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# Acidic Properties and Catalytic Activity of Natural Kaolinitic Clays for Friedel–Crafts Alkylation

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Natural Kaolinitic clays containing transition metals Fe and Ti in their lattice have been examined for their acidic properties and catalytic activity for the alkylation of benzene with benzyl chloride. Calcination of the clays at 550 °C and subsequent acid-activation using 2 M HCl (1 M=1 mol dm$^{-3}$) rendered the kaolinite surface highly acidic with very high acid amount. These clays exhibited high catalytic activity and selectivity for the conversion of benzyl chloride to diphenylmethane. Al(III), Fe(II), and Ti(II) ions exsolved from the lattice of kaolinites by acid activation relocate in the interlamellar space and boost the Brønsted acidity of coordinated hydroxo and proposed to initiate the alkylation. In fact kaolinites having structural transition metal, on acid activation exhibited higher acid amount and enhanced catalytic activity than kaolinites devoid of transition metals and recently studied alkylation catalysts such as synthetic $TiO_2$–$SiO_2$–$Al_2O_3$ and $Fe_2O_3$–$SiO_2$–$Al_2O_3$. Natural kaolinitic clays having transition metals in their lattice possess disordered structure and hence on acid activation results in the generation of larger amounts of relocatable cations, higher surface area and higher acidity compared to an ideal kaolinite. Also their acid amount and catalytic activity retained up to five successive regeneration cycles studied.

There has been a renewed interest in the use of clay aluminosilicates, the earliest known solid acids, as catalysts in various organic transformations because of the ease of handling and work up, low corrosiveness and low cost.[1,2] Also they are suitable for the conversion of relatively larger molecules.[3] Aluminosilicates, synthetic as well as natural (clays) also find utility as catalyst supports. For instance, transition metal oxides $TiO_2$ or $MoO_3$ incorporated on synthetic aluminosilicates are recently found to show remarkable acidic properties and they serve as effective and regenerable catalysts in a wide range of alkylations,[4—8] certain dehydrations, oligomerization and polimerization reactions.[9—11] Similarly montmorillonites, the catalytic activity of which is the most exploited among various clay minerals serve as effective acidic supports for different transition metal compounds.[3,12] The supported systems thus obtained usually exhibit high catalytic activity for acid-catalyzed reactions. In fact, there exists a synergistic effect between the supported compound and the aluminosilicate support. Laszlo et al. have shown that montmorillonites doped or exchanged with the Fe (III) ions is effective for a variety of Diels-Alder reactions and for the chlorination and arylation of adamantane.[13—15] Transition metal atom present in an aluminosilicate system, whether synthetic[4—11] or natural,[16,17] is thought to be seat of impressive and varied catalytic activity and has been the subject of extensive study in recent years. However, studies on acidic properties and catalytic activity of an important group of natural clay mineral, kaolinite, the disordered forms of which some times contain marginal amount of transition metal as a result of isomorphous substitution are not so elaborate as that of other clays or synthetic aluminosilicates. Therefore it is pertinent to evaluate the acidic properties and catalytic activity of such kaolinitic clays and hence the present study. The test reaction selected is the alkylation of benzene with benzyl chloride. This is a convenient screening reaction, since a dominant product, diphenylmethane is formed.[18] Also the reactant and product concentrations are easily measured. The effect of heat treatment and acid activation on the structure, acidic properties and catalytic activities of kaolinites and the mechanism of alkylation are discussed in the present paper. The acidic properties and catalytic activities of kaolinitic clays are compared with that of synthetic $TiO_2$–$SiO_2$–$Al_2O_3$ (Tisial) and $Fe_2O_3$–$SiO_2$–$Al_2O_3$ (Fesial), the recently studied Friedel–Crafts alkylation catalysts.

## Experimental

**Materials:** Two varieties of kaolinitic clays which differ slightly in chemical composition viz. Padappakkara blue kaolin (PBL-K) and Padappakkara black kaolin (PBK-K) are procured from the Padappakkara mine of Quilon District, Kerala, India. A pure white kaolin (EI-K) is supplied by the English Indian Clays Ltd., Veli, Thiruvananthapuram, Kerala, India.

Other materials used are sodium silicate (Scientific Chemicals) aluminium sulfate (BDH), ion(II) sulfate (BDH), titanium tetrachloride obtained from Kerala Metals and Minerals Ltd., Chavara, Quilon, India, benzene (BDH), benzyl chloride (BDH), butylamine (SD Chemicals) and hydrochloric acid and ammonia of AR grade. The indicators used are Neutral Red (p$K_a$=+6.8), Methyl Red (p$K_a$=+4.8) Dimethyl yellow (p$K_a$=+3.3), (phenylazo) diphenylamine (p$K_a$=+1.5), Crystal Violet (p$K_a$=+0.8), dicinnamylideneacetone (p$K_a$=−3.0) benzylideneacetophenone (p$K_a$=−5.6), and anthraquinone (p$K_a$=−8.2).

**Purification of Kaolinites:** Purification method involved the separation of coarser mineral impurities from clay particles. This is achieved by suspending the crude lumps in water (500 g of the clay lump in 5 dm$^3$ water), by vigorous stirring and allowing the coarser mineral particles to settle.

Suspended clay particles are siphoned off, sieved, and particles of size below 45 µm are collected and washed free of solubles.

**Drying:** Clay particles separated from coarser mineral impurities are dried at 110 °C for 12 h. These samples are designated as "dried clay samples" in the present study.

**Calcination:** Dried clay samples are calcined for 6 h at various temperatures viz: 250, 350, 450, and 550 °C.

**Acid Treatment:** The 550 °C calcined clay samples (1 part by weight) are boiled with HCl of 2 M concentration (4 parts by weight) for 45 min. The leached samples are then washed free of chloride ions, dried at 110 °C for 12 h.

**Preparation of $TiO_2$–$SiO_2$–$Al_2O_3$ and $Fe_2O_3$–$SiO_2$–$Al_2O_3$:** Both the ternary oxides were prepared by coprecipitation method as referred elsewhere[5] from aqueous solutions of pH4, dried at 120 °C for 12 h and calcined at 600 °C for 6 h.

**Physicochemical Characterization:** Physicochemical characterization of dried and acid activated clays were done by the measurement of particle size (SEDIGRAPH), surface area (BET, $N_2$ adsorption at −186 °C after degassing at 120 °C), XRD (RIGAKU, Cu $K\alpha$ radiation) and conventional chemical analysis.

**High Gradient Magnetic Separation:** Magnetic impurities (haematite and anatase) were separated from the clay by using the magnetic filter apparatus.[19,20] Clay samples (45 µm) were dispersed using an ultrasonic probe for about 30 s and diluted with water (pH 10) to give a 0.2% suspension. The suspension was passed through the magnetic filter three times at a flow rate of 120—140 $cm^3 min^{-1}$ (flow velocity of 1.5—$1.75\times10^{-2}$ $m s^{-1}$). After the suspension had passed through the filter and was collected, pH 10 water was passed through at the same flow velocity with the magnet on to clean the system. Material collected that was nonmagnetic at 1 T was considered the nonmagnetic fraction. Then the magnet was turned off and the magnetically trapped material, the magnetic fraction, was flushed out. Clay samples were passed through the filter three times. The magnetic and nonmagnetic fractions were flocculated by adjusting the suspensions to pH 3.5—4.0. The clear supernatant solution was siphoned off and the clay material was freeze-dried and stored for subsequent analysis.

**Citrate–Bicarbonate–Dithionite (CBD) Treatment:** This technique is used to remove external Fe impurities from clay by reductive dissolution.[21] 40 ml 0.3 M sodium citrate and 5 ml 1 M sodium bicarbonate solutions were added to 2 g of clay. The temperature of the slurry was maintained at 75—80 °C and 1 g sodium dithionite was added with constant stirring. A second 1 g portion of sodium dithionite was added after 5 min. After 15 min digestion period, 10 ml saturated NaCl solution and 10 ml acetone were added. The suspension was then centrifuged and the supernatant liquid decanted off. The clay was recovered after repeated washings till free from extracted Fe, dried at 110 °C and used for chemical analysis.

**Measurement of Acidity:** The acid amounts and acid strength of samples were measured by titrating the 100—200 mesh powder suspended in dry benzene with butylamine solution in dry benzene using Hammett indicators mentioned earlier.[22] In the case of the raw PBK-K, a mixture of the clay and a white solid, $SiO_2$–$Al_2O_3$, of known acidity distribution, (0.02 g of PBK-K and 0.2 g of $SiO_2$–$Al_2O_3$) was suspended in dry benzene and titrated using butylamine solution in benzene.[23]

**Measurment of Catalytic Activity:** Prior to activity measurements, all catalyst samples were activated at 150 °C under $N_2$ for 2 h. 0.25 g of the catalyst is added to a mixture of 0.2 mol of benzene and 0.01 mol of benzyl chloride and heated to 80 °C with stirring. The conversion of benzyl chloride was checked after a reaction time of 15 min by means of GC-MS and NMR.

## Results and Discussion

**Dried and Calcined Clays:** XRD patterns of dried PBL-K and PBK-K (Fig. 1) show that both are disordered kaolinites, the crystallinity index being 0.59 and 0.53 respectively. The crystallinity index of EI-K is 0.82 and hence has much lower degree of disorder. The non-clay impurities associated with both PBK-K and PBL-K samples are quartz and gibbsite which are present in quantities sufficient for detection by XRD. Table 1 shows that about 85% of these two samples contain particles of size less than 2 µm. Accordingly surface areas of both samples are higher than that expected for an ideal kaolinite (15—20 $m^2 g^{-1}$). The presence of impurities such as quartz and gibbsite in these clay samples also would have contributed to the increase in surface area. The surface areas of both samples increased on increasing the temperature of calcination to 450 °C and then showed a slight decrease on increasing the temperature further (Table 2). The enhancement in surface areas of the clay samples when dried could be attributed to the removal of the coatings of carbonaceous impurities (for instance, humic acid) and water molecules which fill or cover the pores in the case of uncalcined clays. The EI-K sample is devoid of carbonaceous impurities and hence has not shown much increase in surface area on calcination. In fact calcina-

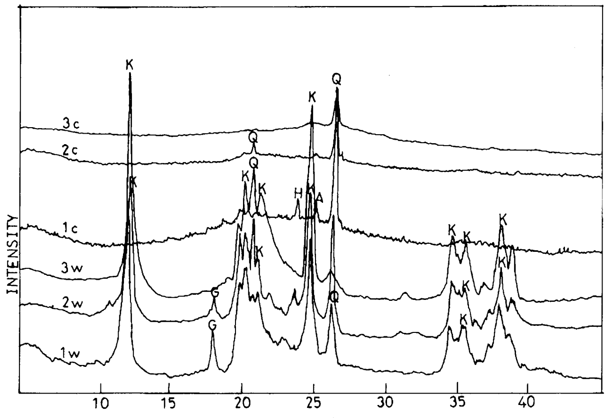


Fig. 1. XRD patterns of PBK-K, PBL-K and EI-K dried at 105 °C and calcined at 550 °C for 6 h. 1 - PBK-K, 2 - PBL-K, 3 - EI-K. W - Washed and dried at 105 °C for 12 h. C - Calcined at 550 °C for 6 h. K - Kaolinite, Q - Quartz, G - Gibbsite, H - Haematite, A - Anatase.

Table 1. Particle Size Analysis (%) of Fraction < 45µm of PBK-K, PBL-K and EI-K Dried at 110 °C, Calcined at 350 °C and 450 °C

| Size/µm | PBK-K | | | PBL-K | | | EI-K | | |
|---|---|---|---|---|---|---|---|---|---|
| < | 110 | 350 | 450 | 110 | 350 | 450 | 110 | 350 | 450 |
| 45 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 25 | 99 | 98 | 96 | 99 | 98 | 95 | 100 | 97 | 93 |
| 20 | 98 | 97 | 96 | 98 | 96 | 94 | 99.5 | 88 | 85 |
| 15 | 97 | 95 | 94 | 95.5 | 94 | 92 | 99 | 79 | 76 |
| 10 | 95.5 | 93 | 92 | 95 | 91 | 89 | 97 | 67 | 66 |
| 5 | 92 | 89 | 87 | 93 | 90 | 88 | 92 | 63 | 61 |
| 3 | 89.5 | 86 | 85 | 91.5 | 89 | 87 | 77 | 57 | 53 |
| 2 | 87 | 85 | 83 | 90 | 87 | 85 | 68 | 49 | 45 |
| 1 | 83 | 81 | 80 | 85 | 83 | 82 | 20 | 18 | 18 |
| 0.5 | 70 | 68 | 66 | 73 | 71 | 69 | 12 | 11 | 10 |

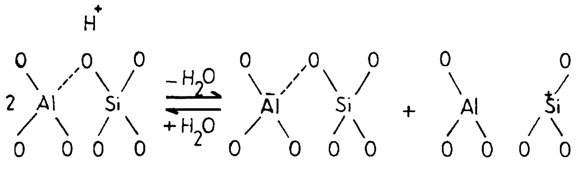
tion increased the size of particles (Table 1). The slight decrease in surface areas at the highest calcination temperature studied (550 °C) could be due to the partial collapse of the layer structure.

Chemical analysis shows (Table 3) the presence of interlayer cations such as $Na^+$ and $K^+$ in appreciable amounts in both PBL-K and PBK-K whereas EI-K contains very less amount of exchangeable cations. The high value of loss on ignition of PBK-K could be attributed to the presence of increasing amounts of carbonaceous impurities inherently present in the clay. This could be a probable reason for its black colour. The percentage by weight of $Fe_2O_3$ present in the raw dried PBK-K and PBL-K are 2.0 and 1.23, respectively. The percentage of weight of $TiO_2$ in these samples are 1.49 and 0.86. The presence of haematite ($d$=3.71) and anatase ($d$=3.52) are evidenced from the XRD patterns of both PBL-K and PBK-K samples taken after dehydroxylation at 550 °C (Fig. 1). It is to be mentioned that haematite and anatase are very effectively separated from dried PBK-K and PBL-K by repeatedly passing the clay samples through high gradient magnetic separator. The separation of anatase by this method is possible because of the presence of Fe, either as coatings on the crystals or within the structure of this mineral.[20] XRD patterns of the nonmagnetic clay fraction (taken after dehydroxylation at 500 °C) are devoid of reflections due to haematite and anatase. Chemical analysis of CBD treated clays and the nonmagnetic clay fraction have shown more or less the same $Fe_2O_3$ content, 1.20 and 1.18% by weight in PBK-K and 0.75 and 0.74% by weight in PBL-K respectively. $TiO_2$ content in the nonmagnetic clay fraction of PBL-K and PBK-K are 0.72 and 0.44% by weight respectively. These results show that Fe and Ti are present in the lattice of PBL-K and PBK-K. Similar studies on EI-K showed that it is practically devoid of lattice transition metals.

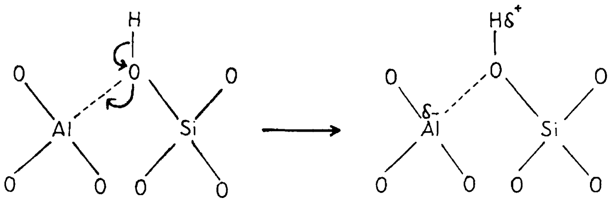
The Brønsted acidity of clays stems from the terminal hydroxyl groups and from the bridging oxygens of which latter have high acid strength.[17] The presence of exchangeable cations in the interlamellar space polarize coordinated water molecules inducing their dissociation.[17] This dissociation reaction is favoured by low water contents since, in this case, only water molecules in direct contact with the cations will be present.[24] This could be a probable reason for the decreased acid amount and acid strength of the kaolins dried at lower temperatures (Table 2). At the edges of platelets which break off, particularly in the octahedral layer, coordinatively unsaturated Al(III), Fe(II), and Fe(III) centres arise which can act as Lewis acid centres.[1] Besides, when clays are activated by heating above 300 °C, a proportion of structural hydroxyl groups (Brønsted acidity) is removed in pair-wise fashion, giving rise to three coordinated Al with the loss of water as shown in Scheme 1(a).[25] Under these anhydrous conditons, the co-existence of Brønsted and stronger Lewis acid sites are highly probable. Accordingly a synergistic interaction between the formed Lewis site and a neighboring weak Brønsted site (silanol group) could occur resulting in the enhancement of Brønsted acidity through an inductive effect exerted by adjacent electron deficient Al, acting as Lewis acid as shown in Scheme 1(b).[25] In other words, the dehydrative activation of clay enhances surface acidity as given in Table 2. The negatively charged aluminosilicate sheets are analogous to the conjugate bases of strong inorganic oxo acids.[1] From the acid amount values it is clear that the extent of total isomorphous substitution (the probable pattern being Fe(II) and Ti(II) in octahedral and Al(III) in tetrahedral layers), which renders a clay surface acidic is high in the case of PBK-K and PBL-K and very low in the case of EI-K.

Calcination of kaolin at 550 °C causes partial collapse of layer structure[26] and dehydroxylation with its accompanying transition to metakaolin and consequently the coordination of Al shifts from octahedral to tetrahedral through pentahedral.[26] Accordingly, the alumina

(a) Generation of Lewis acid site on heating



(b) Enhancement of Brønsted acidity through inductive effect



Scheme 1.

Table 2. Surface Area and Acidity Distribution of Dried, Calcined, and 2 M HCl Activated Clay samples

| Sample | Temperature of drying/ calcination (°C) | Surface area ($m^2\,g^{-1}$) | Acid amount ($mmol\,g^{-1}$) at different $pK_a$'s | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | +6.8 | +4.8 | +3.3 | +1.5 | +0.8 | −3.0 | −5.6 | −8.2 |
| PBK-K | 110 | 40 | 0.36 | 0.33 | 0.29 | 0.16 | 0.07 | 0.00 | 0.00 | 0.00 |
| PBL-K | 110 | 37 | 0.29 | 0.22 | 0.16 | 0.14 | 0.05 | 0.00 | 0.00 | 0.00 |
| EI-K | 110 | 13 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.00 | 0.00 |
| PBK-K | 250 | 62 | 0.41 | 0.40 | 0.39 | 0.29 | 0.14 | 0.04 | 0.02 | 0.00 |
| PBL-K | 250 | 60 | 0.33 | 0.31 | 0.31 | 0.24 | 0.11 | 0.03 | 0.02 | 0.00 |
| EI-K | 250 | 14 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.00 |
| PBK-K | 350 | 78 | 0.46 | 0.44 | 0.41 | 0.34 | 0.21 | 0.17 | 0.06 | 0.03 |
| PBL-K | 350 | 72 | 0.38 | 0.37 | 0.37 | 0.31 | 0.20 | 0.14 | 0.04 | 0.04 |
| EI-K | 350 | 16 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| PBK-K | 450 | 84 | 0.49 | 0.48 | 0.48 | 0.44 | 0.32 | 0.24 | 0.13 | 0.09 |
| PBL-K | 450 | 86 | 0.41 | 0.40 | 0.40 | 0.39 | 0.27 | 0.21 | 0.11 | 0.07 |
| EI-K | 450 | 16 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| PBK-K | 550 | 82 | 0.44 | 0.44 | 0.41 | 0.34 | 0.22 | 0.18 | 0.07 | 0.05 |
| PBL-K | 550 | 85 | 0.36 | 0.36 | 0.36 | 0.36 | 0.19 | 0.15 | 0.05 | 0.04 |
| EI-K | 550 | 15 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| PBK-K | Acid activated | 89 | 0.94 | 0.94 | 0.93 | 0.90 | 0.77 | 0.66 | 0.57 | 0.18 |
| PBL-K | | 95 | 0.78 | 0.76 | 0.75 | 0.74 | 0.67 | 0.54 | 0.42 | 0.08 |
| EI-K | | 17 | 0.24 | 0.23 | 0.23 | 0.21 | 0.21 | 0.14 | 0.06 | 0.05 |
| Tisial-4[a] | | 100 | 0.63 | 0.63 | 0.63 | 0.63 | 0.63 | 0.63 | 0.15 | 0.15 |
| Fesial-4[a] | | 92 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | 0.14 | 0.00 |

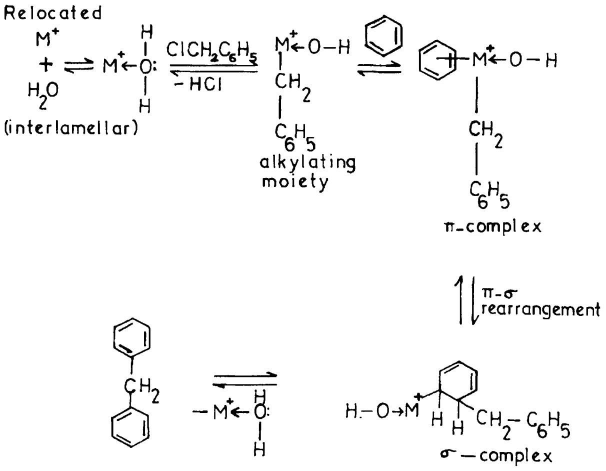
a) Given for comparison.

Table 3. Chemical Composition of Different Clay Samples

| Clay sample | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $Na_2O$ | $K_2O$ | MgO | Loss on ignition at 1025±25 °C |
|---|---|---|---|---|---|---|---|---|
| PBK-K (dried) | 48.32 | 27.51 | 2.07 | 1.49 | 0.98 | 0.44 | — | 19.6 |
| PBK-K (acid activated) | 56.98 | 27.74 | 2.31 | 1.52 | — | — | — | 10.95 |
| PBL-K (dried) | 52.18 | 30.54 | 1.23 | 0.86 | 0.60 | 0.07 | — | 14.43 |
| PBL-K (acid activated) | 60.52 | 26.55 | 1.46 | 1.26 | — | — | — | 10.10 |
| EI-K (dried) | 47.05 | 36.98 | 0.34 | 0.53 | 0.12 | 0.08 | — | 14.31 |
| EI-K (acid activated) | 48.48 | 40.89 | 0.36 | 0.54 | — | — | — | 9.90 |

tetrahedra shows tendency to share edges rather than corners and become uncharged.[27] Hence they do not contribute to the acidity of the clay surface.[27] This could be a probable reason for the decreased acidity of kaolins calcined at 550 °C. Similarly, a divalent cation such as Fe(II) or Ti(II) which is initially present in the octahedral layer of the PBL-K and PBK-K also can change their coordination by calcination at temperatures more than 500 °C. Kaolinitic clays should be calcined before acid activation to get catalysts or adsorbents of superior quality.[27] This is because the meta kaolin with partially collapsed structure is more readily attacked by acid than is the perfectly crystalline kaolin. Also a more favourable pore geometry for reactants or adsorbents are produced when meta kaolin is acid leached.

**Acid Activated Clays:** Chemical analysis shows that a considerable amount of Al has been exsolved out from the lattice by heating with 2 M HCl in the case of PBL-K and PBK-K (Table 3). All the interlayer cations are found to be replaced by $H^+$ by this process. Isomorphously substituted Fe and Ti can also leach out in this way. The relocation of a portion of the leached out Al, Fe, and Ti cations in the partially collapsed interlamellar space is possible.[28] These relocated cations can have coordination with interstitial water molecules rendering them better proton donors and hence enhanced acidity as shown in Table 2. It is known that kaolinite which has isomorphously substituted Fe(II) or Ti(II) have higher degree of disorder (lower crystallinity) than an ideal kaolinite.[29] Hence the structure of the former could be easily attacked and ruptured by the consecutive processes of calcination and acid treatment resulting in the formation of larger amounts of relocatable cations [Al(III), Fe(III) or Ti(IV)]. The surface area and acidity of these kaolinite increase with the exsolving and relocation of these cations. It is specified that EI-K is more or less attributable to an ideal kaolin since the only cation available is the limited amount of Al(III). Moreover it is known that a transition metal cation relocated in such a way can boost the Brønsted acidity to a very great extent.[30] Hence the higher acid amount value at high acid strength of acid activated PBL-K and PBK-K compared to EI-K.



Scheme 2. Mechanism of benzylation of benzene with benzylchloride over acid activated natural kaolinite. $M^+$ is $Al^{3+}$, $Fe^{3+}$ or $Ti^{4+}$.

**Catalytic Activity:** It has been found that both PBK-K and PBL-K in the raw dried form are only marginally active for the alkylation of benzene with benzyl chloride. However both clays on calcination exhibited increased catalytic activity for the conversion and has shown 100% selectivity as the only one product formed is diphenylmethane. On increasing the calcination temperature, the catalytic activity enhanced without altering the selectivity to diphenylmethane. Thus Table 4 shows that PBK-K and PBL-K exhibited higher activity for the conversion of benzyl chloride, when calcined at 450 °C. This could be attributed to the presence of more number of acid sites in these clay surfaces with suitable strength for the aromatic alkylation reaction which usually fall in the range of $H_o \leqq +1.5$.[6–8] However, the EI-K, whether calcined or not is found to be only marginally active for the conversion of benzyl chloride to diphenylmethane which could be attributed to the lower acid amount values. Both the acid activated PBK-K and PBL-K exhibited very high catalytic activity for the conversion, which is even higher than that of the recently studied synthetic $TiO_2$–$SiO_2$–$Al_2O_3$ or $Fe_2O_3$–$SiO_2$–$Al_2O_3$ systems. The enhanced catalytic activity of acid activated PBK-K and PBL-K could be attributed to the significant amount of acidity derived from the Al(III), Fe(II), and Ti(II) ions exsolved from the octahedral layer of the clay structure during acid leaching. It could be depicted that unexsolved Al remaining in the edges of platelets act as Lewis acid centres and exsolved ions relocate in the interlamellar space of the clay as Al(III), Fe(III), and Ti(IV). These relocated ions boost the Brønsted acidity of coordinated hydroxo groups as shown in Scheme 2 and could effectively serve as acid sites for the alkylation reaction. This mechanism of alkylation is analogous to the mechanism of alkylation reaction catalyzed by an $M^+$–H species present on a synthetic transition metal oxide–$SiO_2$–$Al_2O_3$ system.[4–8] The alkylating agent, benzyl chloride interacts with the active species and forms the alkylating moiety $M^+$–$CH_2$–$C_6H_5$ (Scheme 2) which in turn attack the benzene molecule forming a Π-complex. This is possible because of the partially filled p-orbitals of Al(III) and d-orbitals of Fe(III) and Ti(IV).[4–8] This Π-complex rearrange to give the alkylated product, diphenylmethane. The successive platelets of kaolinite can be intercalated by highly polar molecules and are capable of stabilizing highly polar transition states converting it into a product whereas it is formed in lesser amounts or even not obtained when the reaction is performed in homogenous conditions.[1] Thus the intermediate of the alkylating moiety, the Π-complex and the $\sigma$-complex shown in Scheme 2 could be stabilized which in turn enhance the conversion to the product, diphenylmethane. When the reactants are constrained to diffuse in a porous solid which have layered or partially collapsed layered structure like a clay mineral, with the effective dimension (Fractal dimension) being ca. 2,[1,12,17] increased encounter frequencies between reactants occur. Also organic molecules congregate in the compartment like structures of the clay matrix. That is, pores locally increase the interaction between the reactants.[1,12] These features along with the increased amount of acid sites could be cited as the reason for the enhancement of the catalytic activity of PBK-K and PBL-K.

It is to be mentioned that the presence of quartz, gibbsite, haematite and ilmenite do not alter the acidic properties or catalytic activity of the clay surface.[31]

Even though the reaction temperature increases, the conversion to diphenylmethane and the selectivity for the same observed in the present study on acid activated PBK-K and PBL-K are higher than those obtained recently with K10 or KSF montmorillonites or certain Lewis acid catalysts supported on K10 montmorillonites.[32]

Table 4. Catalytic Activity of Dried and Calcined Clays for the Friedel–Crafts Alkylation of Benzene with Benzyl Chloride at 80 °C

| Sample | % Conversion[a] of benzyl chloride to diphenylmethane on clays | | | | | Acid activated |
|---|---|---|---|---|---|---|
| | Dried at | Calcined at | | | | |
| | 110 °C | 250 °C | 350 °C | 450 °C | 550 °C | |
| PBK-K | 15 | 26 | 33 | 41 | 32 | 85 |
| PBL-K | 12 | 21 | 27 | 36 | 24 | 74 |
| EI-K | — | 02 | 03 | 03 | 04 | 20 |

a) Tisial-4 and Fesial-4 under the same experimental conditions 71 and 67, respectively.

Table 5. Effect of Successive Regeneration Cycles on the Acidity Distribution and Catalytic Activity of 2 M HCl Activated PBL-K and PBK-K Samples

| Sample | Number of regeneration cycle | Acid amount ($\mathrm{mmol\,g^{-1}}$) at Different $\mathrm{p}K_\mathrm{a}$'s | | | | | | | | % Conversion to diphenylmethane |
|---|---|---|---|---|---|---|---|---|---|---|
| | | +6.8 | +4.8 | +3.3 | +1.5 | +0.8 | −3.0 | −5.6 | −8.2 | |
| PBK-K | 0 | 0.94 | 0.94 | 0.93 | 0.90 | 0.77 | 0.66 | 0.57 | 0.18 | 85.0 |
| | 1 | 0.94 | 0.94 | 0.93 | 0.90 | 0.77 | 0.65 | 0.56 | 0.18 | 85.0 |
| | 2 | 0.93 | 0.93 | 0.93 | 0.90 | 0.77 | 0.65 | 0.56 | 0.17 | 84.0 |
| | 3 | 0.92 | 0.92 | 0.91 | 0.89 | 0.77 | 0.64 | 0.55 | 0.15 | 83.5 |
| | 4 | 0.92 | 0.92 | 0.91 | 0.89 | 0.77 | 0.63 | 0.54 | 0.13 | 83.5 |
| | 5 | 0.91 | 0.91 | 0.90 | 0.89 | 0.77 | 0.62 | 0.54 | 0.11 | 83.0 |
| PBL-K | 0 | 0.78 | 0.76 | 0.75 | 0.74 | 0.68 | 0.54 | 0.41 | 0.06 | 74.0 |
| | 1 | 0.78 | 0.76 | 0.75 | 0.74 | 0.68 | 0.54 | 0.41 | 0.06 | 74.0 |
| | 2 | 0.78 | 0.76 | 0.75 | 0.74 | 0.68 | 0.54 | 0.40 | 0.05 | 74.0 |
| | 3 | 0.77 | 0.76 | 0.75 | 0.74 | 0.67 | 0.54 | 0.40 | 0.05 | 73.5 |
| | 4 | 0.76 | 0.75 | 0.75 | 0.74 | 0.66 | 0.54 | 0.41 | 0.04 | 73.5 |
| | 5 | 0.75 | 0.75 | 0.75 | 0.74 | 0.66 | 0.54 | 0.40 | 0.04 | 73.0 |

**The Regenerability of Acid Activated PBK-K and PBL-K:** After the alkylation reaction for 15 min, the clay catalyst is filtered off, washed with benzene, dried at 80 °C and heat-treated at 400 °C for 4 h. The catalyst thus regenerated is used again for reaction. The acidity distribution of the clay catalyst after each regeneration is also measured. It was found that the acid amount and acid strength of both samples are negligibly affected by five successive regeneration cycles (Table 5) and accordingly they retained their high catalytic activity and high selectivity for the conversion of benzyl chloride to diphenylmethane (Table 5) in the alkylation of benzene.

## Conclusion

Natural kaolinites having lattice transition metals, Fe and Ti can be converted to excellent solid acid catalysts for the Friedel–Crafts alkylation of benzene with benzyl chloride. The acid amount and catalytic activity of these clays are enhanced by boiling them with 2 M HCL. Catalysts thus prepared exhibit higher activity and 100% selectivity to diphenylmethane than the recently studied synthetic alkylation catalysts such as $\mathrm{TiO_2{-}SiO_2{-}Al_2O_3}$, $\mathrm{Fe_2O_3{-}SiO_2{-}Al_2O_3}$ and clay catalysts used at lower temperatures like K10 montmorillonites exchanged with Lewis acidic cations or supported with Lewis acid. The regenerability of acid activated kaolinite catalysts are such that they retained the initial acid amount and catalytic activity up to five successive regeneration cycles.

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