

Solvent-Free Esterification Of Substituted Benzoic Acids With Alcohols Using Modified Montmorillonite K10 As Solid Acid Catalyst

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Abstract: The easily available Montmorillonite K10 clay is activated with orthophosphoric acid. It has been found that the surface of the clay become more acidic after treating with the orthophosphoric acid. This has been used for esterification of substituted benzoic acids with different alcohols. Benzoic acids having both electron donating and withdrawing groups undergo smooth reaction and provide higher yields with methanol and benzyl alcohol. No solvent and mineral acids have been used in this reported protocol.

Index Terms: Alcohol, Benzoic acid, Esterification, Montmorillonite K10, Solid acid catalyst.

1. INTRODUCTION

Solid materials, especially having definite shape, layering structure, pore volume have been used in many industrially important reactions for better selectivity and reactivity [1]. Further modifications of these materials have been found to give higher reactivity [1-3]. Therefore, modification of the surface or pore volume of a porous material has been acquiring a special domain from last two decades. Modification or activation of these materials with mineral acid, resulted in a new domain, i.e. 'solid acid', which is one of the attractive areas of research, as these replaces mineral acids in many industrially important reactions [4-6]. These solid acids have also been studied for industrially applicable esterification reaction [7-10]. Montmorillonite clay is one of the easily available materials with a definite layered structure. Therefore, it has been used in neat or modified form in many organic reactions [11, 12]. This clay has been modified with phosphoric acid and reported as an efficient catalyst for nitration and Hantzsch reactions [13-15]. Since modification or attachment of phosphoric acid with montmorillonite clay increases the acid strength (low pKa value), it is thought worthwhile to check its activity in an acid demanding reaction, i.e. esterification reaction. Esterification reactions have been tried with various modified solid material. However, their efficiency were checked only for some specific acids and alcohols [16-18]. Few reports established the kinetics of esterification reaction [19]. Apart from that preparation of those materials are found to be tricky. Therefore, we intended to check the activity of phosphoric acid modified montmorillonite clay for esterification reactions with various aromatic acids with alcohols. Herein we report the results obtain from the reaction of benzoic acid derivatives with aliphatic and benzyl alcohols using phosphoric acid modified clay as catalyst.

2 EXPERIMENTAL SECTION

2.1 Chemicals

Montmorillonite K10 (MK) clay was obtained from Merck (98% purity). Ortho phosphoric acid, Benzoic acid, p-chloro Benzoic acid, p-nitro Benzoic acid, p-hydroxy Benzoic acid, p-methyl Benzoic acid, p-methoxy Benzoic acid and Benzyl alcohol were obtained from Loba chemie. Hexane, Ethyl acetate, Sodium hydrogen carbonate, Potassium hydroxide, Toluene, Methanol, Ethanol were purchased from HiMedia. All the chemicals were used without further purification.

2.2 Preparation of the modified Montmorillonite clay (PMK) and characterization

The catalyst (PMK) is prepared following a reported procedure [13]. In a typical procedure 500 mg of Montmorillonite K10 clay, 37.5 mg of ortho-phosphoric acid and 5 mL of toluene are taken in a round bottomed flask, fitted with a reflux condenser. Then mixture is refluxed for around 5 hours and the toluene is removed by distillation under vacuum. The solid material is then dried in oven (110-120°C) and stored in dessicator. To verify the modified material with the reported one, the acidity is determined by titrimetric analysis. In this process, a certain amount of the material (50 mg) is taken in 10 mL water and titrated against standardized sodium hydroxide solution. Perkin Elmer FT-IR instrument is used for recording the FT-IR spectra of the modified clay in the region 4000-500 cm^{-1} using KBr pallets. FESEM analysis of the same catalyst is performed in a Sigma 300 spectrometer.

2.3 Catalytic performance of solid acid catalyst in esterification reaction and characterization

In a typical experiment benzoic acid (1 mmol), alcohol (1 mmol) and catalyst PMK (10 wt%) are added in a round bottom flask equipped with a reflux condenser and an oil bath. Then the mixture is refluxed for 5 h. The progress of the reaction is monitored by TLC. After the completion of reaction, the reaction mixture is filtered to separate the catalyst and extracted the reaction mixture in ethyl acetate. Column chromatographic separation is performed to get the pure product wherever necessary. Melting points are recorded for the solid compounds on μ ThermoCal10 melting point apparatus. ^1H NMR spectra of the samples are taken in CDCl_3 using Bruker 300 MHz instrument.

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2.4 Calculation of percentage conversion

The percentage conversion of acid is calculated using a standard titration method [21]. The reaction mixture is poured in ethanol-diethyl ether mixture (1:2, v/v), to which phenolphthalein solution is added as indicator. Ethanol solution of KOH (0.1 M) is used for titration. The amount of KOH solution consumed is noted, and the percentage conversion of carboxylic acids is estimated using the following expression.

$$\text{Conversion of carboxylic acid (\%)} = 1 - \frac{V - V_2 M_2}{V_1 M_1} \times 100\%$$

V_1 (mL) and V_2 (mL) represent the volume of KOH solution, respectively consumed by benzoic acid gram-1 and catalyst gram-1, which are titrated using ethanol-KOH solution. V (mL) denotes the volume consumed by the reaction mixture after completion of the reaction. M_1 (mol) and M_2 (mol) stand for carboxylic acid and catalyst added in reaction, respectively. Water and low-boiling point solvents are evaporated under rotary evaporator and pure esters are obtained by decompression distillation.

3 RESULT AND DISCUSSION

3.1 Characterization of the catalyst

The freshly prepared catalyst (PMK) is characterized with various physicochemical methods and the results are compared with FTIR (Fig. 1.) analysis shows two significant peaks at 1052 cm^{-1} and 1058 cm^{-1} which may be due to the presence of P-O bond and Si-O vibration respectively. Other peaks are observed for Al-O vibration at 795 cm^{-1} and O-H vibration at 3431 cm^{-1} . These results corroborate well with the earlier reported results [13].

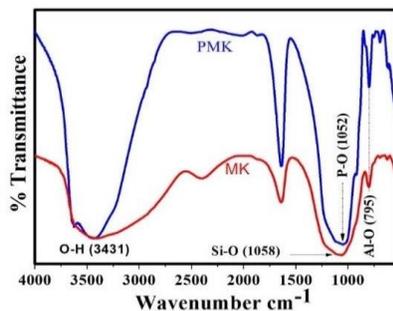


Fig. 1. FTIR spectra of MK and PMK

The SEM micrograph as shown in Fig. 2. reveals that the layered structure of the clay remains intact. The EDX analysis (Fig. 3.) identifies the presence of phosphorus in the PMK catalyst in addition to Al, Si and O elements. The content of P in the modified clay is 6.26 wt%.

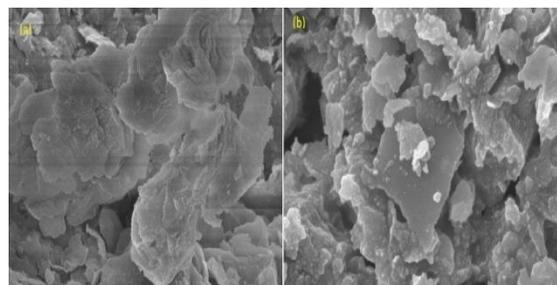


Fig. 2. FTIR spectra of MK and PMK

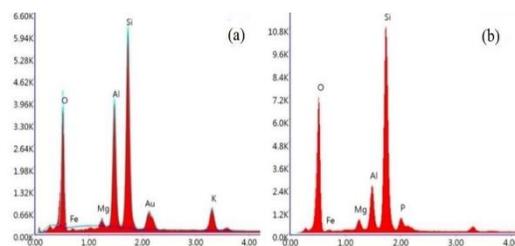


Fig. 3. EDX spectrum of (a) MK and (b) PMK

The acidity of the catalyst is determined with the help of simple titration method. As expected, the acidity of the PMK is found to be more than neat phosphoric acid which is in line with previously reported results [13].

3.2 Optimum reaction condition

The efficiency of PMK is examined with a series of reactions by employing benzoic acid and methanol and the varying amount of catalyst, time of reaction and solvent. The results are summarized in Table 1. It is found that, an equimolar amount of acid and alcohol under solvent-free condition, with 10 wt % of PMK catalyst at reflux temperature for 5 hours is found to be the optimum condition for the esterification reaction and very high yields. Although esterification is an equilibrium process refluxing condition vaporize the water generated from the reaction mixture or form a eutectic mixture with the alcohols. On the other hand, in presence of solvent the temperature of reaction mixture is less than that of boiling point of water even at refluxing condition.

TABLE 1

Optimization of reaction condition of the esterification reaction

Sl. No	Catalyst (wt %)	Solvent	Time	Isolated Yield (%)
1	10	Dichloromethane	6 hrs	39
2	20	Acetonitrile	7.5 hrs	80
3	15	Tetrahydrofuran	5 hrs	65
4	10	Chloroform	7 hrs	60
5	20	Acetone	6 hrs	55
6	10	No solvent	5 hrs	>93

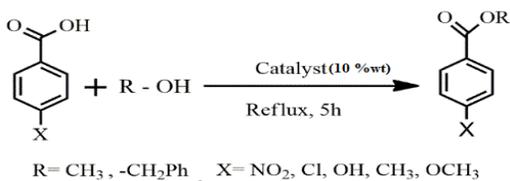
3.3 Catalytic activity

With the optimized reaction condition, several benzoic acid derivatives are subjected to esterification with methanol and

benzyl alcohol. Benzoic acids having both electron donating and withdrawing group reacted and gave the desired products with high yield (Table. 2.). The NMR and IR spectroscopic data along with physical characteristics of some of the products are detailed in Table 3. Electron withdrawing group attached to the benzoic acid gave almost similar yield with electron donating group, that means the substituent has no effect in this reaction condition; this might be due to the temperature and the catalyst, where these two play important role in the formation of the intermediate. The role of the catalyst might be crucial for this important observation. Since acidity of the catalyst is found to be more than neat phosphoric acid, protonation on the benzoic acid is preferred and hence nucleophilic attack of alkoxy group become more feasible. As a result, no difference is observed in conversion with this catalyst. However, the conversion is little bit lower in case of benzyl alcohols. This might be due to bulky benzyl group, which hinder the approach of nucleophile towards the electrophilic carbon.

TABLE 2

Esterification reaction of different benzoic acids with methanol and benzyl alcohol.^a



Sl no	Carboxylic acid	Alcohol	Product	% Conversion
1.		CH ₃ OH		78
2.		CH ₃ OH		92
3.		CH ₃ OH		93
4.		CH ₃ OH		91
5.		CH ₃ OH		95
6.		CH ₃ OH		96
7.		PhCH ₂ OH		72
8.		PhCH ₂ OH		87
9.		PhCH ₂ OH		89
10.		PhCH ₂ OH		88
11.		PhCH ₂ OH		89
12.		PhCH ₂ OH		87

^aAll the products are well known. To record the 1H NMR and IR spectra of some compounds, the compounds are isolated and given as a supporting information and authenticity of the products is established by comparing

with the standard result.

TABLE 3

The spectroscopic data of few products having serial number 2, 8, 3, 9, 5, 11, 6, 12 from Table 2.

	Methyl-4-nitrobenzoate: Yellow Solid, Yield 92%, Mp 94-96°C, IR (KBr) (ν, cm ⁻¹): 3450 (O-H), 1644 (C=O), 1280 (C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 8.23 (d, 2H), 7.267 (d, 2H), 3.89 (s, 3H), 1.63 (s, 3H)
	Benzyl-4-nitrobenzoate: Light yellow Solid, Yield 87%, Mp 165-175°C, IR (KBr) (ν, cm ⁻¹): 3447 (O-H), 1655 (C=O), 1253(C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 8.46 (d, 4H), 7.47 (d, 2H), 7.36 (d, 3H), 4.79 (s, 1H)
	Methyl-4-chlorobenzoate: Colorless liquid, Yield 93%, IR (KBr) (ν, cm ⁻¹): 3450 (O-H), 1718 (C=O), 1277(C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 8.19 (d, 2H), 7.37 (d, 2H), 3.87 (s, 3H)
	Benzyl-4-chlorobenzoate: Light yellowish liquid, Yield 89 %, IR (KBr) (ν, cm ⁻¹) 3463 (O-H), 1729 (C=O), 1270 (C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 7.88 (d, 2H), 7.61(d, 2H), 7.47 (d, 2H), 7.38 (d, 3H), 5.25 (s, 1H).
	Methyl-4-methyl benzoate: Yellowish viscous liquid, Yield 95%, Mp 31-35°C, IR (KBr) (ν, cm ⁻¹): 3450 (O-H), 1640 (C=O), 1260 (C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 7.93 (d, 2H), 7.24 (d, 2H), 3.89 (s, 3H), 2.40 (s, 3H).
	Benzyl-4-methyl benzoate: Yellowish liquid, Yield 89 %, IR (KBr) (ν, cm ⁻¹) 3452 (O-H), 1647 (C=O), 1270 (C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 7.93 (d, 2H), 7.47 (d, 2H), 7.37 (s, 3H), 7.35 (d, 2H), 5.26 (s, 1H), 2.35 (s, 3H)
	Methyl-4-methoxy benzoate: Yellow Solid, Yield 96 %, Mp 48-52°C, IR (KBr) (ν, cm ⁻¹): 3447 (O-H), 1642 (C=O), 1260 (C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 8.00 (d, 2H), 6.90 (d, 2H), 3.861 (s, 3H), 3.84 (s, 3H)
	Benzyl-4-methoxy benzoate: Colorless liquid, Yield 87 %, IR (KBr) (ν, cm ⁻¹): 3449 (O-H), 1622(C=O), 1273 (C-O); ¹ H NMR (300 MHz, CDCl ₃) (ppm): δ 7.47 (d, 2H), 7.38 (s, 3H), 7.09 (d, 2H), 6.82 (d, 2H), 5.26 (s, 1H), 3.83 (s, 3H)

RECYCLIBILITY TEST

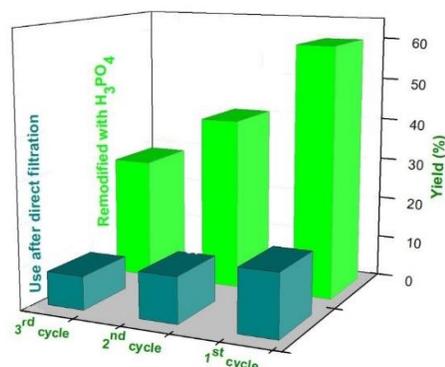


Fig. 4. Reusability test of the catalyst up to three cycles

Reusability tests for the catalyst are performed up to three cycles after recovering the catalysts in two different ways viz. (a) directly by filtration (b) refluxing the regenerated catalyst with Phosphoric acid. The percentage yield for the catalyst recovered by direct filtration method is very nominal (maximum

up to 15% only). However, the same catalyst after refluxing with phosphoric acid gave very good product yield (up to 60%).

CONCLUSION

The Phosphoric acid modified Montmorillonite K-10 clay (PMK) is found to be an efficient catalyst for esterification of aromatic carboxylic acids and alcohols under solvent-free conditions. This catalyst is found to be significantly active for both electron-donating and electron-withdrawing substituents. Another advantage of this catalyst is its easy recovery and reuse again by refluxing with phosphoric acid without losing its activity. Being a cost effective and convenient approach, it can be considered as a better method for the esterification reactions from both academic as well as industrial point of view.

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