

Esterification of dicarboxylic acids to diesters over M^{n+} -montmorillonite clay catalysts

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Esterification of dicarboxylic acids with various alcohols and phenols in presence of metal exchanged montmorillonite clay catalyst (M^{n+} -mont; $M^{n+} = Al^{3+}$, Fe^{3+} , Cr^{3+} , Zn^{2+} , Mn^{2+} , and Ni^{2+}) is studied. Among the catalysts used, Al^{3+} -mont was found to be the most effective, as it gave good to excellent yields of esters under mild reaction conditions. The heterogeneous catalyst presented here can be regenerated and reused. All these features indicate the high potential of the reaction as “green chemistry” process.

KEY WORDS: esterification; dicarboxylic acids; M^{n+} -montmorillonite; catalyst.

1. Introduction

Organic esters have wide applications as intermediates in the synthesis of fine chemicals, drugs, pharmaceuticals, perfumes, cosmetics, plasticizers and solvents [1]. They may be obtained by different routes from a variety of starting materials. However, the reaction between carboxylic acids and alcohols is the most feasible one, as the starting compounds are normally readily available. The common esterification procedure involves the use of sulphuric acid, *p*-toluene sulphonic acid or dry hydrochloric acid vapours as catalyst [2]. However, these catalysts, being highly acidic, can cause damage to other sensitive functional groups, are corrosive, are non-reusable, and pose difficulty in separating them from the reaction mixture. Most importantly, these catalysts generate acid wastes, which cause severe environmental problems. Attempts have been made to overcome these disadvantages by using heterogeneous catalyst systems. The heterogeneous catalyst systems include cationic-exchanged resins like Amberlyst-15 [3], zeolites [4], metal oxides like sulphated zirconia and titania [5], heteropolyacids supported on silica and carbon [6], palladium on charcoal [7], silica chloride [8], aluminophosphate and silicoaluminophosphate molecular sieves [9], and cation exchanged montmorillonite K-10 [10]. 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 [11]. Among smectite clays, montmorillonite, both in natural and exchanged forms, possess both Lewis and Brønsted acidities, which enable them to

function as efficient catalysts in organic transformations. In the present study we are reporting the esterification of dicarboxylic acids with different alcohols, phenol and *p*-cresol using an eco-friendly, high efficient cation-exchanged clay catalyst.

2. Experimental

2.1. 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 exchanging. 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 with cation exchange capacity of 0.8 meq g^{-1} of clay.

Montmorillonite K-10 sample was procured from Sigma Aldrich, dicarboxylic acids, alcohols, phenol and *p*-cresol were purchased from SD Fine Chemicals.

2.2. Preparation of exchanged clays

The cation exchanged clay catalysts were prepared by adopting literature methods [12]. The method involves stirring of 5 g montmorillonite clay sample with 200 mL of 0.5 M required salt solution at room temperature for 24 h. 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 100 °C for 3 h, and subsequently ground to a fine powder. Clay catalysts were activated at 100 °C for 30 min prior to testing of the activity.

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2.3. Characterization

XRD patterns of the clay samples were recorded on Siemens D5005 diffractometer using Cu-K α radiation source and a Ni filter. Basal spacings were calculated to be 15.16, 15.46, 15.77, 14.68, 14.97, and 15.17 Å, respectively for Al³⁺, Fe³⁺, Cr³⁺, Ni²⁺, Zn²⁺, and Mn²⁺-mont catalysts. Specific surface area of catalyst samples was determined by BET method at liquid nitrogen temperature using a Quantachrome NOVA 1000 surface area analyzer and found to be in the range of 25–31 m² g⁻¹. Prior to the surface area analysis, the clay samples were degassed for 2 h at 100 °C. The total acidities of Al³⁺, Fe³⁺, Cr³⁺, Ni²⁺, Zn²⁺, and Mn²⁺-mont catalyst samples were evaluated by *n*-butylamine back titration method [13] and found to be 0.78, 0.78, 0.79, 0.70, 0.79, and 0.74 mmol g⁻¹, respectively. The total cationic content of exchanged clay catalysts was determined according to standard methods [14] after extracting with dilute hydrochloric acid. The exchangeable metal content of Al³⁺, Zn²⁺, Ni²⁺, and Mn²⁺-mont was found to be in the range of cation exchange capacity (CEC) of the parent montmorillonite. However, in the case of Fe³⁺-mont the amount of iron was found to be more than the CEC.

2.4. Typical reaction procedure

The esterification reactions of dicarboxylic acids with alcohols and phenols (Scheme 1) were carried out in 100-mL round-bottom flask fitted with a Dean–Stark trap for water removal and a reflux condenser. The flask was charged with succinic acid (5 mmol), *n*-butanol (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. The clay catalyst was washed with solvent (2 × 5 mL). The combined filtrates were washed with 5% sodium hydroxide (4 × 15 mL) to remove unreacted starting dicarboxylic acid. The organic layer was first washed with water (2 × 15 mL), saturated brine (1 × 15 mL), dried over anhydrous sodium sulphate, and finally concentrated under reduced pressure to obtain pure product. The product was identified by its IR, and ¹H-NMR spectral analyses.

3. Results and discussion

3.1. Effect of different catalysts over esterification of succinic acid with 1-butanol

The results of esterification of 1-butanol with succinic acid over different Mⁿ⁺-mont catalysts are summarized

in table 1. The activity of the Mⁿ⁺-mont catalysts was found to be not in correlation with total surface area and total acidity, but linearly related to the charge to radius ratio of Mⁿ⁺-ion exchanged into montmorillonite clay. The charge to radius ratios of Al³⁺, Fe³⁺, Cr³⁺, Ni²⁺, Zn²⁺ and Mn²⁺ are 6.00, 5.00, 4.69, 2.89, 2.70 and 2.50, respectively. Acidity of cation exchanged clays increases with increase in charge to radius ratio of the exchanged cation due to increase in the polarization of water molecules in the primary coordination sphere [15]. The reactions conducted either in the absence of the catalyst or in the presence of the unexchanged montmorillonite (Na⁺-mont) failed to give the ester. Among the Mⁿ⁺-mont clay catalysts, Al³⁺-mont is the most effective, with an ester yield as high as 94%. The Al³⁺-montmorillonite was also found to be an efficient catalyst in the synthesis of *p*-cresyl phenylacetate [16] and is attributed to the highly polar cation (charge to radius ratio = 6) introduced between the clay layers. Al³⁺- and Fe³⁺-exchanged clays provide Brønsted acid sites, whereas Cr³⁺-exchanged clay provides both Brønsted and Lewis acid sites [17]. Cr³⁺-mont with reduced Brønsted acid sites was found to be effective to the extent of 79% ester yield. The montmorillonite exchanged with dipositive metal ions showed reduced yield of ester, in the range of 18–46%. This is attributed to the small value of charge to radius ratio of the dipositive ions compared to the tripisitive ones.

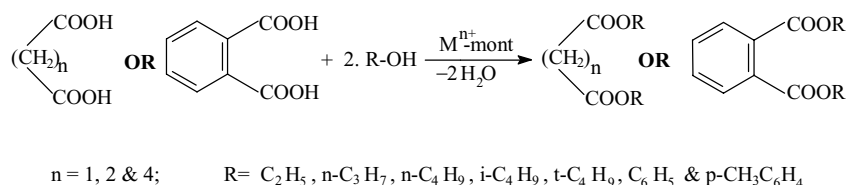
The mechanism of esterification of dicarboxylic acid to diester over Mⁿ⁺-mont is similar to that of

Table 1
Esterification of succinic acid with 1-butanol over Mⁿ⁺-mont catalysts. (acid:alcohol, 1:3 mole; solvent, toluene; reaction, 8 h; catalyst amount, 0.5 g)

| Entry | Catalyst | Charge to radius ratio ^a | Yield of di-(1-butyl) succinate (%) ^b |
|-------|------------------------|-------------------------------------|--|
| 1 | Al ³⁺ -mont | 6.00 | 94 |
| 2 | Fe ³⁺ -mont | 5.00 | 81 |
| 3 | Cr ³⁺ -mont | 4.69 | 79 |
| 4 | Ni ²⁺ -mont | 2.89 | 46 |
| 5 | Zn ²⁺ -mont | 2.70 | 36 |
| 6 | Mn ²⁺ -mont | 2.50 | 18 |
| 7 | Na ⁺ -mont | 1.05 | – |
| 8 | Blank (without clay) | – | – |

^aIonic radii (Å) values are in Pauling's scale.

^bIsolated yields.



Scheme 1.

conventional mechanism involving the formation of protonated dicarboxylic acid, using proton donated by the M^{n+} -mont catalyst, followed by nucleophilic attack of alcoholic group to yield the respective monoester. The second carboxylic group present in monoester gets further esterified by the same mechanism in a repeat reaction, which ultimately results in the diester formation. The proton donating ability of M^{n+} -mont is apparently dependent on the charge to radius ratio of M^{n+} -ion present as aqua complexes. The active sites are perhaps present at the edge sites projecting from the interlayer space.

3.2. Effect of solvents on esterification

The role of different solvents in the esterification of succinic acid and adipic acid with 1-butanol over Al^{3+} -mont catalyst is presented in table 2. Both succinic and adipic acids are sparingly soluble in all the selected solvents except dioxane. Both the acids in *o*-xylene solvent, which has the highest boiling point among the selected solvents, gave almost the same yield of esters (86 and 87%). However, in toluene solvent, succinic acid gave much higher yield of ester (94%) than adipic acid (54%). The reduced yields in benzene are attributable to the low boiling point of the solvent. Both the acids, although soluble in dioxane, did not give the corresponding diesters. This may be due to polar nature of the solvent, which is likely to result in the formation of hydrogen bond between the protonic site of the catalyst and the solvent.

3.3. Esterification of dicarboxylic acids with simple alcohols

The results of esterification of dicarboxylic acids namely malonic, maleic, succinic, adipic and phthalic acids studied with ethanol, 1-propanol, 1-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol over Al^{3+} -mont catalyst in toluene solvent are summarized in table 3. All dicarboxylic acids gave lower yields of diesters with ethanol (3–64%, entries 1–5). The reason for this may be due to the low boiling point of ethanol. Similarly all dicarboxylic acids with 1-propanol gave

slightly higher yields of diesters (19–70%, entries 6–10) compared to ethanol. But all dicarboxylic acids, except phthalic acid, gave reasonably good yields with 1-butanol (54–94%, entries 11–15) and 2-methyl-1-propanol (28–98%, entries 16–20) and relatively poor yields with 2-methyl-2-propanol (16–24%, entries 21–25). Also the results of esterification of adipic and phthalic acids with 1-propanol (entries 9 and 10) indicates toluene (19–35%) is the better solvent compared to *o*-xylene (4–6%), and with 1-butanol and 2-methyl-1-propanol, *o*-xylene (31–87%) is better compared to toluene (29–54%). The reason for this observation is most likely to be due to the high boiling point of *o*-xylene solvent. However, the diesters obtained with 2-methyl-2-propanol are low both in toluene and *o*-xylene. The low yields of diesters with 2-methyl-2-propanol can be attributed to steric bulk of the alcohol or its competitive dehydration over esterification. The tertiary alcohols are known to undergo elimination more easily than primary alcohols in presence of acid clay catalyst [18]. As evidence, the gaseous products formed in the esterification with 2-methyl-2-propanol gave positive test for unsaturation. However, the general trend of diesterification of a particular dicarboxylic acid in respect of alcohols was in the order, 2-methyl-2-propanol < ethanol < 1-propanol < 1-butanol < 2-methyl-1-propanol in toluene solvent. A clear pattern is observable in this trend, that is, the lower boiling alcohols and sterically hindered alcohols give lower yields of esters.

3.4. Esterification of dicarboxylic acids with phenol and *p*-cresol

Esterification of dicarboxylic acids was also studied with phenol and *p*-cresol over Al^{3+} -mont catalyst in presence of toluene solvent (table 4). Malonic, maleic and phthalic acids failed to give diesters with both phenol and *p*-cresol but succinic acid and adipic acid gave low yields of diesters. However, adipic acid gave higher yields in presence of *o*-xylene after 10 h of reaction time. Also in case of *p*-cresol the yields of diesters are more than in phenol. This may be attributed to better nucleophilic nature of *p*-cresol than phenol, which has a positive effect on the rate of esterification. Considering the fact that phenols do not undergo esterification as easily as alcohols using conventional procedures, even the partial success with succinic acid and adipic acid achieved in our present study is significant.

4. Conclusions

Montmorillonite clay exchanged with different cations (M^{n+} -mont; $M^{n+} = Al^{3+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}$, and Mn^{2+}) catalyzes esterification of dicarboxylic acids like malonic, maleic, succinic, adipic and phthalic acid with simple alcohols, phenol, and *p*-cresol to corresponding diesters. The results indicate no correlation

Table 2

Esterification of succinic acid and adipic acid with 1-butanol in different solvents (acid: alcohol, 1:3 mole; catalyst, Al^{3+} -mont; reaction time, 8 h; catalyst amount, 0.5 g)

| Entry | Solvent | Yield of di-(1-butyl) succinate (%) ^a | Yield of di-(1-butyl) adipate (%) ^a |
|-------|------------------|--|--|
| 1 | <i>o</i> -Xylene | 86 | 87 |
| 2 | Toluene | 94 | 54 |
| 3 | Benzene | 11 | 06 |
| 4 | Dioxane | — | — |

^aIsolated yields.

Table 3

Esterification of dicarboxylic acids with different alcohols (acid: alcohol, 1:3 mole; catalyst, Al^{3+} -mont; reaction time, 8 h; solvent, toluene; catalyst amount, 0.5 g)

| Entry | Dicarboxylic acid | Alcohol | Product | Yield (%) ^a | |
|-------|-------------------|---------------------|----------------------------------|------------------------|------------------|
| | | | | Toluene | <i>o</i> -Xylene |
| 1 | Malonic acid | Ethanol | Diethyl malonate | 41 | – |
| 2 | Maleic acid | Ethanol | Diethyl maleate | 18 | – |
| 3 | Succinic acid | Ethanol | Diethyl succinate | 64 | – |
| 4 | Adipic acid | Ethanol | Diethyl adipate | 03 | 07 |
| 5 | Phthalic acid | Ethanol | Diethyl phthalate | 31 | – |
| 6 | Malonic acid | 1-Propanol | Di-(1-propyl) malonate | 70 | – |
| 7 | Maleic acid | 1-Propanol | Di-(1-propyl) maleate | 37 | – |
| 8 | Succinic acid | 1-Propanol | Di-(1-propyl) succinate | 66 | – |
| 9 | Adipic acid | 1-Propanol | Di-(1-propyl) adipate | 35 | 06 |
| 10 | Phthalic acid | 1-Propanol | Di-(1-propyl) phthalate | 19 | 04 |
| 11 | Malonic acid | 1-Butanol | Di-(1-butyl) malonate | 77 | – |
| 12 | Maleic acid | 1-Butanol | Di-(1-butyl) maleate | 88 | – |
| 13 | Succinic acid | 1-Butanol | Di-(1-butyl) succinate | 94 | – |
| 14 | Adipic acid | 1-Butanol | Di-(1-butyl) adipate | 54 | 87 |
| 15 | Phthalic acid | 1-Butanol | Di-(1-butyl) phthalate | 37 | 55 |
| 16 | Malonic acid | 2-Methyl-1-propanol | Di-(2-methyl-1-propyl) malonate | 84 | – |
| 17 | Maleic acid | 2-Methyl-1-propanol | Di-(2-methyl-1-propyl) maleate | 78 | – |
| 18 | Succinic acid | 2-Methyl-1-propanol | Di-(2-methyl-1-propyl) succinate | 98 | – |
| 19 | Adipic acid | 2-Methyl-1-propanol | Di-(2-methyl-1-propyl) adipate | 29 | 31 |
| 20 | Phthalic acid | 2-Methyl-1-propanol | Di-(2-methyl-1-propyl) phthalate | 52 | 79 |
| 21 | Malonic acid | 2-Methyl-2-propanol | Di-(2-methyl-2-propyl) malonate | 24 | – |
| 22 | Maleic acid | 2-Methyl-2-propanol | Di-(2-methyl-2-propyl) maleate | 19 | – |
| 23 | Succinic acid | 2-Methyl-2-propanol | Di-(2-methyl-2-propyl) succinate | 18 | – |
| 24 | Adipic acid | 2-Methyl-2-propanol | Di-(2-methyl-2-propyl) adipate | 16 | 08 |
| 25 | Phthalic acid | 2-Methyl-2-propanol | Di-(2-methyl-2-propyl) phthalate | – | 13 |

^aIsolated yields.

between surface area, *d*-spacing, and total acidity of catalysts with esterification activity, but are found to be linearly related to charge to radius ratio of exchanged cations. Among the M^{n+} -mont clay catalysts studied Al^{3+} -mont is the most active catalyst in the esterification of dicarboxylic acids. The general conversion trend of alcohols to diester with particular dicarboxylic acid

was in the order, 2-methyl-2-propanol < ethanol < 1-propanol < 1-butanol < 2-methyl-1-propanol in toluene solvent with few exceptions. Finally, the advantages of this method include operational simplicity, mild reaction conditions, and eco-friendly character. Thus, the reaction has all the features of “green chemistry”. The technique has the potential for commercial exploitation in the preparation of esters.

Table 4

Esterification of dicarboxylic acids with phenol and *p*-cresol (acid: phenol or *p*-cresol, 1:3 mole; catalyst, Al^{3+} -mont; reaction time, 8 h; solvent, toluene; catalyst amount, 0.5 g)

| Entry | Dicarboxylic acid | Phenol | Product | Yield (%) ^a |
|-------|-------------------|------------------|----------------------------------|------------------------|
| 1 | Malonic acid | Phenol | Diphenyl malonate | Nil |
| 2 | Maleic acid | Phenol | Diphenyl maleate | Nil |
| 3 | Succinic acid | Phenol | Diphenyl succinate | 25 |
| 4 | Adipic acid | Phenol | Diphenyl adipate | 21, 58 ^b |
| 5 | Phthalic acid | Phenol | Diphenyl phthalate | Nil |
| 6 | Malonic acid | <i>p</i> -Cresol | Di-(<i>p</i> -cresyl) malonate | Nil |
| 7 | Maleic acid | <i>p</i> -Cresol | Di-(<i>p</i> -cresyl) maleate | Nil |
| 8 | Succinic acid | <i>p</i> -Cresol | Di-(<i>p</i> -cresyl) succinate | 70 |
| 9 | Adipic acid | <i>p</i> -Cresol | Di-(<i>p</i> -cresyl) adipate | 39, 73 ^b |
| 10 | Phthalic acid | <i>p</i> -Cresol | Di-(<i>p</i> -cresyl) phthalate | Nil |

^aIsolated yields.

^bIn *o*-xylene solvent and 10 h of reaction period.

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