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Preparation of solid acid catalyst from modified Kaolinite and its characterization and catalytic activity

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A new eco-friendly solid acid heterogeneous catalyst has been prepared from Kaolinite clay for the acetylation of cyclohexanol using acetic acid. Catalyst is prepared from purified and calcined Kaolinite, collected from Nileswar, Kerala, by acid activation using different concentrations of sulphuric acid. The physico-chemical characterization of the catalysts has been carried out using XRD, FTIR, SEM, TG/DTA, surface area analysis, acidity measurement and cation exchange capacity measurement. Acid activation increases the number of acid sites on the clay surface. The acid treatment of NS4 is found to give maximum number of acid site with good catalytic activity. The catalytic activity of the same catalyst NS4 has also been tested by using different primary and secondary alcohols.

Keywords: Acid activation, Acidity, Catalytic activity, Kaolinite, Solid acid catalyst

The clay minerals, an important constituent of all soils, are a group of microcrystalline minerals consisting of hydrous aluminum silicates with sheet like structures[1,2]. Clays are highly valued for their adsorptive properties, which depend from their high surface area and their tendency to adsorb water in the interlayer sites[3]. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), tendency to hold water in the interlayer sites, presence of Br¨onsted and Lewis acidity have made the clays excellent adsorbent materials[4,5]. Attempts have been made to further improve the surface properties of the clay minerals by intercalating clays with inorganic clusters[3]. Clay minerals consist of octahedral and tetrahedral structures formed by oxygen or hydroxyl groups, symmetrically disposed in planar layers. Two types of clay mineral exist in nature with respect to their tetrahedral/octahedral ratio: 1:1 structures and 2:1 structures. Kaolinite has a 1:1 layer structure, first suggested by Pauling[6] with the basic unit consisting of a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{+3} as the octahedral cation.

Natural clays such as Kaolinite and Montmorillonite are increasingly used as catalyst or catalyst support in many organic reactions. Kaolinite is one of the important clay mineral, has a wide variety of applications in industry for the production of ceramics, paper, paint, plastics, rubber, ink and adsorbants[7]. The catalytic properties can be improved by using many methods such as acid treatment, metal salt supporting and pillaring[8-11]. Treatment of clay minerals with concentrated inorganic acids usually at high temperature is known as acid activation. Acid treatments of clay minerals are an important control over mineral weathering and genesis[12,13]. Such treatments can often replace exchangeable cations with H^+ ions and release Al and other cations out of both tetrahedral and octahedral sites, but leaving the SiO_4 groups largely intact[14]. It was reported that acid activation followed by thermal treatment increases surface area, porosity, adsorbent capacity and catalytic properties of clays to a good extend[15-20]. Sabu *et al.* investigated the catalytic activity of acid activated calcined kaolinite containing Fe and Ti as transition metal in their lattice, for the alkylation of benzene with benzyl chloride[15, 21].

The catalytic activity of acid activated calcined kaolinite and acid treated montmorillonite showed the same but the surface area of the former is about half of the latter[22.] Sabu *et al.* studied the acidic properties and catalytic properties of acid treated natural Kaolinite clays containing transition metals in their lattice[23]. Alcohols are converted to esters by acylation with anhydrides or acyl chlorides in the presence of tertiary amine bases such as either triethylamine or pyridine[24]; Lewis or protonic acids[25-29]; or sometimes solid acid catalysts[30,31]. Tributyl phosphine was introduced as a less basic catalyst than amines in the acetylation of alcohols[32,33]. In recent years, it has been shown that several metal triflates such as $In(OTf)_3$, $Cu(OTf)_2$, $Bi(OTf)_3$, $ZrO(OTf)_2$, $Ce(OTf)_4$, $Gd(OTf)_3$, $Sc(OTf)_3$ as well as Me_3SiOTf (Ref.34) are excellent catalysts for efficient acetylation of various types of structurally diverse alcohols with acetic anhydride. There have also been reports on the acylation of alcohols using acetic anhydride, catalyzed by silica gel supported $Ce(SO_4)_2$, $Ti(SO_4)_2$, $Fe_2(SO_4)_3$ and $NaHSO_4$ (Ref. 35). Clay supported $InCl_3$, $GaCl_3$, $FeCl_3$ and $InCl_2$ (Ref. 36) and commercial clay catalysts like K-10 and KSF/0 (Ref. 37) also were reported to catalyze acetylation reaction. Although the majority of these methods ensure good results, there is still a great need for simple, mild, less toxic and easy-to-handle catalysts to generate esters. Development of easily separable and reusable solid catalyst having high activity for the acylation reaction is of great practical importance. The most economically and eco friendly way for the acetylation of alcohols is by using acetic acid instead of acetic anhydride or acetyl chloride. Recently Choudary *et al.* reported acetylation of alcohols with acetic acid using ion exchanged Monmorillonite[38]. Narendar *et al.* reported it over ion exchanged zeolites (LaY)[39] and Pushpaletha *et al.* reported acid treated Attapulgites catalyze acetylation of alcohols using acetic acid in excellent yield[40]. It is important to note that acid treated clays remain one of the most important classes of acid solid catalysts available in the industry[41].

Literature reveals a number of works on the systematic examination of porous silica prepared from mechanically and thermally amorphized kaolinite by sulphuric acid leaching. However, a systematic analysis of the chemical activation of untreated crystalline kaolin with sulphuric acid of different concentrations, with a wide characterization of the obtained solids and a complete discussion of the phenomena governing this process, is sparsely available in the literature. The increasing interest in looking for new applications of clays justifies such a systematic study of this process.

So the objective of this work is to study the preparation and characterization of acid treated Kaolinite clay and their utilization as catalysts for the acetylation of alcohols using acetic acid.

Experimental Section

Materials

The clay sample kaolinite was obtained from Kerala Clays and Ceramic Products Ltd. Pappinissery, Kannur, Kerala. Kaolinite was mined from Nileswer, Kasaragod district, Kerala, and the laboratory reagents are commercially available from Lobacheme.

Catalyst preparation

Catalysts were prepared from metakaolin by acid activation. Metakaolin was obtained from calcinations of Kaolinite. Kaolinite is resistant to acid activation due to its high octahedral aluminium content, and the transformation of kaolin into metakaolin would increase the susceptibility of the former to the aluminium and iron cations leaching from the octahedral layer[42]. Acid activation of metakaolinwas carried out by treating with different concentration of sulphuric acid (0.5, 1, 2, 3, 4 and 5N). Twenty five grams of clay was refluxed with 100 mL of sulphuric acid for 45 min. The resulting residue was filtered and washed with water several times and dried at 110°C. Catalysts prepared were designated as NS1, NS2, NS3, NS4, NS5 and NS6 (Table 1).

Characterization

Characterization of the raw sample was done by chemical analysis. The structural details were studied by Scanning electron microscopy (SEM) and Infrared spectroscopy (IR). SEM images of the catalysts were recorded on a JEOL Model JSM- 6390 LV microscope. The X-Ray Diffraction (XRD) data was collected using a model Bruker AXS D8 advance, X-ray instrument (λ 1.5406 Å). The IR spectra were obtained by Bruker (alpha) KBr Fouriertransform infrared spectroscopy.

The thermal behaviour was determine

d by TG/DTA analysis. The analysis was carried out with a Perkin Elmer, Diamond TG/DTA instrument. A known weight of the sample was heated in an alumina crucible at a constant rate of 10°C/min. from 40°C to 740°C.

Table 1 — Catalysts prepared by acid activation of calcined Kaolinite

Acid concentration (N)	Catalysts
0.5	NS1
1	NS2
2	NS3
3	NS4
4	NS5
5	NS6

The surface areas for the catalysts were estimated according to Sears' method[43,44]. A sample containing 0.5 g of clay was acidified with 0.1N HCl to a *p*H 3-3.5. The volume was made up to 50 mL with distilled water after addition of 10 g of NaCl. The titration was carried out with standard 0.1M NaOH in a thermostatic bath at 298±0.5 K to *p*H 4.0 and then to *p*H 9.0. The volume, V, required to raise the *p*H from 4.0 to 9.0 was noted and the surface area was computed from the following equation:

$$S\ (m^2/g) = 32V-25$$

Acidity measurements were carried out by Potentiometric titration[45], Potassium hydroxide titration method and Cation exchange capacity by the ammonium adsorption technique[46]. In potentiometric titration, the catalyst was mixed with acetonitrile and was titrated against n-butylamine taken in the burette. Using a Beckmann digital *p*H meter, electrode potential variation was recorded. To get acidity distribution curve, potential was plotted against the concentration of *n*-butylamine. In potassium hydroxide titration method, the clay was equilibrating with potassium hydroxide for 48 h at room temperature. After filtering, the amount of base determines by titrating with hydrochloric acid.

Cation exchange capacity was measured by exchanging the cation by ammonium ions. The exchanged clay was washed with alcohol and refluxed with magnesium oxide. The ammonia thus liberated was collected in saturated boric acid solution containing mixed indicator. The distillate was titrated against standard hydrochloric acid solution to determine the cation exchange capacity.

Catalytic reaction

The catalytic activity of synthesised catalyst was tested by acetylation of cyclohexanol using acetic acid. Before the experiment started, the catalyst were activated at 110°C in an oven for 2 h. The catalytic test was performed by refluxing 0.5 g of the catalyst with 0.05 molcyclohexanol and 0.15 mol glacial acetic acid for 3 h. The solid catalyst was separated by filtration. The filtrate was washed with saturated sodium bicarbonate solution in order to make it free from acid and dried over anhydrous sodium sulphate. The conversion of cyclohexanol was determined by saponification. Efficiency of the catalyst was also tested by using different alcohols.

Result and Discussion

Characterization of catalysts

XRD analysis

The structural changes that occurred in the clay mineral due to calcination and acid treatment were studied using XRD technique (Fig. 1). Calcination and acid treatment influences some changes in to the crystal structure of the clay mineral. These diffractograms also exhibit the characteristic peaks of Kaolinite (7.17 Å; 3.59 Å; 1.49 Å). When the sample was calcined at 600°C, water was lost and the characteristic peak of Kaolinite disappeared. The impurity quartz (3.34 Å; 4.28 Å; 1.81 Å) present in the initial Kaolinite are resistant to the acid attack and the corresponding peaks remain unmodified after the treatment with sulphuric acid. The XRD analysis also showed the breakdown of the crystalline structure of the acid activated metakaolins compared to the raw sample and a structural water loss that facilitated the transformation of octahedral AlO_6 into tetra and penta-coordinated Al units. The literature reports that these Al units are more reactive and susceptible than hexa-coordinated Al units that is responsible for the partial dissolution of Al^{3+} and, consequently, for the observed increase of the amorphous phase[47].

Chemical analysis

In chemical analysis, the composition of the raw clay expressed in oxides (SiO_2: 47.08%; Al_2O_3: 37.12%; Fe_2O_3: 0.86%; TiO_2: 0.70%; and Loss of ignition: 13.08) was found comparable with the reported values of standard raw samples. About 84% from the total content contains silica and alumina. So it showed that the major components for Kaolinite are silica and alumina.

Scanning electron microscopy (SEM)

The scanning electron micrograph showed the morphological features. The SEM micrograph of samples revealed the presence of large particles that have been formed by several flaky particles stacked together in the form of agglomerates.

Infrared spectroscopic studies

The IR spectra of raw and acid treated clay samples are shown in the Fig. 2. In the raw sample, the band at $3683 cm^{-1}$ corresponds to Al-OH stretching. When the clay was treated with sulphuric acid it showed some of the bands were removed or shifted and their

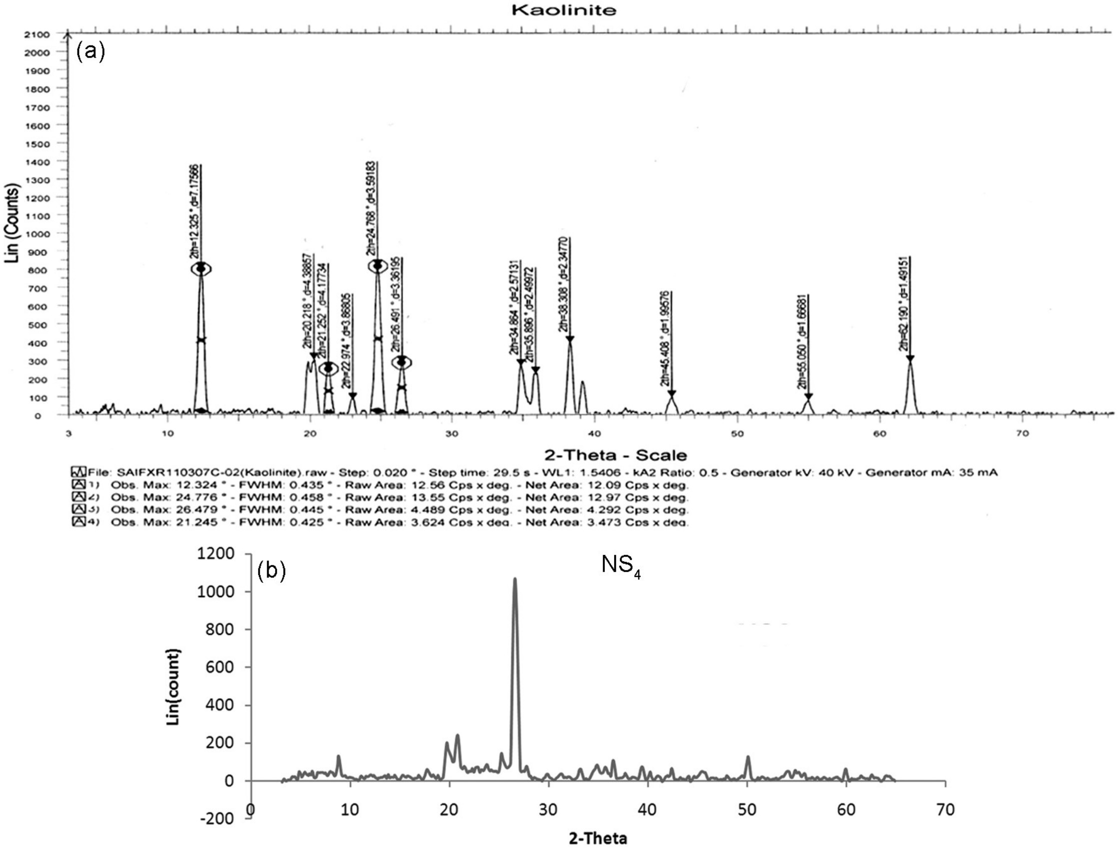

Fig. 1 — XRD pattern of (a) Raw sample and (b) NS4

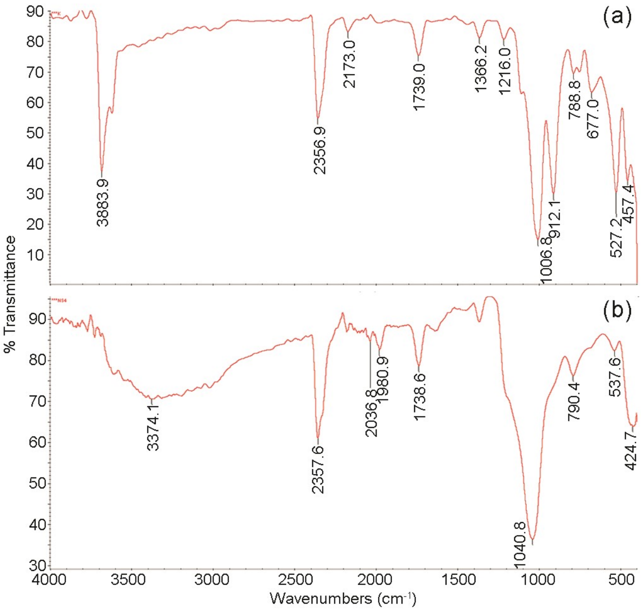

Fig. 2 — IR spectra of (a) Raw sample and (b) NS4

intensities also changed. During acid treatment of the clay, the protons from the acid medium penetrate into the clay structures attacking the OH groups, thereby causing the alteration in the adsorption bands[48]. In the bending region, the raw sample shows IR bands at 173, 912 and 788 cm^{-1}. The IR peak at 912 and 527 cm^{-1} can be due to the Al-Al-OH and Si-O-Al vibration of the clay. The absorption band of acid activated clay samples at 1040 and 790 cm^{-1} are respectively attributed to asymmetric and symmetric vibrations of Si-O-Al and Si-O-Si bonding of AlO_2 and SiO_4 tetrahedrons[49,50]. The band at 527 and 912 cm^{-1} is absent and the appearance of a new band at 790 cm^{-1}can be related to the change from octahedral coordination of Al^{3+} in kaolinite to tetrahedral coordination in metakaolinite. It can be concluded that, when the acid strength is more, the de-alumination process is facilitated rapidly, during acid treatment[51.]

TG/DTA analysis

Figure 3 represents the TG/ DTA curves of the raw and acid activated catalyst samples. The raw kaolinite sample show two well defined weight loss regions due to the loss of physisorbed water (below 100°C) and dehydroxylation of structural water (above 500°C). In the case of acid activated clay catalyst shows only a one step weight loss correlated to the endothermic peak centered below 100°C due to the dehydration of the kaolin to metakaolin. That is on acid treatment, the endotherm was shifted to lower temperature region.

Measurement of surface properties

Surface area analysis

Upon acid treatment the surface area of the catalyst samples increases from 7 to 19.8 m^2/g and are given in the Table 2. Activation of clay by acid treatment has been shown to be effective in the decomposition of the crystalline structure and in increasing the specific surface area[52]. The acid activation opens up the edges of the platelets and consequently the surface area and pore diameter increases[53]. Generally the surface area increases with increasing severity of acid treatment upto a maximum and then falls regularly. This decrease at higher concentration is due to the strong penetration of acid into the crystal structure of the individual layers, resulting in partial collapse of the clay structure[54].

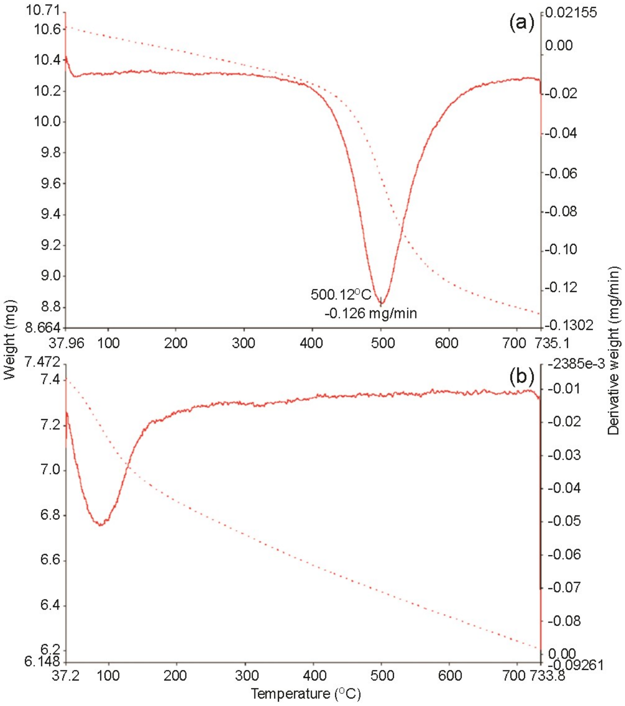

Fig. 3 — TG/DTA of (a) Raw sample and (b) NS4

Acidity measurement

Acidity of raw and acid treated samples was determined by potentiometric titration and potassium hydroxide titration method. Potentiometric titration gives relative strength and types of acid sites present in the solid acid catalyst[55]. Acidity distribution curve of raw and acid treated catalyst are given in Fig. 4. Here the initial electrode potential indicates the maximum acid strength of the surface site and the quantity of base (*n*-butyl amine) indicates the total number of acid sites present in the sample. On acid activation, both strength and number of acid sites increased. From these two acidity measurement analysis, it was found that raw sample showed low acidity than acid treated sample. From the Table 2, it was noted that, acidity of the catalyst increased up to a maximum and then decreased regularly. Maximum acidity was shown by the sample treated with 3N sulphuric acid (NS4). These results are in agreement with those obtained by Sabu *et al.*[56].

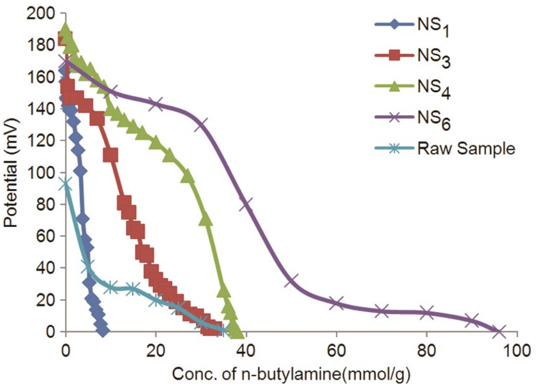

Fig. 4 — Acidity distribution curves of Raw sample, NS1, NS3, NS4 and NS6.

Table 2 — Surface area, surface acidity, CEC and catalytic activity (acetylation of cyclohexanol) of acid activated samples

Catalyst	Surface area (m2/g)	Surface acidity(mequiv/100g)	CEC (mequiv/g)	Conversion (%)
Raw sample	6	109	32	72.26
NS1	19.8	197	26	79.96
NS2	39	207	52	81.47
NS3	71.4	218	58	82.36
NS4	125	229	68	85.46
NS5	131.8	226	64	81.56
NS6	109.4	223	54	76.69

Table 3 — Catalytic activity of NS4 in the acetylation of different alcohols

Alcohol	Conversion (%)
Benzyl alcohol	77.94
Isopropanol	20.68
n-Butanol	76.47
n -Hexanol	85.81
n - Heptanol	84.92
n -Octanol	78.57
Sec–Butanol	22.13
Lauryl alcohol	29.15

Cation exchange capacity

The CEC of raw and acid activated catalyst samples showed that they increase with increase in concentration of activating acid (Table 2). Clay minerals have the property of sorbing certain anions and cations and retaining them in an exchangeable state. On acid activation, these ions are replaced by hydrogen ions. On acid treatment, the CEC of the catalyst increases and maximum CEC is shown by NS4.

Clays contain both Bronsted and Lewis acid sites with the interlamellar region and the edge sites respectively. When the clay is heated, interlamellar water is removed results in complete dehydroxylation of the aluminosilicate lattice, and the Lewis acidity increases at the expense of the Bronsted acidity[57]. The CEC of calcined clay samples is mostly contributed by the Lewis acid sites arising from structural defects, broken bonds and hydroxyl transfers[58].

Catalytic activity

Acetylation of cyclohexanol using acetic acid was selected to evaluate the catalytic activity of acid activated clay catalyst (Table 2). The analysis of the results obtained shows that the final percentage conversion of product is directly related to the severity of acid treatment, surface acidity and cation exchange capacity. The result showed that the catalytic activity increases with increase in concentration of acid treatment up to an optimum value and then decreases[59]. Acid activated sample NS4 gave the maximum activity. In this case the same sample showed the maximum acidity and cation exchange capacity.

Because of the result of the first catalytic tests, the catalyst NS4 chose to test the acetylation of different alcohols with acetic acid (Table 3). Effect of catalyst loading, reaction time on the percentage conversion and reusability of the catalyst was also checked (Table 4). This data indicates that the minimum amount of catalyst required is 0.5 g for 0.05 mol acetic acid. The reaction time for maximum conversion was 3 h.

Table 4 — Catalytic activity of NS$_4$: Catalyst loading and reaction time (acetylation of cyclohexanol)

Reaction time 3 h.		Catalyst loading 0.5 g	
Catalyst loading (g)	Conversion (%)	Reaction time (h)	Conversion (%)
0.25	63.49	1	48.29
0.50	85.46	2	76.96
0.75	62.20	3	85.46
0.10	76.23	4	75.55

Table 5 — Reusability of the catalyst NS4 (acetylation of cyclohexanol)

Cycle	Conversion (%)
One	85.46
Two	84.98
Three	84

From the result (Table 5), the catalytic activity of the regenerated catalysts showed that, no significant decrease in the catalytic activity and product selectivity of the catalyst observed.

Conclusion

Chemical analysis and XRD studies show that Kaolinite is the major component in the studied samples. Acid activation enhances the catalytic activity compared to the untreated clay mineral due to increased surface area, acidity and cation exchange capacity. All the acid activated metakaolins studied, showed catalytic activity for the acetylation of cyclohexanol using acetic acid. Among the studied catalysts, the maximum number of acid sites could be imparted when the clay sample is activated with 3N sulphuric acid. The same catalyst is also active for the acetylation of different alcohols. The result obtained in this work indicates that the solid acid catalysts prepared from modified Kaolinite are highly efficient, environmentally begin, cheaper and reusable for the acetylation of alcohols using acetic acid.

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