J. Mol. Catal. A: Chem. 98 (1995) 101.
[13] J.A. Ballantine, J.H. Purnell, J.M. Thomas, J. Mol. Catal. 27 (1984) 157.
[14] J.M. Adams, D.E. Clement, S.H. Graham, Clays Clay Miner. 30 (1982) 129.
[15] J. Tateiwa, H. Horiuchi, S. Uemura, J. Org. Chem. 60 (1995) 4639.
[16] M.L. Kantham, V. Bhaskar, B.M. Choudary, Catal. Lett. 78 (1–4) (2002) 185.
[17] K.V.N.S. Srinivas, Biswanath Das, J. Org. Chem. 68 (2003) 1165.

[18] J.M. Adams, D.E. Clement, S.H. Graham, Clays Clay Miner. 3 (2) (1983) 129.

[19] H.A. Benesi, J. Phys. Chem. 61 (1957) 970.

[20] A.I. Vogel, Textbook of Quantitative Inorganic Analysis, 4th ed., ELBS/Longman, 1978.

[21] R.D. Laura, Clay Miner. 11 (1976) 331.

[22] C. Ravindra Reddy, B. Vijayakumar, P. Iyengar, G. Nagendrappa, B.S. Jai Prakash, J. Mol. Catal. A: Chem. 223 (2004) 117.

[23] C. Breen, A.T. Deane, J.J. Flynn, Clay Miner. 22 (1987) 169.