Brønsted and Lewis acidity of modified montmorillonite clay catalysts determined by FT-IR spectroscopy

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ABSTRACT

The surface acidity of different modified montmorillonite clay catalysts, Al^{3+}-exchanged montmorillonite (Al^{3+}-Mont) and aluminium pillared montmorillonite (Al-PILC) was determined by DRIFTS (diffuse reflectance Fourier transform infrared spectra) using pyridine as probe molecule. The method involved treating the clay sample directly with pyridine, drying the sample at 120 °C and recording FT-IR spectra in the region 1650 and 1350 cm^{-1}. The spectra obtained showed well resolved absorption bands for Lewis and Brønsted acid sites in the clay catalysts. In order to understand the role of acid sites present on clay catalysts, esterification of propionic acid with p-cresol has been studied. The Brønsted acidity data obtained by FT-IR study for modified montmorillonite clay catalysts correlated well with the catalytic activity in the esterification reaction. Among the modified clay catalysts, Al^{3+}-Mont and H^{+}-Mont clay catalysts showed good activity and Al-PILC showed negligible activity in esterification. The inactivity of Al-PILC catalysts is attributed to the absence of Brønsted acidity.

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1. Introduction

Acidity on catalyst surface plays an important role in bringing about various organic transformations. The origin and nature of acidity in zeolites and oxide surfaces have been studied and understood well [1–3]. The nature of acidic sites in clays is different from that of metal oxides and zeolites. The study of acid centers on clays is still a subject of investigation primarily because of the presence of different kinds of water molecules and their indefinite contribution to different types of acidities on the surface.

There are several methods to determine the surface acidity of clay minerals such as Hammett indicator technique [4], n-butylamine back titration [5], microcalorimetry [6] and FT-IR spectroscopy of adsorbed basic probe molecules [7–9]. Thermal desorption analysis of bases, such as butylamine, cyclohexylamine and pyridine, can also be used for rapid evaluation of the amount and type of acid sites in clay minerals [10]. Another widely used method to study the surface acidity of a solid catalyst is through the product distribution analysis of some model catalyzed reactions [11]. Isomerisation, catalytic dehydration, and dehydrogenation are the most common typical model reactions used for investigating the acid–base properties of heterogeneous catalyst systems [12,13].

Brønsted and Lewis acid sites can be distinguished from the IR spectrum of pyridine adsorbed on the clay surface. The spectrum shows well resolved and characteristic bands for pyridine adsorbed on both the types of acid sites [14]. The methods used by earlier workers to study the acidity by IR measurements on pyridine adsorbed surfaces are tedious, which include preparation of very thin self-supporting wafers of the catalyst material under high pressure and then exposing the wafer to pyridine vapour at room temperature followed by desorption of physisorbed pyridine at 100 °C under high vacuum [15–17]. Recently, Jankovic and Komadel reported a relatively simple procedure to access Brønsted and Lewis acidity of clay catalysts [9]. In the present study, the method that is employed is similar to the method adopted by Jankovic and Komadel but is further simplified by treating the catalyst samples directly with pyridine and recording the spectra after thermal desorption of physisorbed pyridine at 120 °C. The main objective of this paper is to examine whether the acidity measured by the simplified method correlated with the activity of in the esterification of propionic acid with p-cresol.

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 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) of montmorillonite was found to be 0.8 meq g^{-1}. The enriched clay containing less than 2 μm fraction was used for catalyst preparation. Commercially available acid clay, montmorillonite K-10 (procured from Sigma–Aldrich) was also used for comparative study in this investigation.

2.2. Preparation of catalysts

2.2.1. Preparation of Al-exchanged clays

The Al-exchanged montmorillonite clay was prepared by adopting standard procedure reported in the literature [18]. The method involves stirring 5 g of montmorillonite clay sample with 200 mL of 0.5 M $AlCl_3$ solution for 24 h. The clay was then centrifuged and washed with distilled water repeatedly until the washings showed negative test for chloride. The clay sample was then dried at 100 °C for 3 h and subsequently ground to a fine powder and used as Al^{3+}-Mont (100) catalyst. In order to study the effect of thermal treatment on acidity as well as activity, the Al^{3+}-Mont (100) was further thermally treated at 200 °C and 400 °C for 3 h. The catalysts thus obtained were referred to as Al^{3+}-Mont (200) and Al^{3+}-Mont (400) respectively. However, in preparation of H^+-Mont, 0.5 M HCl was used as a source of H^+-ions and the rest of the procedure is same as followed above. Commercially available montmorillonite K-10 was also modified into Al^{3+}-exchanged form, which is labeled as Al^{3+}-Mont K-10. The procedure is similar to the one followed for the preparation of Al^{3+}-Mont (100) catalyst except parent clay.

2.2.2. Preparation of Al-PILC

A solution of aluminium hydroxy oligomer cations was prepared by adding 0.4 M NaOH to 0.4 M $AlCl_3$. The rate of addition of NaOH to $AlCl_3$ was maintained at 1.0 mL min^{-1} and OH^-/Al^{3+} ratio was maintained at 2.5 using peristaltic pump [19]. The resulting solution was aged for 24 h at ambient temperature (pH 3.8). The aluminium oligomeric cations, formed under these conditions predominantly contained ions of Keggin-type $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ [20]. The pillared clay material was prepared by stirring 1 g of clay sample with 125 mL of aluminium oligomeric solution for 12 h. After pillaring reaction, the clay sample was separated by centrifugation and washed repeatedly with distilled water. Centrifugation and washing operations were continued till the washings show negative test for chloride ions. The resulting clay sample was dried at 100 °C for 4 h and ground to a fine powder and identified as Al-PILC (100). Finally, the Al-PILC (100) clay was calcined at 500 °C for 4 h and used as Al-PILC (500) catalyst.

2.3. Methods

XRD patterns of the clay samples were recorded on a Siemens D5005 diffractometer using Cu Kα radiation source 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 BET methods 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 100 °C. The diffuse reflectance Fourier transform infrared spectra (DRIFTS) of modified montmorillonite clay catalysts were recorded in the spectral range 1650–1350 cm^{-1} using a diffuse reflectance accessory at room temperature on a Nicolet Avatar 320 FT-IR spectrometer.

2.4. Catalytic study

The liquid phase esterification reaction of propionic acid with p-cresol was carried out in 100 mL round-bottomed flask fitted with Dean-Stark trap for water removal and a reflux condenser. The flask was charged with propionic acid (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, filtered to separate the clay catalyst and the latter was washed with ethyl acetate (2 × 5 mL). The combined filtrates were washed with 5% sodium hydroxide solution (4 × 15 mL) to remove unreacted reactants. The organic layer was washed with water (2 × 15 mL) and saturated brine (1 × 15 mL), dried over anhydrous sodium sulphate. The solvent was finally distilled out under reduced pressure. The product was extracted with diethyl ether and identified by IR and ^{1}H NMR. The IR data of p-cresyl propionate (cm^{-1}) is 2983, 1759, 1585, 1488, 1075, 915, 753 and 698, and ^{1}H NMR data of compound is 1.26 (t, 3H), 2.3 (s, 3H), 2.6 (q, 2H), 6.8 (d, 2H) and 7.1 (d, 2H).

2.5. FT-IR spectroscopic measurements

The DRIFTS of modified montmorillonite clay catalysts were recorded using a diffuse reflectance accessory at room temperature on Nicolet Avatar 320 FT-IR spectrometer. The modified montmorillonite clay catalysts were dried in a hot air oven for 1 h at 100 °C prior to pyridine treatment for IR measurements. The catalyst samples (~50 mg each) were poured loosely into a sample cup. The loosely filled sample was brought in contact with pyridine (~0.1 cm^3) directly. Then the sample cup was kept in a hot air oven at 120 °C for 1 h to remove physisorbed pyridine. After cooling the catalyst sample, the IR spectrum was recorded in the spectral range 1650 and 1350 cm^{-1} with 256 scans and at a resolution of 4 cm^{-1} using KBr background.

3. Results and discussion

Table 1 presents the basal spacing, specific surface area, and activity of different montmorillonite clay catalysts. The basal spacing values of Raw-Mont and some modified forms such as Al^{3+}-Mont (100), Al^{3+}-Mont (200), H^+-Mont and Al-PILC (100) are found to be in same order between 14.7 and 15.7 Å. The Al^{3+}-Mont (400) showed absence of $d_{0\,0\,1}$ plane indicating layered structure collapse on thermal treatment of Al^{3+}-Mont at 400 °C. However, Al-PILC (500) showed characteristic intense peak for $d_{0\,0\,1}$ plane with basal spacing 17.5 Å. Also as expected the specific surface area values are low (21–34 $m^2\,g^{-1}$) and of same order for Raw-Mont and some modified forms such as Al^{3+}-Mont (100), Al^{3+}-Mont (200), Al^{3+}-Mont (400), H^+-Mont and Al-PILC (100) catalysts.

Table 1
Basal spacing, specific surface area, and activity[a] of montmorillonite clay catalysts

Catalyst	Basal spacing (Å)	Surface area ($m^2\,g^{-1}$)	Ester yield (%)[b]
Blank (no catalyst)	–	–	Nil
Raw-Mont	14.7	20.9	Nil
Al^{3+}-Mont (100)	15.5	22.8	88
Al^{3+}-Mont (200)	15.5	36.2	56
Al^{3+}-Mont (400)	$d_{0\,0\,1}$ peak absent	35.4	Nil
Al-PILC (100)	15.7	22.2	Nil
Al-PILC (500)	17.5	201.0	Nil
H^+-Mont	15.1	30.7	85
Mont K-10	$d_{0\,0\,1}$ peak absent	254.0	19
Al^{3+}-Mont K-10	–	267.0	52

[a] Concentration of propionic acid, 5 mmol; concentration of p-cresol, 15 mmol; amount of catalyst, 0.5 g; solvent, toluene (35 mL); reaction time, 8 h.
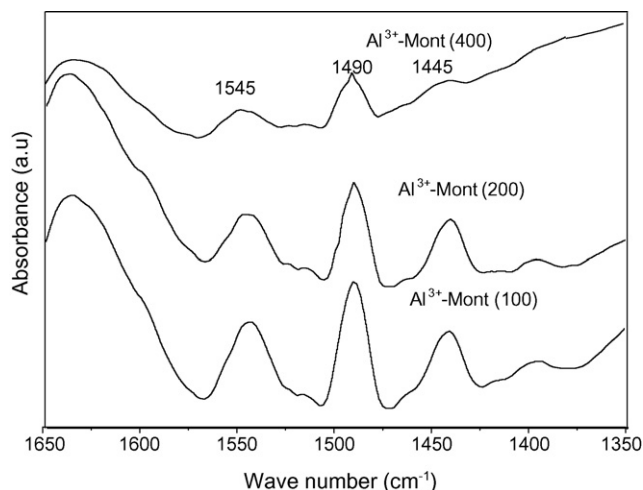[b] Isolated yields.

Fig. 1. DRIFT spectra of pyridine treated Al³⁺-Mont (100), Al³⁺-Mont (200), and Al³⁺-Mont (400) clay catalysts.

Fig. 3. DRIFT spectra of pyridine adsorbed on Mont K-10 and Al³⁺-Mont K-10 catalysts.

The Al-PILC (500) showed characteristic high surface area (201 m^2 g^{-1}). Commercial acid clay, montmorillonite K-10 and its Al³⁺-exchanged form also showed high specific surface area (254–267 m^2 g^{-1}).

The catalytic activities of montmorillonite clay catalysts in the esterification of propionic acid with p-cresol are presented in Table 1.

The DRIFT spectra in the spectral region 1350 and 1650 cm^{-1} after pyridine treatment of modified clay catalysts followed by thermal desorption at 120 °C for 1 h are presented in Figs. 1–4. The IR absorption bands are assigned according to Breen et al. [8]. Physisorbed pyridine was assigned to the bands at ∼1577 and ∼1440 cm^{-1}; hydrogen-bonded pyridine to ∼1440 and 1590 cm^{-1}; Lewis acid-bound pyridine to ∼1450, 1490, 1590 and 1620 cm^{-1}; pyridine coordinated through its aromatic π-electrons to ∼1607 cm^{-1}, and the Brønsted acid-bound pyridinium cation to ∼1540 and 1640 cm^{-1}. The spectra of modified montmorillonite clay catalysts exhibit major absorption bands similar to those observed by Jankovic and Komadel [9]. Spectra of all samples both before and after pyridine treatment show broad absorption band at ∼1640 cm^{-1} due to bending vibrations of –OH group of water molecules. However, there were no other absorption bands for clay catalyst samples before pyridine treatment except 1640 cm^{-1} band. Since the samples were subjected to thermal desorption at 120 °C before taking the spectra, they show
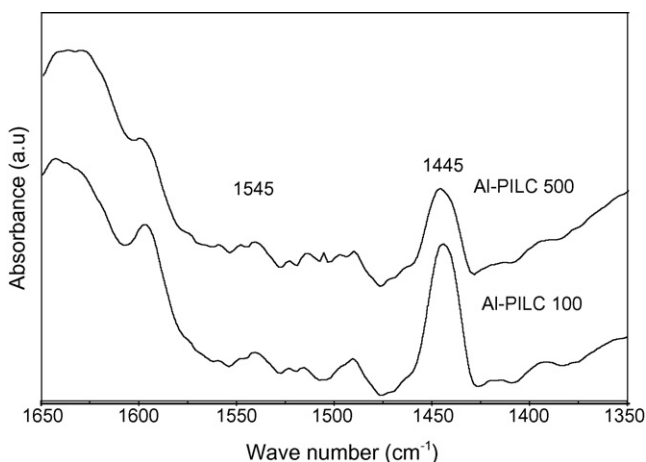
the absence of physisorbed pyridine (band at ∼1577 and ∼1440 cm^{-1}) and hydrogen bonded pyridine (band at ∼1440 and ∼1590 cm^{-1}) that are otherwise observed. The catalyst samples did not show any color changes on pyridine treatment and/or on heat treatment. The DRIFT spectral and activity results of montmorillonite clay catalysts are presented under different headings.

3.1. DRIFT spectra of Al³⁺-Mont catalysts

The DRIFT spectra of pyridine treated Al³⁺-Mont (100), Al³⁺-Mont (200), and Al³⁺-Mont (400) clay catalysts are presented in Fig. 1. The spectra of these catalysts show three major absorption bands at 1545, 1490, and 1450 cm^{-1} corresponding to Brønsted, both Brønsted and Lewis, and Lewis acidity respectively. Among these three catalysts, Al³⁺-Mont (100) showed a slightly more intense absorption bands compared to Al³⁺-Mont (200), which in turn was more intense compared to Al³⁺-Mont (400). On thermal treatment at 200 °C the spectrum of Al³⁺-Mont (200) indicates slight reduction in the intensity of the peaks of both Brønsted and Lewis acidity. Further, the spectrum of Al³⁺-Mont (400) reflects the destruction of both Brønsted and Lewis acidity to a larger extent on thermal treatment at 400 °C. The intensity of absorption band at ∼1545 cm^{-1}, specifically, is high in the case of Al³⁺-Mont (100) indicating presence of Brønsted acidity in high concentration. The intensity reduces for the sample thermally treated at 200 °C and becomes almost negligible for that treated at 400 °C.

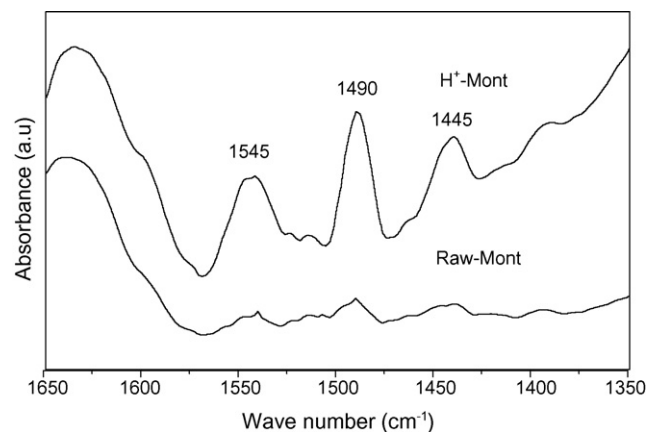Fig. 2. DRIFT spectra of pyridine treated Al-PILC (100) and Al-PILC (500) catalysts.

Fig. 4. DRIFT spectra of pyridine adsorbed on Raw-Mont and H⁺-Mont clay catalysts.

The observed variations in Brønsted acidity concentration are reflected in their activity in the esterification of propionic acid with p-cresol (Table 1). A very good activity (88% ester yield) observed with Al^{3+}-Mont (100) is attributed to its higher Brønsted acidity as shown by the intensity of the peak at 1545 cm^{-1}. Similarly the reduced activity (56% ester yield) in case of Al^{3+}-Mont (200) is attributed to its reduced Brønsted acidity as shown by the peak at 1545 cm^{-1}. Negligible activity was observed in the case of Al^{3+}-Mont (400) due to its insignificant Brønsted acidity. The reduced activity due to insignificant Brønsted acidity of Al^{3+}-Mont upon thermal treatment beyond 200 °C is obviously due to the loss of water molecules attached to the hydration shell of the cation [7,21]. Similar relationship was observed in esterification of succinic acid with iso-butyl alcohol and DRIFT spectra for Al^{3+}-exchanged montmorillonite clay catalyst [22].

3.2. DRIFT spectra of Al-PILC

The DRIFT spectra of pyridine treated Al-PILC (100) and Al-PILC (500) clay catalysts are presented in Fig. 2. Both the samples show only one prominent absorption band at 1450 cm^{-1} and very feeble bands at 1545 and 1490 cm^{-1} indicating low concentration of the Brønsted acidity and significant amount of Lewis acidity. Also both the catalysts failed to give ester when used in esterification of propionic acid with p-cresol. The inactivity of catalysts is due to the absence of Brønsted acidity and that the Lewis acidity although present in high concentration, apparently, does not catalyze the esterification. Pillared montmorillonite clays are known to exhibit high Lewis acidity [23].

3.3. DRIFT spectra of Mont K-10 and Al^{3+}-Mont K-10

The DRIFT spectra of pyridine treated Mont K-10 and Al^{3+}-Mont K-10 clay catalysts are presented in Fig. 3. The spectra of these catalysts also exhibited weak absorption bands at 1545, 1490, and 1450 cm^{-1} indicating presence of both Brønsted and Lewis acidity in low concentrations. Of the two catalysts, aluminium-exchanged montmorillonite K-10 (Al^{3+}-Mont K-10) displayed slightly more intense absorption bands compared to the parent clay, Mont K-10. Cation exchange of Mont K-10 has apparently resulted in the enhancement of both Brønsted and Lewis acidity. The activity of the Mont K-10 catalyst was also observed to be low as only 19% yield of product was obtained when used in the esterification. The Al^{3+}-exchanged Mont K-10 (Al^{3+}-Mont K-10) showed increased activity with 52% ester yield which could be attributed to its enhanced Brønsted acidity by the inclusion of Al^{3+}. However, the increase in ester yield was not very significant compared to the yield obtained using Al^{3+}-exchanged form of Raw-montmorillonite. The reason for this observation may be due to the reduced cation exchange capacity of Mont K-10 [24].

3.4. DRIFT spectra of Raw- and H$^+$-Mont

The DRIFT spectra of pyridine treated H$^+$- and Raw-Mont clay samples are presented in Fig. 4. The spectra of H$^+$-Mont observed to be similar to that of Al^{3+}-Mont catalyst with respect to intensity of absorption bands at 1450, 1490 and 1540 cm^{-1}. Acid treatment of clays is known to result in the removal of Al^{3+}-ions from the octahedral sheet and possibly other soluble ions which subsequently migrate into the interlayer [25,26]. The spectrum of H$^+$-Mont indicates presence of both Brønsted and Lewis acidities to the same extent as Al^{3+}-Mont. Also, the activity of H$^+$-Mont was observed to be high (85% ester yield) and is in the order observed for Al^{3+}-Mont. The Raw-Mont in its Na$^+$-form exhibited absence of all those absorption bands observed for its modified forms. However the sample revealed a broad absorption band at 1640 cm^{-1}, which is due to bending vibrations of –OH group of water associated with the clay surface. The results of surface acidity measurements by DRIFTS using pyridine probe indicated that the modified forms of clay exhibited better Brønsted and Lewis acidity as compared to its natural form.

4. Conclusion

A simplified method of acidity determination is found to give well resolved and reproducible DRIFT spectra arising from the interaction of pyridine with Brønsted and Lewis acid sites on the surface of montmorillonite. The intensity of peak due to Brønsted acidity (1545 cm^{-1}) correlated well with the activity of the modified montmorillonite catalysts for the esterification of propionic acid with p-cresol. The decrease in the area of the Brønsted peaks with the thermal treatment and consequent reduction in the activity of the Al-exchanged montmorillonite clearly demonstrates the role played by the interlamellar water coordinated to the metal ions in the esterificaton. The water molecules coordinated to the exchangeable Al^{3+}-ions dissociate generating the Brønsted acid sites which in turn are able to protonate the carboxylic acid to effect esterification. Aluminium pillared clay fail to bring esterification due to very low intensity peak for Brønsted acidity and strong peak for Lewis acidity. A simple approach developed here for acidity measurement can be advantageously used for a quick evaluation of Brønsted acidity of layered materials where interlamellar water determines the acidity.

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