

Catalyst Preparation, Characterization and Catalytic Activity of Kaolinite Clay from Nileswar, Kerala

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Abstract

A new economically and environmentally benign clay catalyst for benzylation of benzene with benzyl chloride has been prepared from thermally calcined Kaolinite, that was activated with different concentration of sulphuric acid. The activated samples were characterized by acidity measurements, XRD, SEM, FTIR, TG/DTA and surface area measurement. The sample activated with 3N sulphuric acid showed maximum acidity and maximum activity. The activity of this catalyst was enhanced by metal chloride supporting using FeCl₃, ZnCl₃, MnCl₃, CoCl₃ and SnCl₃. The activity also monitored by using different solvents

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

INTRODUCTION

The replacement of homogeneous catalyst with heterogeneous catalyst is very essential for the development of clean environment. The use of eco-friendly solid acid catalysts cause only reduced pollution and waste disposal problems compared to their toxic and corrosive counter parts. In this point of view, the study on clay based eco-friendly catalysts become the need of the day. Clay catalysts are less expensive, reusable, and non-corrosive and have no disposal problems. Catalytic activity of clay minerals from Kerala is less studied. Even though Kerala has a vast deposit of clay minerals there are only few reports on their catalytic activity.

The crystal structure of clay minerals was first proposed by Pauling [1] and the validity of his model was confirmed by the powder X-ray diffraction technique [2]. Clays are naturally occurring layered silicates. They are essentially crystalline materials of very fine particle size, catalyst supports, ion exchangers and adsorbents [3]. Clay catalysts are interesting materials, not only for the low cost of the raw material [4] but also for their lack of harmful effects on the environment [5]. Clay catalysts have been shown to contain both Brønsted and Lewis acid sites [6, 7] with the Brønsted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites. The acidity of ion exchanged clays is very much influenced by the quantity of water between the sheets.

A catalyst does not initiate the reaction; it merely accelerates the rate of a reaction which is thermodynamically feasible. A number of reactions that are catalyzed by acids and bases in solutions can also be catalyzed by solids having acidic and basic properties. Solid acid catalysts usually employed are mixed oxides, zeolites and clays. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Brønsted and Lewis acidity, etc., have made the clays excellent materials for adsorption [8]. 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 [9] with the basic unit consisting of a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{+3} as the octahedral cation.

One of the most common chemical modifications of clays, used for both industrial and scientific purposes is their acid activation. The so-called acid activation, used as a chemical treatment to improve the surface area and catalytic properties of clays [10-14], consists of the leaching of the natural clays with inorganic acid. The result is an increase of the surface area, porosity, and of the number of the acid sites with respect to the parent clays, depending on the intensity of the treatment

Acid activated bentonites were among the earliest known solid acid catalysts. Natural clays such as Kaolinite and Montmorillonite are increasingly used as catalyst or catalyst support in many organic reactions. Extremely efficient solid catalysts of remarkable acidic properties can be produced by the activation of metakaolinite with H_2SO_4 , HNO_3 and HClO_4 [15]. Metakaolinites were also prepared by calcination of natural kaolinites at 600–9000°C and are more reactive than the parent kaolinite after acid activation. 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 [16]. Sabu et al. studied the acidic properties and catalytic properties of acid treated natural Kaolinite clays containing transition metals in their lattice [17].

Friedel–Crafts alkylations, which are usually catalyzed by Lewis acids in the liquid phase, constitute a very important class of reactions which are of common use in organic chemistry [18]. Among these reactions, the alkylation of benzene by benzyl

chloride or alcohol is interesting for the preparation of substitutes of polychlorobenzenes used as dielectrics. This reaction is presently catalyzed in the homogeneous phase at the industrial scale by FeCl_3 [19]. The substitution of liquid acid catalysts in the case of the Friedel–Crafts alkylation is an important challenge that is on the way to being successful. Indeed, several solid acid catalysts have already been proposed which are efficient catalysts such as: Fe-modified ZSM-5 and H-zeolites; Fe_2O_3 or FeCl_3 deposited on micro-, meso and macro-porous [20]; Fe-containing mesoporous molecular sieves materials [21,22]; Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts [23]; Ga and Mg-oxides and chlorides derived from Ga–Mg-hydrotalcite [24]; Ga-SBA-15 [25]; Ga-HMS [26]; InCl_3 , GaCl_3 , FeCl_3 and ZnCl_2 supported on clays and Si-MCM-41 [27]; supported thallium oxide catalysts [28]; clayzic [29]; solid superacids based on sulfated ZrO_2 [30]; H-ZSM-5 [31] and FeCl_3 , MnCl_2 , CoCl_2 , NiCl_2 , CuCl_2 , ZnCl_2 supported on acidic alumina [32] for the benzylation of benzene and other aromatic compounds. The use of eco-friendly acid catalysts for benzylation under mild conditions is of great industrial significance. Solid acids are the most widely studied of supported reagents. The emergence of zinc chloride supported on acid treated montmorillonite (K 10), ‘Clayzic’ was a definite breakthrough in the search for environmentally friendly Friedel Crafts catalysts [33]. Initial screening of various metal reagents supported on acid treated montmorillonite revealed that while most reagents reduced the already low activity of acid treated clay, supported CuCl_2 , NiCl_2 and ZnCl_2 give a definite enhancement in activity. Impregnation of metal chlorides onto natural kaolinite and its modified forms results in efficient Friedel Crafts alkylation catalysts [34].

So the objective of this work is to study the preparation and characterization of acid treated Kaolinite clay collected from Nileswaram, Kerala and their utilization as catalysts for the benzylation of benzene with benzyl chloride

METHODS AND MATERIALS

Materials

Clay sample used for the present study was collected from Kerala Clays and Ceramic Products Ltd. Pappinisseri, Kannur, Kerala. The clay was mined from Nileswar, Kasaragod district, Kerala and all other products used are Loba Cheme.

Preparation of catalysts

Catalysts were prepared from metakaolin by acid activation. The purified Kaolinite was calcined at 600°C for two hours for converting it to metakaolin. Acid activation was done by refluxing the sample with various concentration of Sulphuric acid (0.5, 1, 2, 3, 4 and 5N) in the solid to liquid ratio 1:4 for 45 minutes. All the samples were washed till the disappearance of sulphate anions (barium chloride test). It was then filtered and dried at 110°C . Catalysts prepared were designated as NS1, NS2, NS3, NS4, NS5 and NS6 and listed in Table 1.

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

Activity can be further improved by metal salt supporting. Acid activated sample is further modified by metal chloride supporting. The sample is stirred with metal chloride salt (FeCl_3 , ZnCl_3 , MnCl_3 , CoCl_3 and SnCl_3 1 mmol/g) in 60 ml Acetonitrile and stirred for 3h. Then the solvent is evaporated and oven dried for 6h at 110°C . The metal chloride catalysts prepared are listed in Table 2.

Table 2. Catalysts prepared by the metal chloride supporting of acid activation of kaolinite

Metal chloride	Catalysts
Ferric chloride	NSF
Stannous chloride	NSS
Manganese chloride	NSM
Cobalt chloride	NSC
Zinc chloride	NSZ

Characterization of the catalysts

Characterization of the raw sample was done by chemical analysis. 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 determined 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 10⁰C/min. from 40°C to 740°C.

The surface areas for the catalysts were estimated according to Sears' method [35,36]. A sample containing 0.5g of clay was acidified with 0.1N HCl to a pH 3-3.5. The volume was made up to 50 ml with distilled water after addition of 10g of NaCl. The titration was carried out with standard 0.1M NaOH in a thermostatic bath at 298± 0.5 K to pH 4.0 and then to pH 9.0. The volume V, required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation

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

Acidity measurements were carried out by Potentiometric titration [37]. Potassium hydroxide titration method and Cation exchange capacity by the ammonium adsorption technique [38]. In potentiometric titration, the catalyst was mixed with acetonitrile and was titrated against n-butylamine taken in the burette. Using a Beckmann digital pH 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 hour 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.

Catalyst test

The activity of the catalyst was measured by the benzylation of benzene. In this experiment the reaction mixture benzene and benzyl chloride was refluxed in the presence of activated catalyst for 3h. After the completion of the reaction, the catalyst was removed by filtration. The excess benzene was distilling off and the percentage of conversion was determined. The efficiency of the best catalyst was also tested by using substrate such as toluene, biphenyl, naphthalene, p- xylene and anisole.

RESULT AND DISCUSSION

Chemical composition of the raw clay was determined and the values are compared with those of theoretical Kaolinite. About 84% from the total content contains silica and alumina.

The scanning electron micrographs (SEM) show the morphological features of the sample. The SEM micrographs points out the presence of agglomerates formed by several flaky particles stacked together (FIG.1)

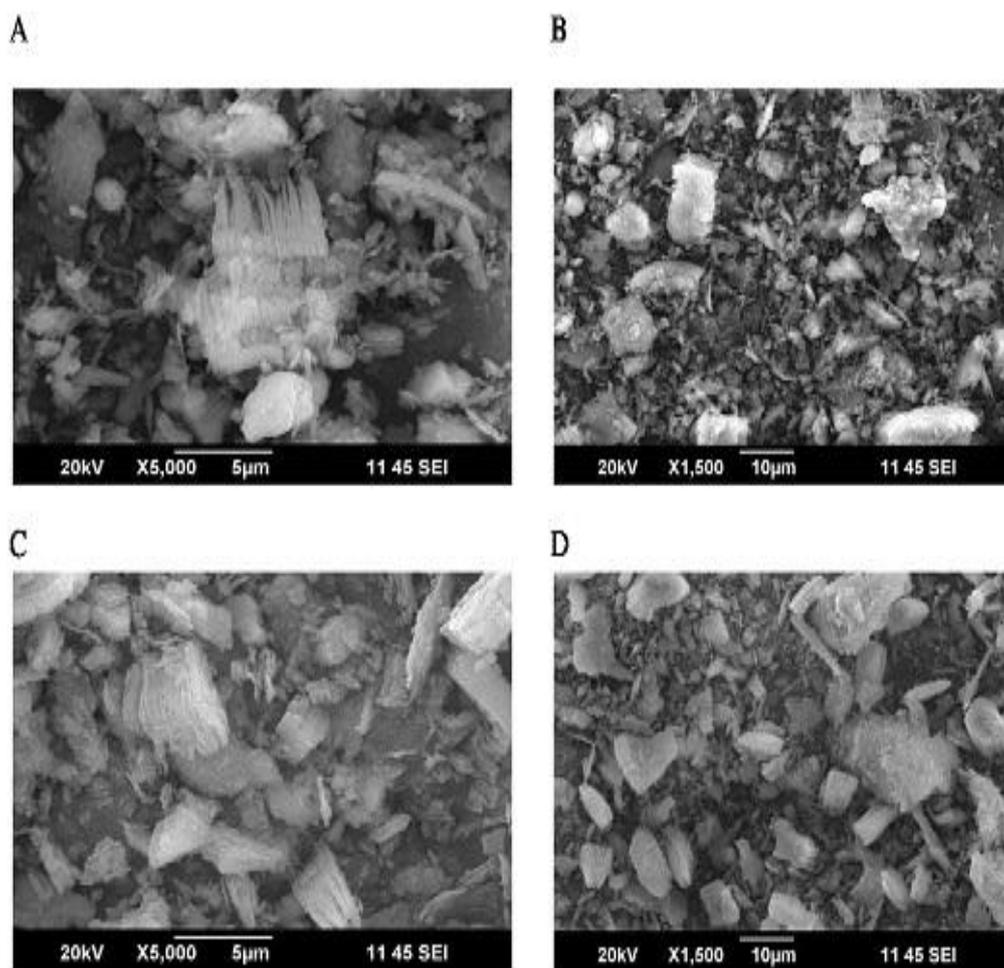


Fig.1: SEM images of Raw sample (A,B) and NS4 (C,D) at different magnifications

Acid activation of metakaolin resulted in a structural dealumination. During acid activation the composition of the parent clay changes considerably. As the strength of the acid increases the alumina content decreases, simultaneously the silica content increases. The decrease in the alumina content is due to the leaching of Al^{3+} ions from the octahedral layer.

Acidity was measured by titration with Potassium hydroxide solution, Potentiometric titration method and Cation exchange capacity measurements. Surface acidity calculated by potassium hydroxide titrations is given in Table3.

Table 3. Surface Area, Surface Acidity, CEC and Catalytic Activity (alkylation of benzene) of Acid activated samples

Catalyst	Surface Area (m ² /g)	Surface Acidity(mequiv/100g)	CEC (mequiv/g)	Conversion (%)
Raw Sample	6	109	32	20.77
NS1	19.8	197	26	55.52
NS2	39	207	52	57.74
NS3	71.4	218	58	67.54
NS4	125	229	68	74.17
NS5	131.8	226	64	70.86
NS6	109.4	223	54	72.87

This technique determines the total number of surface acid sites. From this measurement, it was found that raw sample showed low acidity than acid treated sample. That is 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 [39].

Potentiometric titration gives relative strength and types of acid sites present in the solid acid catalyst [40]. Acidity distribution curve of raw and acid treated catalyst are given in Fig.2.

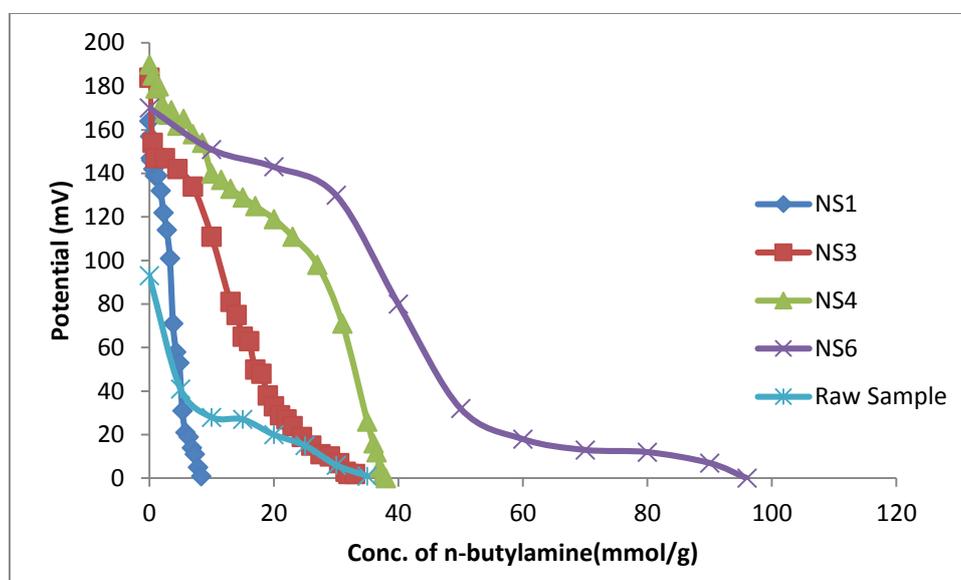


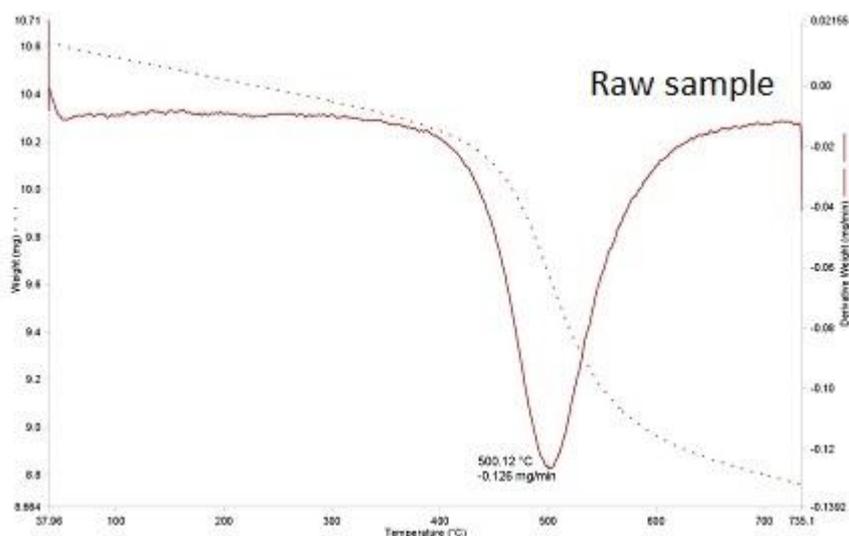
Fig. 2 Acidity distribution curves of Raw sample, NS1, NS3, NS4 and NS6.

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.

CEC of raw and acid treated samples are given in the table 3. On acid treatment there is an increase in the CEC. By acid treatment, the cations are replaced by hydrogen ions. Acid activation significantly increased the surface area. Clays contain both Bronsted and Lewis sites within the interlamellar region and the edge sites. When the clay is heated most of the interlamellar water is removed and the Bronsted acidity increases and the interlayer structure of the clay is collapses if the temperature is raised to 473- 573 K and the Lewis acidity increases at the expense of the Bronsted acidity [41]. The CEC of calcined clay samples is mostly contributed by the Lewis acid sites arising from structural defects, broken bonds and hydroxyl transfers [42].

The most important physical changes in acid-activated clay included increase in the SSA and the average pore volume. The extent of these changes depended on the acid strength, time of the treatment and the heating mode. The SSA and porosity of the samples were similar for comparably dissolved materials [37]. The measured surface areas of the samples are given in Table 3. The surface area of Kaolinite was reported as 5 to 25 m²/g [40]. Similar results have been reported by other authors [38, 43] suggesting that intercalation creates a porous framework increasing the surface area [44]. The specific surface area of Kaolinite was only 7m²/g, but it increased to 19.8 m²/g during acid activation. 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. The acid activation opens up the edges of the platelets and consequently the surface area and pore diameter increases [45].

Thermogravimetry is the measurement of some physical parameter of a system as a function of temperature. The hydroxyl groups attached with the aluminium ions get dehydroxylated. The endothermic loop occurring at mid temperature range is associated with the major loss of hydroxyls from the octahedral layer and this varies considerably from clay to clay. In the Kaolinite group, endothermic loop is an intense reaction which probably starts at a much lower temperature at about 450°C [46] and to peak at about 600°C (FIG.3).



The raw Kaolinite sample shows 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.

X-ray is one of the most important tools and is used extensively for investigation of phase transformation behaviors of Kaolinite during heating. The structural changes that occurred in the clay due to calcination and acid activation were studied using X-ray diffraction technique. XRD measurements indicated acid activation with different concentration of sulphuric acid had considerable influence on Kaolinite. Systematic studies of heating effect on Kaolinite which vary in their crystallinity were made by John (1953) [47]. Calcinations followed by acid activation influences the crystal structure of the clay minerals. The XRD pattern of raw sample shows the characteristic peaks of Kaolinite (7.17Å; 3.59Å; 1.49Å) (FIG.4). When the sample was calcined at 600°C the characteristic peak of Kaolinite disappeared. The impurity quartz present in the raw sample are resistant to the acid attack remains unmodified after acid activation.

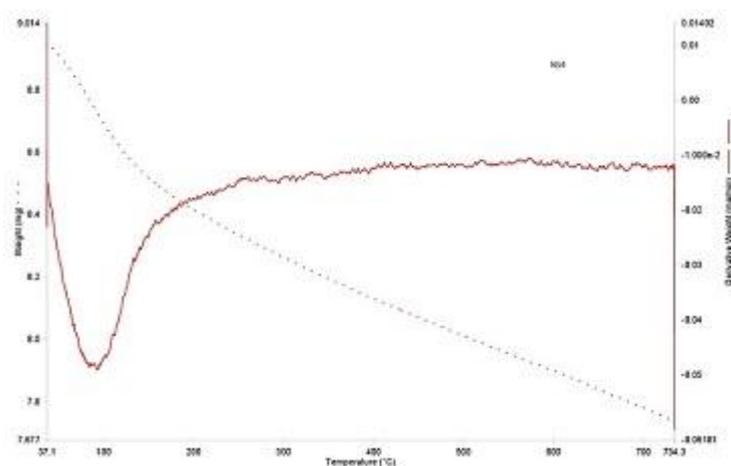


Fig. 4 XRD pattern of Raw sample and NS4

Catalytic activity

Catalytic activity of the samples was examined in benzylation of benzene with benzyl chloride. The analysis of the result obtained showed that the activity increases with increase in the concentration of acid treatment up to an optimum value and then decreases. Acid activated sample NS4 gave the maximum activity are listed in Table 3. The same sample showed the maximum acidity also. Here the raw sample has poor activity. This explains the greater performance of NS4 as a catalyst which also be attributed to its greater number of acid sites. The catalytic activity of the catalyst NS4 has also been tested by using toluene, biphenyl, naphthalene and anisole (Table 4).

Table 4. Catalytic activity of NS4 in the benzylation of aromatic compounds

Sl No.	Substrate	%
1	Benzene	74.17
2	Toluene	94.31
3	Biphenyl	90.22
4	Naphthalene	90.93
5	Anisole	91.34
6	p-Xylene	92.13

The catalyst characterization and activity of metal chloride supported catalyst was given in the Table 5. From these it was clear that metal salt supporting can introduce more acid sites into the catalyst surface. The data shows that there is an increase in the acid sites on metal chloride supporting. The maximum acidity and catalytic activity was shown by ferric chloride supported catalyst. Stannous chloride Supported sample

also showed good improvement in the activity. Benzylation of benzene of this catalyst is in the order NSF > NSS > NSZ > NSM > NSC. It is reported that the catalytic activity of metal supported catalysts depends on the redox potential of the metal in the metal chloride catalyst. Among the metal salt used Iron is having the highest redox potential. Moreover ferric chloride supported sample showed the maximum acidity and activity. Activity of FNS in the benzylation of different solvent was also tested (Table 6).

Table 5. Surface Area, Surface Acidity, CEC and Catalytic Activity (alkylation of benzene) of Acid activated samples

Catalyst	Surface Area (m ² /g)	Surface Acidity(mequiv/100g)	CEC (mequiv/g)	Conversion (%)
NSF	157.4	328	58	76.63
NSS	285.4	307	66	72.69
NSM	138.2	299	60	65.72
NSC	231	305	64	45.70
NSZ	253.4	270	62	69.66

Table 6. Catalytic activity of NSF in the benzylation of aromatic compounds

Sl No.	Substrate	%
1	Benzene	76.63
2	Toluene	92.55
3	Biphenyl	91.69
4	Naphthalene	92.13
5	p-Xylene	93.01

CONCLUSION

Acid activated Kaolinite clay from Nileswar, Kerala was successfully utilised as a low cost solid acid heterogeneous catalyst for the benzylation of benzene with benzyl chloride. Solid acid catalysts from clays were prepared by calcination of natural kaolinite at 600°C followed by acid treatment with different concentration of sulphuric acid. Chemical analysis and XRD pattern of the sample showed that the major component was Kaolinite. The results show that acid modification of Kaolinite enhances its surface acidity. From the different samples, the maximum acidity was shown by 3N sulphuric acid treated sample. This same sample was also showed a

good catalytic activity in benzylation of benzene. The catalytic activity of the best sample was also tested by using different substituted benzene. The catalytic activity was increased by metal chloride supporting. The metal salt supported catalysts were highly active in the benzylation of benzene. Ferric chloride supported sample, NSF, showed maximum percentage conversion and acidity. There for the use of eco-friendly solid acid clay catalyst from Nileswer is of great industrial significance for the benzylation of aromatic compound

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