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Acid Activated Indian Bentonite, an Efficient Catalyst for Esterification of Carboxylic Acids

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Abstract The preparation, characterization, and catalytic properties of acid activated Indian bentonite (AAIB) are reported. AAIB has been characterized by XRD (basal spacing, 15.05 Å), specific surface area (273 m^2/g), pore volume and pore diameter using BET method, TGA, SEM, and surface acidity by *n*-butylamine back titration method and infrared spectroscopy using pyridine as a probe molecule. The activity of Montmorillonite K10, ZrO_2, S–ZrO_2, *p*-toluenesulfonic acid (*p*-TSA), Indian bentonite (IB), and AAIB was investigated by the esterification of *p*-cresol with stearic acid. Among the catalysts, AAIB was found to be more active. The esterification of various carboxylic acids with phenols and alcohols was studied on AAIB to obtain corresponding esters in good yields. The regeneration and reusability of AAIB has also been investigated.

Keywords Acid activated Indian bentonite · *p*-Cresyl stearate · Esters · Catalyst

1 Introduction

Esterification reaction is one of the most important processes in organic synthesis and has been extensively used [1, 2]. A number of methods including microwave applications have been developed for esterification process and new methods continue to appear. Esterifications are usually catalysed by Brønsted acids like H_2SO_4 and HCl in liquid phase [3] and have several disadvantages. The present tendency is to replace these catalysts by solid acid catalysts. Several heterogeneous catalysts have been reported to synthesize industrially important esters. Zeolites in different forms have been studied in esterification reactions [4–6]. Filtrol-24, Amberlyst-15, sulphated zirconia and heteropolyacids have been used as catalysts in the synthesis of phenethyl acetate and cyclohexyl acetate [7]. Esterification of cresols catalysed by lipase enzyme has been reported [8]; the method however has drawbacks like long reaction times and poor to average yields. Smectite clays and their modified forms have been reported as efficient catalysts in the esterification of alkenes with carboxylic acids [9]. Kantam et al. [10] and Srinivas and Das [11] have carried out esterification reactions on Fe^{3+}-montmorillonite clay. Kawabata et al. [12] have reported highly efficient esterification of carboxylic acids with alcohols by montmorillonite-enwrapped titanium as a heterogeneous acid catalyst. Recently, esterification of succinic anhydride with *p*-cresol and dicarboxylic acids to diesters has been reported over cation exchanged montmorillonite clay catalysts [13, 14]. Very few of these are environmentally safer, the clays and zeolites being particularly so.

A common method of preparing esters is to react the required carboxylic acid and alcohol in presence of an acid catalyst, such as conc. H_2SO_4. Hirose et al. [15] have employed imidazole as a promoter for microwave assisted esterification of carboxylic acid anhydrides with alcohols.

The modified clays are versatile heterogeneous catalysts for a wide variety of organic reactions [16]. The acidity of a clay matrix can be improved by acid activation. The acid

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activation process increases the number of Brønsted acid sites on the clay due, partly, to the introduction of lattice protons [17]. The usefulness of microwave radiation in activating a wide range of organic reactions is well established [18]. In addition, the importance of heterogeneous catalysts is becoming more significant, because of their enhanced selectivity and use of milder reaction conditions compared to conventional ones [19, 20].

We report here the liquid phase esterification of some carboxylic acids with phenols or alcohols using acid activated Indian bentonite as an acid catalyst.

2 Experimental

2.1 Materials

Smectite rich clay sample from Bhuj area in Gujarat (supplied by Ashapura Chemicals Ltd., India) has been used in this study. The composition of the Indian bentonite was found by XRF to be 53.44% SiO_2, 16.12% Al_2O_3, 13.65% Fe_2O_3, 2.84% MgO, 2.31% Na_2O, 0.27% K_2O, 1.28% CaO, 1.24% TiO_2, 0.02% Cr_2O_3, 0.11% MnO, 0.01% NiO, 0.04% P_2O_5, 0.16% S, and ignition loss 8.03%. The cation exchange capacity (CEC) value was found to be 0.98 meq g^{-1}.

2.2 Preparation of Catalysts

Acid activated Indian bentonite was prepared by following the method reported elsewhere [21–24]. To prepare acid activated Indian bentonite, the Indian bentonite was slurried with water and then mixed with conc. H_2SO_4 (98%) at predetermined acid/clay ratio of 0.30 so as to form a clay slurry, which was heated on a water bath at 90 °C for 16 h with constant stirring (pH 1.84). At the end of the reaction time the activation was stopped by adding a large amount of cold water (~250–300 mL). The resulting slurry was repeatedly centrifuged in fresh hot deionised water until free of SO_4^{2-} ions (as tested using $BaCl_2$). The resulting AAIB was dried at 100 °C and subsequently ground to a fine powder. ZrO_2 and S–ZrO_2 were prepared by following the methods reported in literature [25]. Mont. K10 was purchased from Sigma-Aldrich Company.

2.3 Characterisation

A Siemens D5005 diffractometer utilizing CuKα radiation was used for obtaining powder X-ray diffraction (XRD) patterns. Specific surface area, pore volume, and pore size distributions were obtained using a Quantachrome NOVA 1000 surface area analyzer. The samples were degassed for 2 h at 200 °C prior to analysis. A Polymer Laboratory make STA 1500 thermo gravimetric analyzer was used for obtaining TGA curves and materials were examined using a JEOL JSM-840A scanning electron microscope and an energy-dispersive X-ray analysis system (EDX). All sample stubs were coated with a thin layer of colloidal graphite prior to deposition of the clay sample, which in turn was coated with a thin film of gold to prevent charging. Surface acidity was measured using *n*-butylamine (0.01 M) back titration method [26, 27] and IR spectroscopy method by pyridine thermodesorption [28, 29].

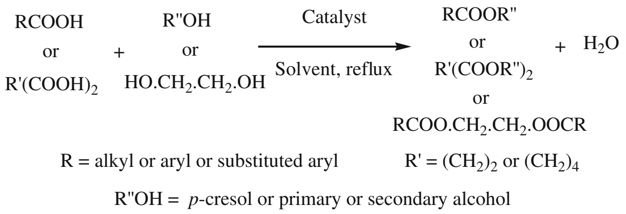
2.4 IR Spectroscopy Method by Pyridine as a Probe Molecule (DRIFTS)

IR spectroscopy was performed using a Nicolet Avatar 320 FTIR spectrometer. The samples were taken into a sample cup of 2 mm depth and 8 mm diameter. The samples were activated at 120 °C prior to saturation with 0.05 mL freshly distilled pyridine and then heated at 120 °C for 1 h. After this treatment the infrared spectra were recorded between 2,000 and 1,200 cm^{-1} at room temperature. Each spectrum consisted of 256 scans at a resolution of 4 cm^{-1}.

The band at 1,545 cm^{-1} was considered as characteristic of Brønsted acidic site, the band at 1,455–1,450 cm^{-1} of Lewis acid site and the band at 1,490 cm^{-1} of Brønsted and Lewis acid sites [28].

2.5 Procedure for the Esterification in Liquid Phase

In a typical experiment (Scheme 1) 5–15 mmole of carboxylic acid and 5–20 mmole of *p*-cresol or alcohol were dissolved in dry *o*-xylene or toluene (30 mL) to which 500 mg of the catalyst was added. The resultant mixture was refluxed for appropriate time with azeotropic removal of water. After cooling the reaction mixture, the catalyst was filtered off and washed with the solvent (10 mL). The unreacted starting compounds were removed by washing the filtrate with 5% NaOH [with saturated $NaHCO_3$ solution in 4-hydroxybenzoic acid reaction] (4 × 10 mL) followed by water (2 × 10 mL) and saturated NaCl (2 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the product was purified by recrystallising from ethanol.



Scheme 1 Esterification of carboxylic acids with *p*-cresol or alcohols

The esters were identified by their melting points and ^{1}H NMR and IR spectra. All acids and alcohols (except myristic acid, which was procured from Merk-Schuchardt, Germany) and solvents were purchased from S. d. fine-chem. Limited, India. All solvents were distilled prior to use. The IR spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer and ^{1}H NMR spectra on a Brüker–AMX 400 MHz NMR spectrometer.

3 Results and Discussion

3.1 Characterization

The acid activation process is often quite severe and destroys much of the clay layer structure [30] as it removes iron, aluminium, and magnesium from the octahedral sheet. The exchangeable cations are replaced mainly by Al^{3+} and H^+- cations [31, 32]. The CEC decreases with increasing acid treatment [33]. Treatment of montmorillonite clays with cold dilute acids has little effect on the elemental composition of the host layer and results in an essentially proton-exchanged clay, whereas activation with hot concentrated acids results in the removal of ions associated with the octahedral sheet and may not produce an exclusively proton-exchanged clay [34–36]. Acid activation causes little damage to the silicate layer and consequently the structure in the centre of the platelet, at the limit of acid attack, remains intact [31, 34, 37]. The acid activation process followed in the present work is a mild acid treatment and the catalyst showed reduced CEC, which is about half of the exchange capacity of the parent clay.

The basal spacings of the catalysts are presented in Table 1. The intensities of basal reflections of acid activated Indian bentonite are decreased due to partial decomposition of layers and it is an indication that montmorillonitic structure of Indian bentonite is partially preserved.

3.1.1 *Adsorption Measurements*

Figures 1 and 2 show the pore size distribution curve and nitrogen adsorption–desorption isotherm for IB and AAIB respectively. The sorption isotherms for the catalysts are type IV in the classification of Brunauer et al. [38] indicating the presence of pores. The catalysts exhibit a narrow pore size distribution characteristic of mesopores. It is important to note that the surface area of the reused acid activated Indian bentonite catalyst has decreased from 273 m^2/g before use to 103 m^2/g and so as the activity after 5th reuse. This may be attributed to saturation of the reaction product in the catalyst pores thereby reducing active sites on the catalyst available for the reaction.

3.1.2 *TGA of IB and AAIB*

Figure 3 shows the TGA curves of IB and AAIB respectively. The TGA curve of IB exhibits an initial sharp decrease due to the loss of hydration water and a second one beyond about 120 °C due to the gradual loss of the hydroxyl groups. The loss at 300–450 °C is hydroxyl water associated with Indian bentonite's structure. Between 450 and 650 °C, an additional amount of water is lost. There is negligible weight loss above 700 °C.

The TGA curve of AAIB exhibits an initial sharp decrease due to the loss of hydration water and a second one beyond about 150 °C due to the gradual loss of the hydroxyl groups. The loss at 500 °C is hydroxyl water associated with acid activated Indian bentonite's structure. Between 500 and 700 °C, an additional amount of water is lost. There is negligible weight loss above 700 °C.

3.1.3 *SEM of IB and AAIB*

Figure 4 shows SEM pictures of Indian bentonite and acid activated Indian bentonite. The particle size of Indian bentonite is 5.5–45.5 µm, whereas the particle size of acid activated Indian bentonite is 0.5–35 µm indicating

Table 1 Esterification of stearic acid with *p*-cresol over different catalysts

Entry	Catalyst	Basal spacing (Å)	Sp. surface area (m^2/g)	Surface acidity mmol/g	% Yield of *p*-cresyl stearate
1	Mont.K10	d_{001} peak absent	254	–	23
2	ZrO_2	–	23	0.09	Nil
3	$S–ZrO_2$	–	76	0.35	60
4	*p*-TSA	–	–	–	78
5	IB	12.83	75	0.44	Nil
6	AAIB	15.05	273	0.96	96
7	No catalyst	–	–	–	Nil

Molar ratio *p*-C: SA, 2:1 [10: 5 mmol]; solvent, *o*-xylene; time, 6 h; amount of catalyst, 0.5 g

Fig. 1 **a** Mesopore size distribution curve and **b** Nitrogen adsorption–desorption isotherm of IB

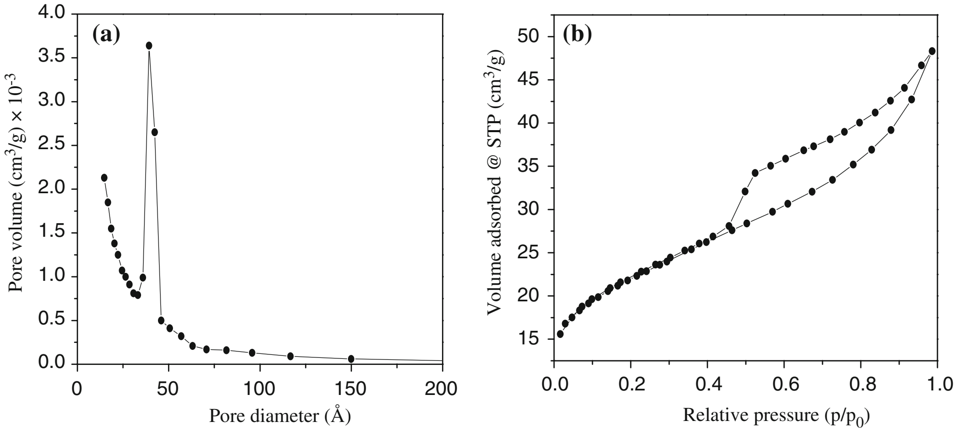


Fig. 2 **a** Mesopore size distribution curve and **b** Nitrogen adsorption–desorption isotherm of AAIB

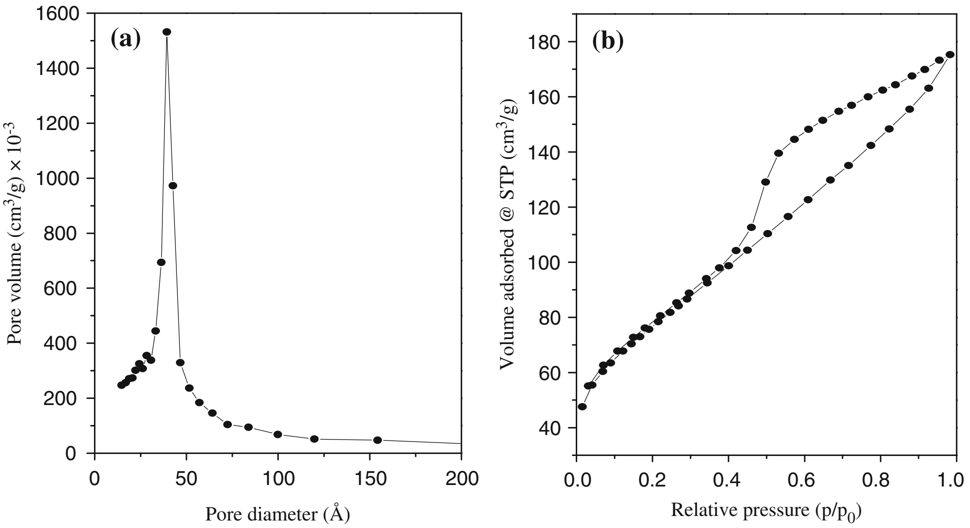
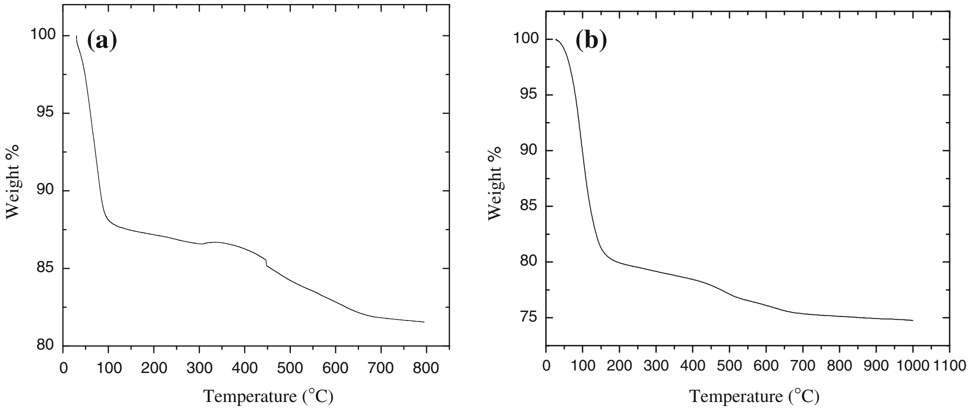


Fig. 3 Thremogravimetric curves of **a** IB and **b** AAIB



decrease in particle size and enhancement in surface area after acid treatment.

3.1.4 Acidity Measurements

The acidity of the catalysts has been investigated by *n*-butylamine back titration method, and infrared spectroscopy using pyridine as a probe molecule.

3.1.4.1 n-Butylamine Back Titration Method *n*-Butylamine back titration method gives the total surface acidity of the catalysts. However, it is not possible to distinguish between the Lewis and Brønsted acid sites. Total acidity of Indian bentonite (IB) and acid activated Indian bentonite (AAIB) was measured by *n*-butylamine (0.01 M) back titration method. The results (Table 1) clearly indicate that modification by acid treatment is advantageous for improving the acidity of IB.

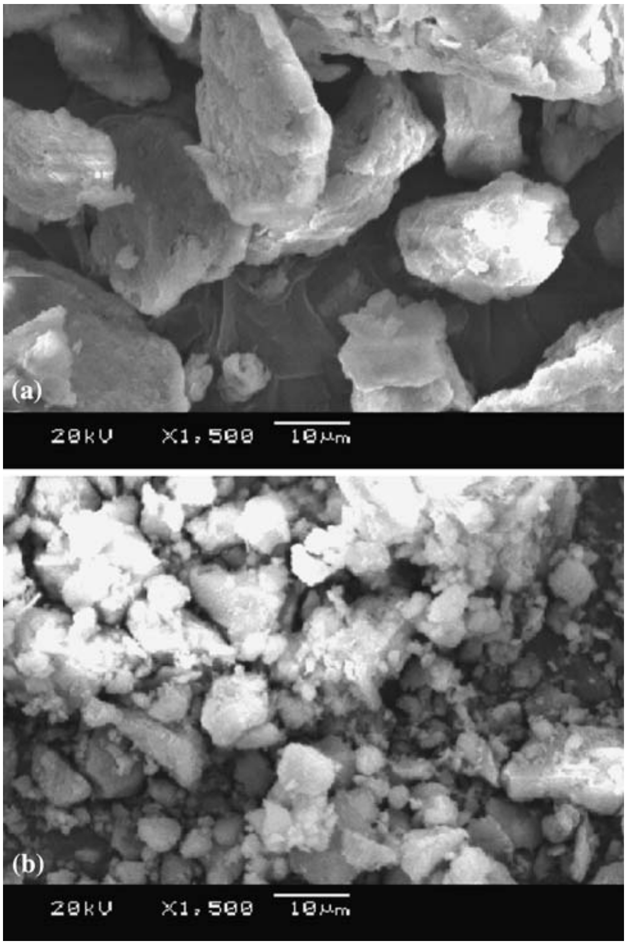


Fig. 4 SEM pictures of **a** IB and **b** AAIB

Total acidity of the catalysts is found to follow the sequence: AAIB › Indian bentonite › S–ZrO_2 › ZrO_2.

3.1.4.2 Infrared Spectroscopy After Pyridine Adsorption Surface acidity was determined using pyridine as a probe molecule by FT-IR. Pyridine has been used as a probe molecule for the determination of the nature of acid sites on the surface of solid catalysts. The adsorption of pyridine in the gas phase, followed by infrared spectrometry is reported by earlier workers as one of the probe molecules to establish the nature of the acid sites. There are also reports that the adsorption of pyridine ($pK_a = 5.3$) method gives only the strong acid sites [39]. In this study, bands are observed at 1,540–1,545, 1,490, and 1,444–1,453 cm^{-1} for catalysts activated at 120°C. The vibrations at 1,444–1,453 cm^{-1} are associated with pyridine coordinated to Lewis sites, the vibration at 1,540–1,545 cm^{-1} is associated to pyridine bound to Brønsted sites (pyridinium ions), and the vibration at 1,490 cm^{-1} is associated to pyridine bound to both Brønsted and Lewis acid sites. Hydrogen-bonded pyridine, which typically absorbs at 1,440 and 1,490 cm^{-1}, may be contributing in these regions of the spectra [40].

The infrared spectra of the catalysts after pyridine adsorption are shown in Fig. 5. From the acidity data, the density of the Brønsted acid sites in acid activated Indian bentonite is increased over raw Indian bentonite because of the substitution of Na^+, K^+ and Ca^{2+}, present as interlamellar cations, with the H^+ and/or the lattice ions, e.g., Al^{3+} and the protons that replace leached octahedral cations on the clay matrix [41]. The infrared spectra of the catalysts with adsorbed pyridine showed both Brønsted and Lewis acid sites. AAIB and S–ZrO_2 showed more acidity than their parent materials IB and ZrO_2 respectively. However, spectra of pyridine adsorbed on Mont. K10 and ZrO_2 exhibited only weak bands in these regions after activation at 120°C. The spectra revealed a broad absorption band at 1,640 cm^{-1}, which is due to bending

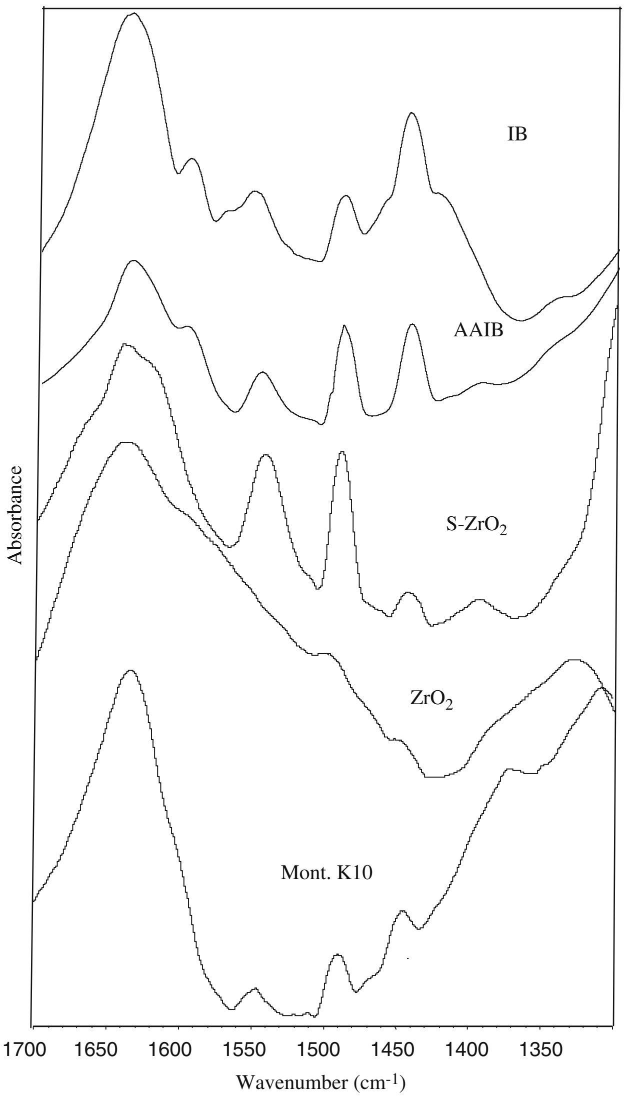


Fig. 5 Infrared spectra of the catalysts after pyridine adsorption

Table 2 Synthesis of esters of various carboxylic acids catalyzed by acid activated Indian bentonite

Entry	Carboxylic acid	*p*-Cresol or alcohol	Molar ratio	Solvent	Time (h)	Yield (%)[a]
1	Succinic acid	1-Butanol	1:4	Toluene	8.0	94
2	Succinic acid	*p*-Cresol	1:4	*o*-Xylene	6.0	77
3	Adipic acid	*p*-Cresol	1:4	*o*-Xylene	6.0	71
4	Myristic acid	Ethane-1,2-diol	3:1	*o*-Xylene	6.0	94
5	Stearic acid	Ethane-1,2-diol	3:1	*o*-Xylene	6.5	76
6	Stearic acid	2-Methyl-1-propanol	1:2	Toluene	8.0	73
7	Benzoic acid	1-Butanol	1:2	Toluene	8.5	56
8	Benzoic acid	*p*-Cresol	1:2	Toluene	12.5	74
9	4-Nitrobenzoic acid	1-Butanol	1:2	Toluene	8.5	17
10	4-Nitrobenzoic acid	*p*-Cresol	1:2	Toluene	11.5	37
11	4-Nitrobenzoic acid	*p*-Cresol	1:2	*o*-Xylene	6.0	10
12	2-Chlorobenzoic acid	*p*-Cresol	1:2	Toluene	10.5	66
13	2-Chlorobenzoic acid	1-Butanol	1:2	Toluene	8.5	67
14	4-Hydroxybenzoic acid	1-Butanol	1:2	Toluene	8.0	87
15	Palmitic acid	2-Propanol	1:4	Toluene	8.0	54
16	Phenylacetic acid	2-Propanol	1:4	Toluene	8.0	84

Amount of catalyst, 500 mg; molar ratio [acid: *p*-cresol or alcohol]

[a] Isolated yields

vibrations of –OH group of water associated with the solid surface.

3.2 Catalytic Activity

3.2.1 *Esterification of Stearic Acid with p-Cresol*

The activity of the catalysts was tested on the esterification of stearic acid with *p*-cresol. Table 1 summarises the results. From the results it is clear that in the AAIB catalysed reaction the ester was obtained in 96% yield after 6 h and therefore it is selected as catalyst for other esterifications.

The activity of the catalysts for esterification of stearic acid with *p*-cresol is found to follow the sequence: AAIB › *p*-TSA › S–ZrO_2 › Mont.K10 › Indian bentonite = ZrO_2. The activity of the catalysts for the esterification of stearic acid with *p*-cresol has also correlated with the data of Brønsted acid sites obtained from Infrared spectroscopy after pyridine adsorption.

3.2.2 *Esterification of Various Carboxylic Acids with p-Cresol*

Table 2 shows the results of esterification of various carboxylic acids with *p*-cresol and different alcohols catalysed by acid activated Indian bentonite. The esters are obtained in 10–94% yield in *o*-xylene and toluene. From the results, it is clear that the yields in the esterifications of *p*-cresol or 1-butanol with 4-nitrobenzoic acid are low compared to those with benzoic acid, 2-chlorobenzoic acid or 4-hydroxybenzoic acid. This is attributed to the presence of an electron withdrawing nitro group.

The AAIB is recovered by filtration, washed with the solvent and water. The recycled catalyst (after activation at 110°C for 2 h) is used in subsequent reactions for three times without much loss in activity.

4 Conclusions

Acid activated Indian bentonite, ZrO_2, and its sulphated form have been prepared and characterised by XRD, surface area, pore volume and pore diameter using BET method and surface acidity by *n*-butylamine back titration method and through infrared spectroscopy after pyridine adsorption. Further, Acid activated Indian bentonite was characterized by TGA and SEM. Both Brønsted and Lewis acid sites are present on the acid activated Indian bentonite catalyst. These results clearly indicate that the acidity of the catalysts increases after modification and so as their activity in the esterification. The process of synthesizing the esters presented here employs the reusable, inexpensive and totally eco-friendly Indian bentonite as catalyst. The catalyst is easily regenerated and the regenerated catalyst is found to retain the same activity even after three experimental cycles.

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