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Active Site Accessibility Aspect in Montmorillonite for Ketone Yield in Ester Rearrangement

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Abstract:

Removal of Al from the octahedral layer of montmorillonite by organic acid treatment results in increased microporosity generating a material with different surface features from the virgin clay. Micropores thus generated are found to be responsible for ester to ketone transformation. Various parameters of the newly generated pores such as, pore diameter, pore structure, pore volumes and acidity by pyridine-FTIR were evaluated with respect to ester to ketone formation. Best correlation was found between volume accessibility factors (VAF) and the ketone yield. The VAF reflects the extent of volume space available around the acid site for the reactant to orient in a specific way for the transformation to occur within the pore to form a specific product. This acid site accessibility aspect was further verified by extending to micropores with large VAF generated by treatment with phenoldisulfonic acid (PDSA).

Keywords: micropore, accessibility, acidity, ester rearrangement, citric acid, p-toluenesulfonic acid, phenoldisulfonic acid.

1. Introduction

Solid acid catalysts are widely used in the acylation of phenolic compounds with carboxylic acids. Phenolic esters and aromatic ketones find use in the synthesis of fragrances and pharmaceuticals[1-4]. The acylation reaction involves the formation of acylium ion by the protonation of carboxylic acid with subsequent dehydration[5]. In the industrial practice, acylation reactions are carried out using corrosive, homogenous acid catalysts, such as $FeCl_3$, $SnCl_4$, $TiCl_4$, $AlCl_3$, HF, BCl_3 and $ZnCl_2$, in stoichiometric amounts invariably generating waste products.[6-9] Efforts have also been made to use, eco-compatible, reusable, heterogenous catalysts for acylation. Heteropoly acids,[1,6] acidic zeolites,[10,11] metal oxides,[12,13] cation-exchange and acid treated clays are the most studied heterogeneous catalysts.[9,14] Activity and selectivity of these catalysts have been investigated in the direct acylation as well as rearrangement of several organic substrates such as aromatic ethers (anisole, thioanisole, veratrole, and 2-methoxy naphthalene), heterocyclic compounds (thiophene and benzofuran), phenolic compounds (phenol, p-cresol, naphthol and resorcinol) and aromatics[15-20] (toluene, biphenyl and naphthalene).

Acidic clays are promising solid acid catalysts for aromatic acylation owing to their easy modification and generation of acidity, cation exchange capacity and unique layered structure. Modification of layered clays involves interlayer cation exchange,[21-24] acid treatment,[15, 25-27] surfactant treatment and pillaring.[28-30] One of the commonly used surface modifications is treatment with mineral and organic acids to generate acid sites. Mineral acid treatment results in decrease in the cation exchange capacity and increase in surface area but severe treatment results in the removal of structural elements leading to the collapse of the layered structure. Treatment with organic acids, however, results in a layered clay material with increased surface area having altered pore structure exhibiting higher acid characteristics without much change in the cation exchange capacity.[15,25,31] It will be of interest to exploit such enhancement in the surface and acid characteristics for improving the yield of the desired products.

The aim of the present investigation is to study the role of the micropore generated by the displacement of structural Al in the organic acid treated montmorillonite on the ketone selectivity in the acylation of p-cresol with decanoic acid in solvent-less liquid phase microwave irradiation.

2. Experimental

2.1Catalyst preparation

The used montmorillonite obtained from Bhuj area, Gujarat, India supplied by Ashapura Group of Industries, India. The clay was treated with 1 M NaCl solution to convert sodium form. The composition

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was found using ICP-OES to be 42.86% SiO_2, 10.14% Al_2O_3, 6.08% Fe_2O_3, 1.69% MgO, 1.91%Na_2O, with idealized structural formula $Si_4[Al_{1.432}\ Fe_{0.416}\ Mg_{0.266}]\ O_{10}\ (OH)_2Na_{(0.318)}$.

Acid treated montmorillonite clay catalyst was prepared by treating with different acids. Typical procedure for acid treatment followed is discussed elsewhere.[15,25,27] Briefly, the method involved treatment of 10 g Montmorillonite clay with 100 ml of 1M solution of p-toluenesulfonic acid (p-TSA) and stirring the mixture at 110 ^{0}C for 30 min under the microwave irradiation, centrifuged, washed with deionized water to remove excess of acid from the clay and dried in hot air oven at 120 ^{0}C. Di-sodium salt of ethylenediaminetetraacetic acid (EDTA), citric acid (CA) and phenoldisulfonic acid (PDSA) treatment were also carried out for comparison and the resulting samples were labeled as p-TSA-clay, EDTA-clay, CA-clay and PDSA-clay. Clay samples treated with different concentration of p-TSA ranging from 0.1M, to 0.5M p-TSA were prepared and named as 0.1p-TSA-clay, 0.3p-TSA-clay and 0.5p-TSA-clay.

For the preparation of ion-exchange clay with Al, reported procedure was followed.[21-24]. The procedure involved stirring 10 g clay with 100 ml 1M aluminium chloride for 24 hours, then centrifuged and washed with distilled water to remove the chloride ions. The sample was dried at 120 ^{0}C for 5 hours in hot air oven, then ground and labelled as Al-clay. The catalytic activities of all the prepared catalyst samples were evaluated for acylation followed by rearrangement.

2.2 Characterization

The prepared catalysts were characterized using pyridine-FTIR, XRD, TEM and BET surface area. Acidity was measured by FTIR spectroscopy using pyridine as probe molecule. All the samples were activated by degassing at 110 ^{0}C for 2 h and then saturated with pyridine. The catalyst samples were then evacuated at 120 ^{0}C for 1 h to remove physisorbed pyridine. The amount of pyridine adsorbed on the acid sites of the clay samples was determined gravimetrically which was taken as a measure of the total acidity. FTIR spectra of the samples were then recorded in the range 1400–1600 cm^{-1} using IRAffinity-1 spectrometer having resolution of 4 cm^{-1} with 40 scans.[15-17] The Brønsted and Lewis acidity were quantified based on the peak areas of the two sites with respect to the total acidity. The acidity was

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expressed in micromole per gram of clay. The molar extinction coefficient of the pyridine adsorbed on the acid sites was found to be 5.8 x 10^4 kg mol^{-1} cm^{-1}.

Surface area and porosity measurements were carried out using Quanta chrome Nova-1000 surface analyzer under liquid nitrogen temperature. N_2 adsorption-desorption isotherm measurements were done in order to study the evolution of porosity and textural properties of the acid treated and ion-exchange clay samples. Full adsorption-desorption cycles were determined up to the saturation vapor pressure of nitrogen at -196 ^{0}C. Pore size distribution was calculated from adsorption data using BJH and deBoer t-method.[26,32, 33, 34]

Structural integrity of the catalyst samples was checked by powder XRD. The data were recorded by step scanning at $2\theta = 0.020^0$ per second from 3^0 to 80^0 on PANalytical X'Pert PRO MPD X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.15406 nm).

Morphology of montmorillonite before and after PDSA modification was recorded using Tecnai-G2 Transmission Electron Microscope (TEM) under 120KV, transmission mode.

The amount of interlayer aluminium in different acid treated clay samples was estimated by the method reported elsewhere.[35] It involved treatment of 2 g of clay sample with 0.1M HCl for 60 min at 60 ^{0}C. After treatment, the mixture was centrifuged and the solid was repeatedly washed with deionized water. Al was estimated in the centrifugate by aluminon reagent method spectrophotometrically using Chemito UV-2100 Spectrophotometer.[25, 36]

2.3 Catalytic activity tests

The activity of catalysts was studied under microwave irradiation, using microwave lab station "START-S" model from Milestone, Italy, having software which enables the control of reaction mixture and temperature with aid of infrared sensor by regulation of microwave power output in such a way that the reaction mixture was exactly in line with infrared sensor that monitors the temperature. Variable power up to 1200 W was applied by microprocessor-controlled single-magnetron system.

Ten mmol of p-cresol (PC) and five mmol of decanoic acid (DA) were mixed with 1 g catalyst in a microwave reactor vessel with magnetic stirring bar. Reactor vessel was kept in microwave reactor and an

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initial power of 1200 W was applied for 1 minute to attain the reaction temperature of 190 ^{0}C. The reaction temperature was then maintained for 59 minutes to get maximum conversion. The mixture was then cooled for 10 minutes, and the mixture of reactants and products was extracted by stirring with 10 mL of toluene for 30 minutes and filtered to remove the catalyst. The reaction mixture was analyzed using Chemito GC-1000 gas chromatograph with TR-Wax capillary column of length 30 m, 0.32 mm thickness and 0.55 µm internal diameter with flame ionization detector. The ester product, p-cresyldecanoate (O-acylation) and the ketone product 1-(2-hydroxy-5-methylphenyl) decan-1-one (C-acylation) were analyzed using n-heptane as internal standard.The products were also confirmed by GC-MS analysis.[15,26] Catalytic activity, measurement of acidity and surface characteristics were performed three times on each sample and the mean of the measurements were used for calculating the standard deviation (< ±2.3).

3. Results and discussion

3.1 Acylation with ion-exchange and acid treated montmorillonite clay catalyst samples

Acylation involves formation of ester in the initial stages. The ester formed subsequently undergoes transformation into ketone through rearrangement as shown in scheme 1. Under the experimental conditions, interphase and intraparticle heat and mass transfer as calculated using Koros-Novak, Mears and Weisz- Prater criteria were negligible.[37, 38] The Al-clay and the acid treated clays showed different behavior in the formation of products. These are discussed below.

Al-exchange clay: Under optimized reaction conditions, acylation reaction was carried out with Al-clay and the per cent conversion of DA and yields of ester and ketone were recorded. While untreated clay was ineffective, the conversion of DA in presence of Al-clay was found to be quite high (68%). It was observed that the ester (62%) was the major product accompanied by small amounts of ketone (6%), the latter formed due to subsequent rearrangement of the former.

Al-clay had a CEC 0.83 meq/g, surface area 28-32 m^2/g, average pore diameter (50.27 Ǻ) and micropore volume (0.011 cm^3/g). These surface features were not different from the untreated clay, but the acidity was very much higher than the untreated clay, 150 µmol/g as measured by pyridine-FT-IR method.[15,21,22] Ion-exchange clays are known to accelerate the rate of acid-catalyzed reactions through their Brønsted

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acid sites present in the form of polarized hydrated cations on the edge sites. In the same way, the conversion of DA is also catalyzed by the polarized water molecules of the hydrated Al cations. Although high amounts of ester were formed, the Al-clay was not effective in bringing about the ester's conversion to ketone through rearrangement, both reactions being known to be catalyzed by acid catalysts. Ketone formation is not assisted by the mesopores is clearly seen in the case of Al-clay as shown by its BJH curve (Fig.1). Apparently, rearrangement of the ester to ketone is not facilitated by the mesopores.

Organic acid treated clays: The picture, however, is different in the presence of acid treated clay catalysts. Organic acid treated clays, unlike Al-exchange clay, showed more amount of ketone formation resulting from the rearrangement of the ester. In order to understand the formation of ketone, it was necessary to look at the surface characteristics and acidity after acid treatment. Acid treatment of montmorillonite clay brings about many types of changes in (i) surface area (ii) pore size and pore volume (iii) CEC and (iv) acidity. It is reported that organic acids and chelating agents remove the structural Fe, Al and Mg from the octahedral layer of the untreated (Na-) clay resulting in micropores on the clay surface enhancing its surface area. The structural elements that get dislodged forming complex species hydrolyze, on subsequent washing, releasing a part of the cations into the interlayer. The hydrated Al and Fe ions, which displace the sodium ions in the interlayer, act as Brønsted acid sites thus enhancing the acidity.[25] Removal of structural elements would create voids in the structure resulting in increase in porosity, pore volume and surface area. It is known that when structural aluminium is removed, there is no reduction in CEC while the removal of isomorphously replaced Fe and Mg causes a reduction in CEC. Tables1 and 2 give the structural elements and their amounts removed from the clay samples along with the increase in surface area and pore volume after the acid treatment. It can be seen from Table 2, that p-TSA and PDSA remove more Al, but very little structural Fe and Mg than CA and EDTA. Hence the CECs of the former two treated clays were not very much different (0.70-0.72) from the untreated clay (0.83). Among the acids used for treatment, PDSA removed more structural Al (1.04 meq/g) generating more porous regions and higher amounts of interlayer Al than the other acids. On the other hand, CA and

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EDTA removed more Fe and Mg than Al resulting in a considerable reduction in CEC (≈0.2 to 0.4). As a result, the interlayer Al was much less and proportionate to the reduced CEC in these two treated clays. CA however removed relatively a large quantity of Fe resulting in a clay material with high surface area (156 m^2/g) and micropore volume (0.031 cm^3/g) but having a low CEC value (0.42 meq/g) and consequently low interlayer Al. Most of the Al that is removed has migrated to the interlayer in CA-clay. Among the acids used, EDTA was able to remove the least amount of structural elements. In this case almost all the Al removed has migrated to the interlayer resulting in a material having relatively low surface area and pore volume.

Table 2 shows the CEC calculated based on the loss of structural Fe and Mg. CEC, as calculated based on the total amount of Fe and Mg leached out, was in agreement with the experimentally determined CEC values within experimental errors.

Decrease in average pore diameter on acid treatment clearly shows the formation of micropores on the surface (Table1). This could also be seen in Figs.1 and 2, where the nitrogen adsorption-desorption isotherms and BJH plots show the pore size distribution curves of the acid treated clays. TEM images in fig.3 show surface morphology of the clay before and after the PDSA treatment.

The acidity of clays was dependent on the interlayer Al after the acid treatment. It was almost the same for the p-TSA and PDSA treated clays with similar interlayer Al which was around 0.70 meq/g, but the CA-clay and EDTA-clay showed much less interlayer Al (0.36 meq/g and 0.22 meq/g respectively). Consequently the acidity values of the latter two clays were low (Table 3).

In order to study the effect of generated porosity and enhanced acidity on the catalytic activity, the acylation reaction studies were considered with different acid treated clay catalysts that is, PDSA-clay, CA-clay, p-TSA-clay and EDTA-clay. Fig.4 summarizes the DA conversion which increases from EDTA-clay to p-TSA-clay catalyst. Clay catalysts treated with different concentration of p-TSA showed increased surface area, interlayer Al and decreased average pore diameter.[25] In addition, the present study showed an increased micropore volume, mesopore volume and pyridine FT-IR acidityas the concentration of p-TSA used for treatment was increased from 0.1 to 0.5 M (Table 3).

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Among the three treated clays, DA conversion (Fig.4) was found to increase in the order EDTA-clay<CA-clay< p-TSA-clay though the formation of ketone which follows the ester rearrangement indicated variation in its yield. p-TSA-clay showed higher ketone yield (32%) than the other two (EDTA-clay 4% ; CA-clay 14%). Variation in the ester rearrangement to form ketone may be attributed to higher acidity and the generated porosity of the acid treated clay catalyst samples.

3.2 Role of porosity and acidity in ester rearrangement.

In order to understand the role of acidity and porosity in the ester rearrangement to form ketone, a sample of the prepared phenolic ester mixed with different modified clay catalyst samples was separately subjected to microwave irradiation. The results in Table 3 show that p-TSA-clay was more effective in ester conversion into ketone. The rearrangement of the ester into ketone on the surface of the catalysts was apparently influenced by the pores and the acidity of the catalyst samples. This is based on the fact that (i) ketone formation was accelerated only after the formation of pores (shown by the increased pore volumes) due to acid treatment and (ii) that the ketone formation requires acid sites. This is substantiated by the results in Table 3. Al-clay, having almost the same acidity as p-TSA-clay with relatively small pore volume showed less conversion. On the other hand, CA-clay showing a high pore volume, but having low acidity, yielded less ketone than p-TSA-clay, the latter having both high acidity and pore volume. The results show clearly that rearrangement of the ester to ketone is the resultant of both pore volume and acidity. Apparently, the newly generated pores facilitate the orientation of the ester molecules in such a fashion to access the acid sites thus accelerating the conversion to ketone. This is supported by the average turnover frequency (TOF) for ketone (Table 3).

3.3 Volume Accessibility Factor (VAF):

Correlation factor (r) was calculated between the amounts of ketone formed, pore volumes and the different types of acidities for the Al-clay and acid treated clays. The results are given in Table 3.The objective was to evaluate the role played by the different types of acidities, Brønsted (B) at 1550 cm^{-1} and Lewis (L) at 1445 cm^{-1}(fig 5), the combination of the acidities and also the mesopore and micropore

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volumes. This would throw light on the mechanism of the orientation of the ester molecule to form ketone within the pore.

The results in table 3, 4 and 5 reveal very poor correlation between the different types of acidities and pore volumes with the amount of ketone formed, clearly showing that neither the micropore and mesopore volumes, nor the acidity, when individually considered facilitate the ketone formation. Among the correlations, best correlation (r= 0.77) was shown by micropore volume and a poor correlation (r=0.32) was shown by mesopore volume. Since, micropores alone cannot bring about the rearrangement, possibly a combination of micropore and acidities are involved in the process. A factor called Volume Accessibility Factor (VAF), therefore, was obtained by multiplying the micropore volume with the different types of acidities. VAF was correlated with the amounts of ketone formed for all the clay catalyst samples which developed pores upon acid treatment and also with Al-clay which had negligible micropores.

To further establish the relation between the ketone yield and VAF, the ketone yield was measured under different conditions of temperature, reaction time and catalyst amount (shown by R1, R2 and R3 in Table 6). The purpose was to find the relation between VAF and the formation of ketone under different conditions. 10 mmol of the ester (p-cresyldecanoate) was irradiated with MW radiations for 30 min at 160 ^{0}C with 0.5 g of the catalyst (R1), 0.5 g catalyst for 60 min at 190 ^{0}C (R2) and with 1 g of the catalyst for 30 min at 190 ^{0}C (R3). The yield of ketone was measured and found to increase with the temperature, reaction time and the amount of catalyst. Table 6 shows the correlation between VAF, product of micropore volume and Brønsted (B), Lewis (L) and (B+L) with the ketone yield. $VAF_{(B+L)}$ calculated by multiplying microporosity with combination of Brønsted and Lewis acidities (B+L) showed a better correlation with the yield of ketone for all the sets of experiments conducted at different reaction conditions. This clearly suggests involvement of both the Brønsted and Lewis acid sites. There are several reports on the ester to ketone transformation catalyzed by both Brønsted and Lewis acid sites [39, 40]. In the present study the ester to ketone transformation involves acid sites which are made accessible through micropores. Based on this, a mechanism, as shown in scheme 2 is proposed involving both the Lewis and

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Brønsted acid sites. The micropores apparently make way for the ester molecules to rearrange to ketone where in the ester is coordinately bonded either to the Lewis acid sites or get protonated at the Brønsted sites. Thus the pores formed due to dealumination provide access for the ester molecules to reorient within the pore facilitating the rearrangement process to form ketone. Access to both Lewis and Brønsted acid sites are scarcely available on the surface of the clay, as for instance on Al-exchange clay which explains its low effectiveness in the ketone formation when compared with the dealuminated clays with more pores. XRD patterns of the clays after the reaction did not show any change in the d(001) reflection indicating no layer swelling and therefore no intercalation of reactant or product molecules into the interlayer.Thus, volume accessibility factor, VAF of micropore provides a parameter to interpret the mechanism of reactions that take place within the pores which possibly could find application in micropore acid-base catalyzed reactions.

The role of mesopores in the formation of ketone is of less consequence is shown by the poor correlations of the VAFs obtained by multiplying mesopore volumes with acidities (Table 5). This can be clearly seen in the case of Al-clay which shows the least ester transformation to ketone which could be attributed to higher proportion of mesopores that do not facilitate the accessibility to acid sites. Thus the acid site accessibility and the number of acid sites apparently determine the transformation which indicates that a linear increase in the two favours the transformation till thermodynamic equilibrium of the reaction is attained, whereas in cases where one of the parameters is high and the other is low, the lower parameter limits the transformation of the ester to ketone.This suggests a limiting range of a relation linking the acid sites and their accessibility for the rearrangement of the ester.

Limiting factor: Large micropore volumes (0.203 cm^3/g) for PDSA-clay upon treatment with PDSA, showed a moderate increase in the ketone formation (Table 7). Apparently, the ketone formed reaches a maximum value, determined by the acidity factor, irrespective of the pore volume. This could be mathematically presented as

$$y = \begin{cases} k \times VAF, & 0 < v < v(\max)\ and\ 0 < z < z(max) \\ k \times VAF(max), & v \geq v(\max)\ and\ z \geq z(\max) \end{cases}$$

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Where, y = percent product formed, VAF = maximum pore volume v × acidity z , z(max) = maximum acidity and k is a proportionality constant characteristic of the catalyst.

Conclusion:

In the present study, there is evidence for the micropore to accelerate the ester rearrangement to form ketone. Favorable factors such as accessibility to the acid sites and number of acid sites facilitate the ester to reorient it to transform to ketone. A new term called volume accessibility factor, VAF which is the product of micropore volume and different types of acidities showed improved correlations with the amount of ketone formed. Experimental results suggest that volume accessibility factor may possibly be used to throw light on the organic transformations occurring exclusively in porous catalysts.

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Figures:

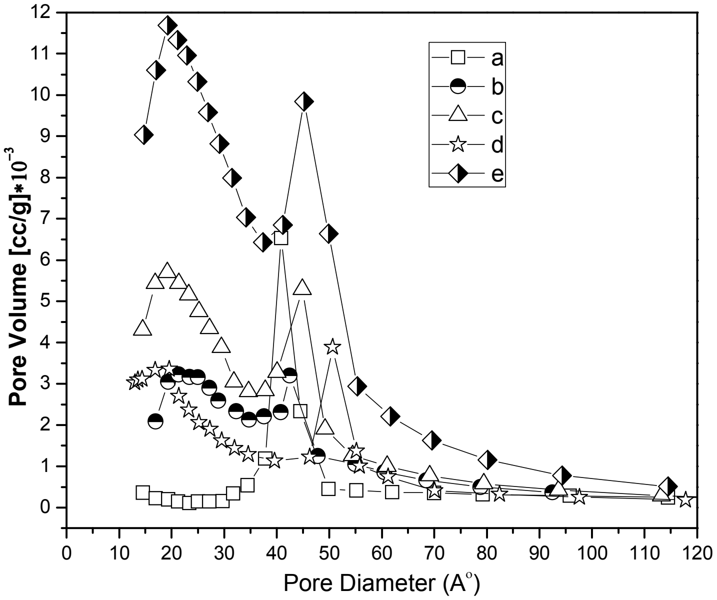

Fig.1 BJH plots of (a) Al-clay (b) EDTA-clay (c) CA-clay (d) p-TSA-clay and (e) PDSA-clay catalysts.

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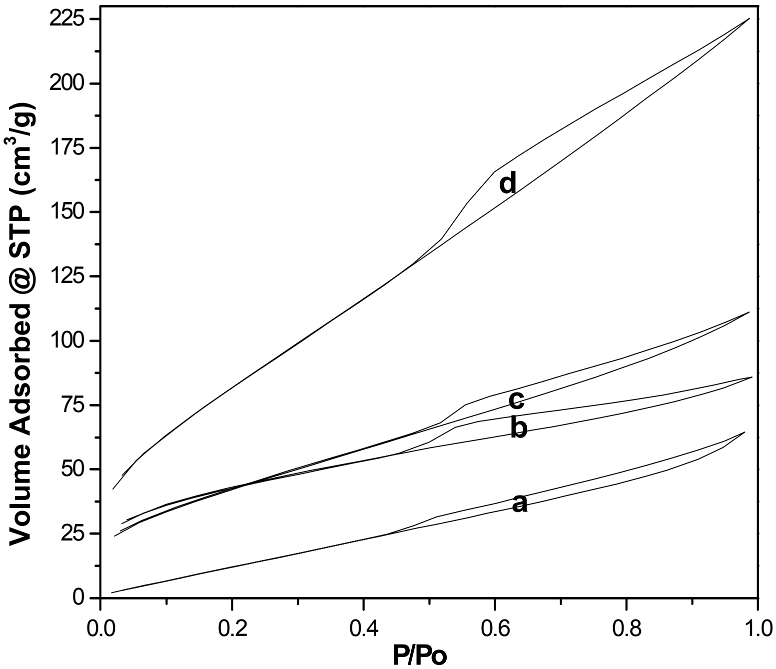

Fig.2BET N_2 adsorption isotherm plots of (a) EDTA-clay (b) p-TSA-clay (c) CA-clay and (d) PDSA-clay catalysts

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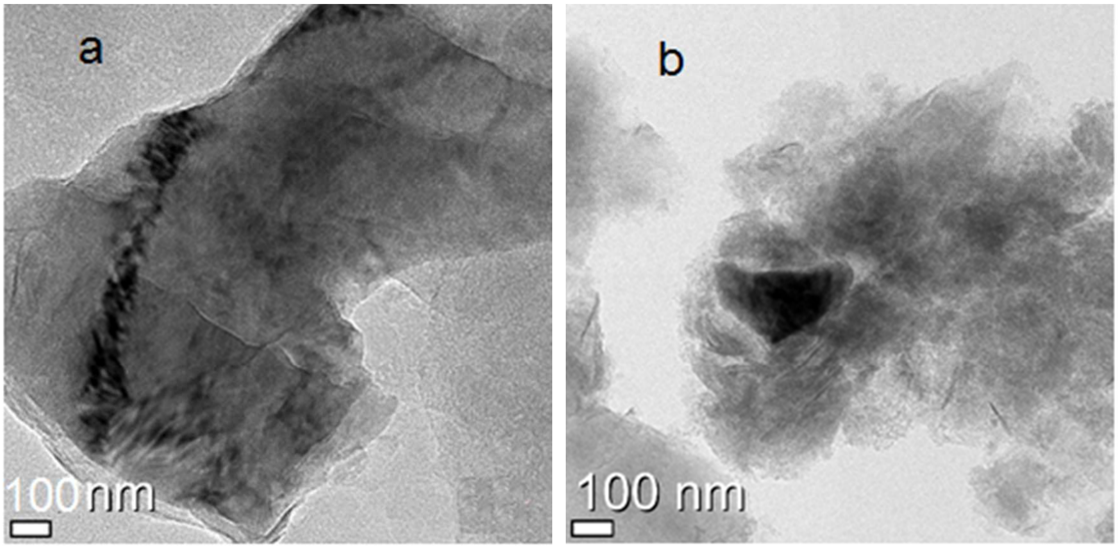

Fig.3 TEM images of montmorillonite clay (a) before treatment (b) after treatment with PDSA

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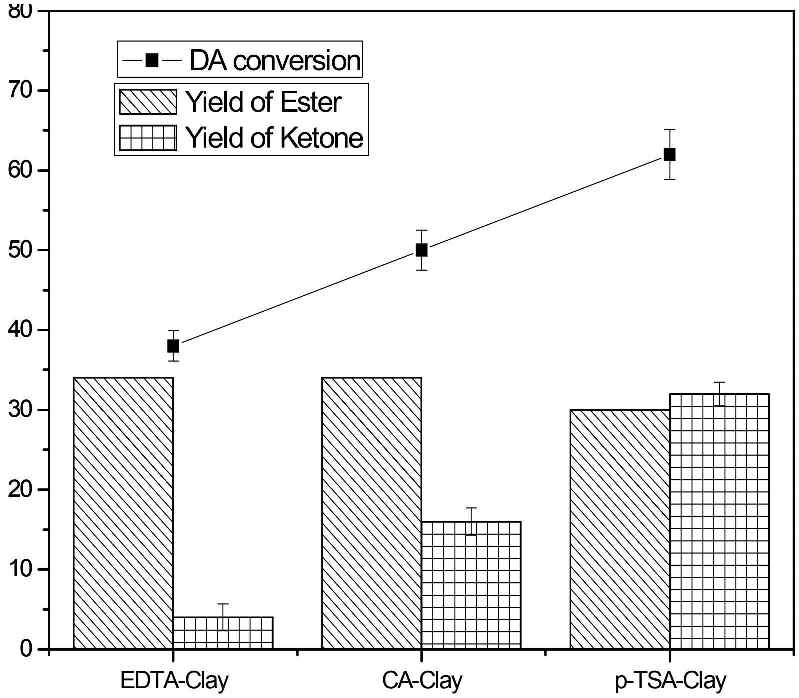

Fig.4 Effect of different acid treated montmorillonite clay catalyst on the acylation of PC with DA. Reaction condition: mole ratio PC: DA, 2:1; reaction time, 60 min; temperature 190^{0}C; catalyst amount, 1 g.

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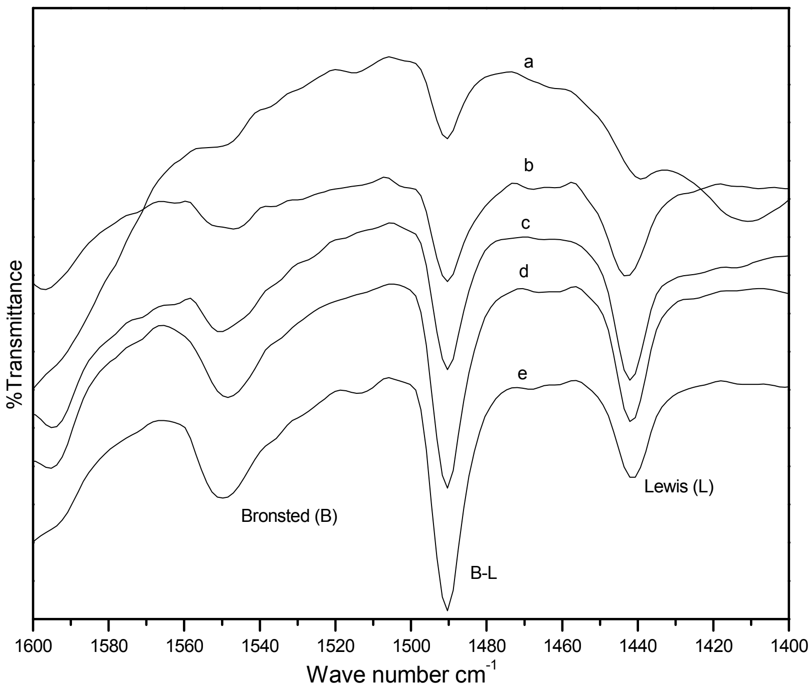

Fig.5 Pyridine FT-IR acidity plots of (a) EDTA-clay (b) CA-clay (c) p-TSA-clay (d) PDSA-clay and (e) Al-clay montmorillonite clays.

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Tables

Table.1 CEC, surface area, average pore diameter and micropore volume of different acid treated clays.

Acid treated clay samples	**CEC (meq/g)**	**Surface area (m^2/g)**	**Average Pore diameter (Å)**	**Micropore volume (cm^3/g)**	**Mesopore volume (cm^3/g)**
Untreated	0.83	28	50.3	0.011	0.067
EDTA-clay	0.64	80	46.9	0.017	0.073
CA-clay	0.42	156	32.2	0.031	0.159
p-TSA-clay	0.72	135	35.3	0.026	0.094
PDSA-clay	0.71	276	24.0	0.203	0.140

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Table.2 CEC, Interlayer Aluminium and ICP elemental analysis of untreated and Acid treated clay samples

Elements	**Unteated clay (Wt%)**	**Amount of elements removed by acid treatment (meq/g)**			
		EDTA-clay	**CA-clay**	**p-TSA-clay**	**PDSA-clay**
Al	10.14(Al_2O_3)	0.235	0.463	0.97	1.04
Fe	6.08 (Fe_2O_3)	0.046	0.242	0.044	0.058
Mg	1.69 (MgO)	0.103	0.187	0.022	0.044
CEC (calculated) (meq/g)	0.83	0.68	0.404	0.760	0.720
CEC (experimental) (meq/g)	0.83	0.64	0.42	0.72	0.71
Interlayer Al, (meq/g)	-	0.22	0.36	0.70	0.71

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Table.3 Correlation between amounts of ketone formed, micropore volume and acidity factors for ester rearrangement.

Catalysts	**Micropore volume (cm^3/g)**	**Ketone yield (%)**	**Pyridine FT-IR acidity (μmol/g)**			**Average TOF(min^{-1})**
			B	**L**	**B+L**	
Al-clay	0.011	6	74	70	144	0.04
EDTA-clay	0.017	10	12.2	20.8	33	0.32
CA-clay	0.031	22	18.02	66	84.02	0.47
p-TSA-clay	0.026	32	70	68	138	0.58
0.1p-TSA-clay	0.015	15	30	26	56	0.29
0.3p-TSA-clay	0.019	21	49	44	93	0.24
0.5p-TSA-clay	0.024	30	67	63	130	0.55
Correlation factor, r	0.77	-	0.31	0.41	0.39	-

r = correlation factor between yield of ketone and other factors
TOFs were calculated for yield of ketone with B+L Pyridine FT-IR acidity
Reaction conditions; 10mmol of p-cresyldecanoate; reaction time, 30 min; temperature 190^0C; catalyst amount, 0.5 g.

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Table.4 Correlation between amounts of ketone formed with micropore volume and volume accessibility factor.

Catalysts	**Micropore volume (cm^3/g)**	**Ketone yield (%)**	**Volume Accessibility Factor (VAF)**		
			Pyridine FT-IR acidity		
			B	**L**	**B+L**
Al-clay	0.011	6	0.81	0.77	1.58
EDTA-clay	0.017	10	0.21	0.35	0.56
CA-clay	0.031	22	0.56	2.05	2.61
p-TSA-clay	0.026	32	1.82	1.77	3.59
0.1p-TSA-clay	0.015	15	0.45	0.39	0.84
0.3p-TSA-clay	0.019	21	0.93	0.84	1.77
0.5p-TSA-clay	0.024	30	1.61	1.51	3.12
Correlation factor, r	0.77		0.79	0.74	0.86

Reaction conditions; 10mmol of p-cresyldecanoate (ester); reaction time, 30 min; temperature,190^0C; catalyst amount, 0.5 g.
*r = Correlation factor between ketone formed and VAF
*VAF = (micropore volume × acidity, (eg. for Al-clay, VAF-B = 0.011 x 74 = 0.81)

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Table.5 Correlation between amounts of ketone formed with mesopore volume, total pore volume and volume accessibility factor of mesopore volume.

Catalysts	**Ketone yield (%)**	**Mesopore volume (cm^3/g)**	**Total pore volume (cm^3/g)**	**Volume Accessibility Factor (VAF)**		
				FT-IR Acidity × mesopore volume		
				B	**L**	**B+L**
Al-clay	6	0.067	0.078	4.95	4.69	9.65
EDTA-clay	10	0.073	0.090	0.88	1.52	2.41
CA-clay	22	0.159	0.190	2.86	10.49	13.36
p-TSA-clay	32	0.094	0.120	6.58	6.39	12.97
0.1p-TSA-clay	15	0.068	0.083	2.04	1.77	3.81
0.3p-TSA-clay	21	0.074	0.093	3.63	3.26	6.88
0.5p-TSA-clay	30	0.076	0.100	4.79	4.33	9.88
Correlation factor, r		0.32	0.41	0.57	0.43	0.57

Reaction conditions; 10mmol of p-cresyldecanoate (ester); reaction time, 30 min; temperature,190^{0}C; catalyst amount, 0.5 g.

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Table.6 Correlation between volume accessibility factor (VAF) and yield of ketone from ester rearrangement reaction at different reaction conditions.

Catalyst	**Ketone yield (%)**			**VAF**		
				Pyridine FT-IR Acidity		
	R1	**R2**	**R3**	**B**	**L**	**B+L**
Al-clay	4	11	9	0.81	0.77	1.58
EDTA-clay	8	19	16	0.21	0.35	0.56
CA-clay	16	36	28	0.56	2.04	2.60
0.1p-TSA-clay	10	24	19	0.45	0.39	0.84
0.3p-TSA-clay	14	31	24	0.93	0.84	1.77
0.5p-TSA-clay	25	44	39	1.61	1.51	3.12
p-TSA-clay	27	46	41	1.82	1.77	3.59
Correlation factor, r(R1)	-	-	-	0.83	0.74	0.88
r(R2)	-	-	-	0.74	0.77	0.85
r(R3)	-	-	-	0.79	0.74	0.86

*VAF = FTIR acidity x micropore volume

Reaction conditions:

R1: 10 mmol of p-cresyldecanoate (ester) reaction time 30 min, temperature 160 ^{0}C, catalyst amount 0.5 g
R2: 10 mmol of p-cresyldecanoate (ester) reaction time 60 min, temperature 190 ^{0}C, catalyst amount 0.5 g
R3: 10 mmol of p-cresyldecanoate (ester) reaction time 30 min, temperature 190 ^{0}C, catalyst amount 1 g

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Table.7 Amount of ketone formed, acidity and average TOF for PDSA-clay catalyzed ester rearrangement.

Catalyst	**Micropore volume (cm^3/g)**	**Total acidity (µmol/g)**	**Brønsted acidity (µmol/g)**	**Lewis acidity (µmol/g)**	**Ketone yield (%)**	**Average TOF (min^{-1})**
PDSA-clay	0.203	140	72	68	48	0.76

Reaction conditions; 10mmol of p-cresyldecanoate; reaction time, 30 min; temperature 190^0C; catalyst amount, 0.5 g.

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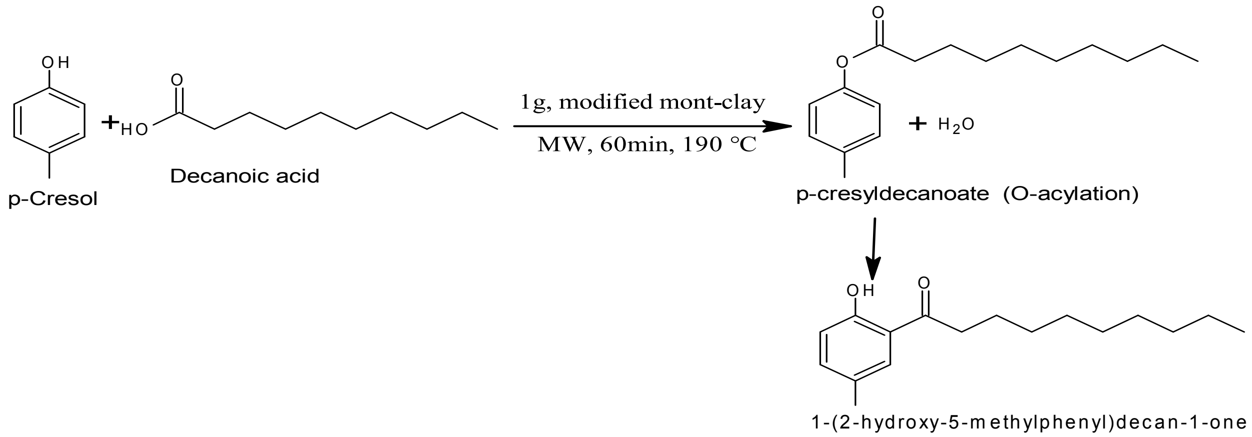
Schemes



Scheme 1: reaction carried out using modified clay catalysts samples.

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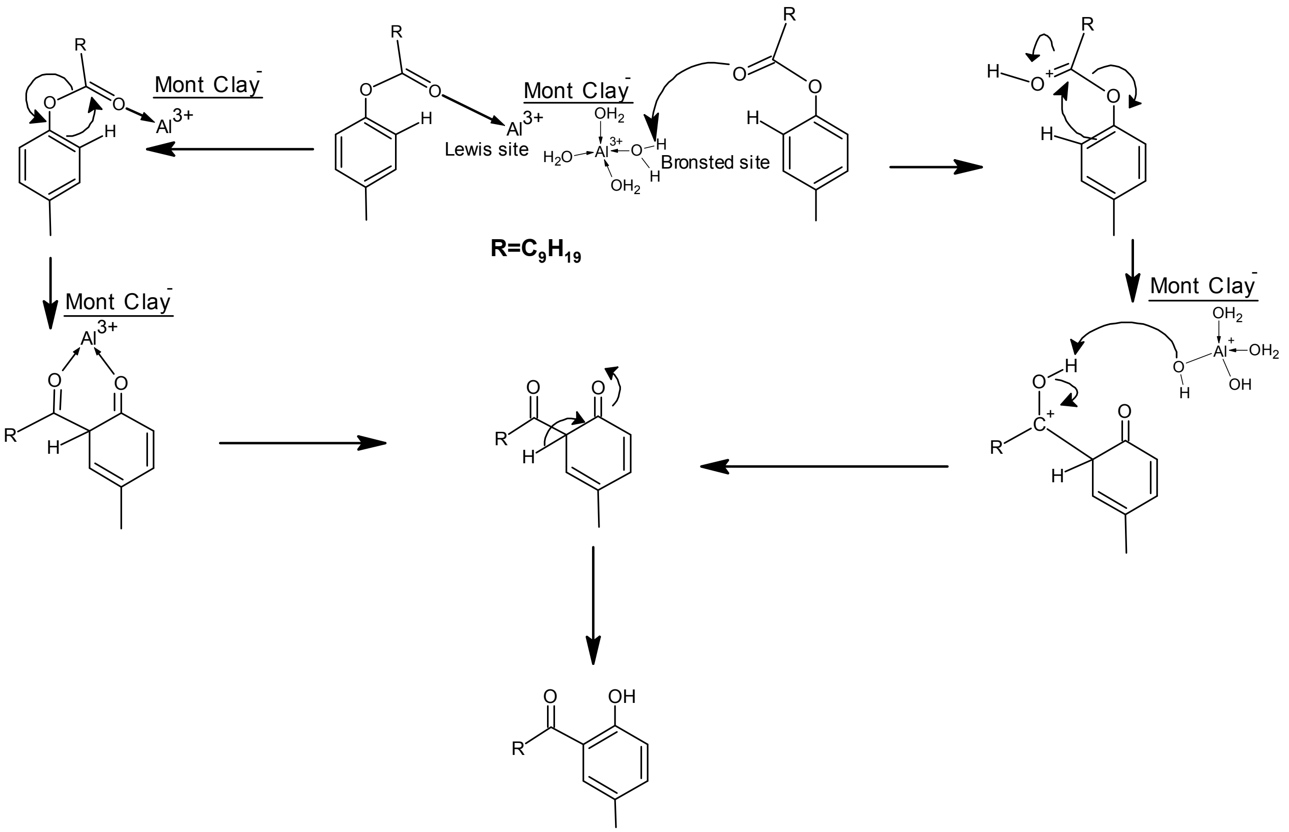

Scheme 2: Possible reaction mechanism for the rearrangement catalyzed by both Brønsted and Lewis acid sites.

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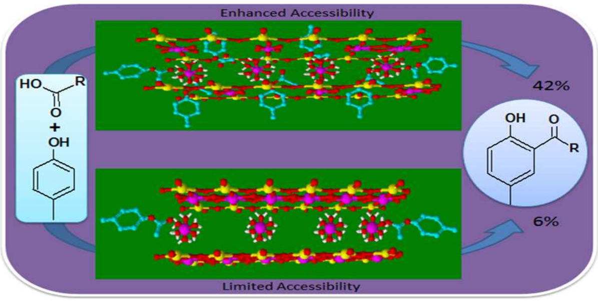
Abstract Graphics:



A new term Volume Accessibility Factor (VAF), product of micropore volume and acidity correlates with ketone formation in modified montmorillonite.