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A comparative study on H_2SO_4, HNO_3 and $HClO_4$ treated metakaolinite of a natural kaolinite as Friedel–Crafts alkylation catalyst

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Abstract

A natural kaolinitic clay from Padappakkara mine of Quilon District of Kerala, India, has been metakaolinized at 550°C and activated separately with H_2SO_4, HNO_3 and $HClO_4$ of varying concentrations. The chemical composition, BET surface area, acidity distribution as well as alkylation activity of these activated metakaolinites are studied. Silica to alumina molar ratio, surface area and the number of strong acid sites increased on increasing the concentration of acid used for activation. Metakaolinite activated with 4 M HNO_3 is found to possess the highest surface area and surface acidity. Alkylation of benzene with benzyl chloride at reflux was chosen as the test reaction. All the catalyst samples prepared were active for the benzylation reaction giving above 75 mol% conversion of the alkylating agent. Metakaolinite activated with 4 M HNO_3 gave 87 mol% conversion of benzyl chloride to diphenylmethane with 100% selectivity within 30 min of reaction time. This could be correlated well with the greater surface acidity of this sample. It is concluded that extremely efficient solid catalysts of remarkable acidic properties could be produced by the activation of metakaolinite with H_2SO_4, HNO_3 and $HClO_4$. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Friedel–Crafts alkylation; Metakaolinite; Benzyl chloride; Diphenylmethane; Mineral acid activation

1. Introduction

Layer silicates, montmorillonite clays are well exploited as catalysts for a variety of organic transformations [1–7]. The usual method of catalyst preparation is treatment of the natural clay with acid solutions of suitable concentration which produce solid acids of required acidic properties [8–10]. K 10 is a well-known commercial montmorillonite clay catalyst, the surface acidity as well as catalytic activity of which can be enhanced considerably by exchanging with transition metal ions [11–14]. However, the catalytic activity of another major group of clay mineral, kaolinite is comparatively not well studied. Recent studies in our laboratory have shown that certain kaolinites which are isomorphously substituted (eventhough the percentage of substitution is low compared to montmorillonites) could be converted to efficient acid catalysts by suitable thermal and chemical activation [15–17]. Kaolinites from Padappakkara and Thonnakkal mines of Kerala State, India, are isomorphously substituted, the main element being Fe in octahedral layers. These clays after metakaolinization and proper acid treatment served as effective

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catalyst for Friedel–Crafts alkylation of benzene with benzyl chloride in the liquid phase and several other organic transformations [15].

The present work deals with the preparation, physicochemical characterization, surface acidity evaluation, and alkylating activity measurements of solid acid catalysts from the natural kaolinite, PBK-K procured from the Padappakkara mine of Kerala, India [15–21]. The objective of the study is to compare the acidic properties and catalytic activity of a series of catalysts prepared from the same source kaolinite using several mineral acids of different concentrations. The test reaction chosen was Friedel–Crafts alkylation of benzene with benzyl chloride in the liquid phase.

2. Experimental

Chemicals used are AR grade sulphuric acid, nitric acid and perchloric acid (E. Merck), benzene and benzyl chloride (BDH), acetonitrile and butylamine (SD fine chemicals).

The natural kaolinite PBK-K was purified by separating coarser mineral impurities from clay particles. This is achieved by suspending the crude lumps in water (500 g of clay lump in 5 dm^{-3} of water) by vigourous stirring and then allowing the coarser mineral particles to settle. Suspended particles are siphoned off, sieved and particles of size below 45 μm were collected and washed free of soluble impurities. The separated clay particles are dried at 110±5°C for 12 h and then calcined at 550±5°C for 5 h. The calcined clay is refluxed separately with sulphuric, nitric and perchloric acids of varying concentrations (1–4 M) in the solid to liquid ratio 1:4 for 45 min. The samples were then washed thoroughly with distilled water and made anion free, dried at 110±5°C in an air oven for 12 h and then calcined at 400°C for 3 h. The samples prepared are listed in Table 1. Characterization techniques involved wet chemical analysis, X-ray diffraction (XRD) (Rigaku, Cu K_α radiation), and surface area analysis by BET, N_2 adsorption at -196°C (Micromeritics Gemini-2360). Acidity measurements were carried out by means of potentiometric titration in acetonitrile [15–21]. One drop of 0.1 M *n*-butylamine in dry acetonitrile was added to 1 g of the catalyst in 10 ml of dry acetonitrile and stirred for 3 h. The initial electrode potential (*E* (mV)) was noted and subsequently, by adding 0.05 ml butylamine solution at regular intervals, the change of electrode potential was noted until a constant *E* (mV) value was obtained. The benzylation of benzene was carried out in the liquid phase. Prior to activity measurement, all the catalyst samples were activated at 100°C for 1 h. One gram of the catalyst was added to a mixture of 0.025 mol of benzyl chloride and 0.25 mol of benzene and refluxed at 80°C with constant stirring till the complete evolution of HCl occurred. The reaction products were filtered while hot to remove the catalyst and analysed by GC–MS and NMR.

Table 1
Samples prepared from metakaolinized PBK-K for the present study

Sample	Acid used for activation	Concentration of the acid used (M)	Time of activation (h)	Solid/liquid (w/w)
A	H_2SO_4	1	0.75	1:4
B	H_2SO_4	2	0.75	1:4
C	H_2SO_4	3	0.75	1:4
D	H_2SO_4	4	0.75	1:4
E	HNO_3	1	0.75	1:4
F	HNO_3	2	0.75	1:4
G	HNO_3	3	0.75	1:4
H	HNO_3	4	0.75	1:4
I	$HClO_4$	1	0.75	1:4
J	$HClO_4$	2	0.75	1:4
K	$HClO_4$	3	0.75	1:4
L	$HClO_4$	4	0.75	1:4

3. Results and discussion

3.1. Physicochemical characteristics of PBK-K

XRD pattern of the clay is discussed in detail in [15]. It was found that kaolinite is the chief mineral content of PBK-K. The major non-clay mineral present is quartz. Minor quantities of gibbsite also is present. Hinckley crystallinity index of the kaolinite was calculated to be 0.56, which indicates that PBK-K has only a low degree of order. The chemical composition of the kaolinite in the dried state is given in Table 2. Higher percentages of SiO_2, Fe_2O_3, TiO_2 and the presence of alkali metal ions were seen compared

Table 2
Chemical composition and surface area of raw, calcined and mineral acid activated clay samples

Sample	SiO_2 (wt%)	Al_2O_3 (wt%)	Al_2O_3/SiO_2 (w/w)	Fe_2O_3 (wt%)	TiO_2 (wt%)	LOI[a] at 1025±25°C (wt%)	Surface area ($m^2\,g^{-1}$)
PBK-K[b] (raw)	48.32	27.51	0.57	2.07	1.49	19.6	26.62
PBK-K (calcined)	42.90	36.58	0.85	7.52	1.02	10.58	31.92
A	46.98	34.70	0.74	6.92	1.98	7.83	39.18
B	54.47	27.77	0.51	6.62	2.02	8.12	41.67
C	63.54	20.47	0.32	6.06	2.15	6.78	50.05
D	70.20	14.20	0.20	6.02	2.19	6.39	70.42
E	49.96	33.70	0.68	6.93	2.01	6.90	37.92
F	53.75	28.67	0.53	6.75	2.03	7.80	44.17
G	64.79	18.32	0.28	5.93	2.13	7.84	53.28
H	72.90	12.81	0.18	5.82	2.15	6.32	100.88
I	50.32	33.12	0.66	7.05	2.09	5.42	44.38
J	56.66	26.74	0.47	6.62	2.11	6.87	49.27
K	62.31	20.47	0.33	6.52	2.14	7.56	57.19
L	69.96	14.65	0.21	6.20	2.17	6.02	76.69

[a] Loss on ignition.
[b] Na_2O (wt%)=0.95; K_2O (wt%)=0.40.

to a standard kaolinite. The kaolinite in the raw dried state is black in colour due to the presence of carbonaceous impurities which in turn is the cause of high LOI value. Surface area of the raw and calcined kaolinites (metakaolinite) are shown in Table 2. The surface area of PBK-K in the raw dried state is much higher (26.6 $m^2\,g^{-1}$) than that of an ideal kaolinite (13–14 $m^2\,g^{-1}$). Reasons for the enhanced surface area are disorderness resulting in finer particles and the presence of fine ancillary minerals.

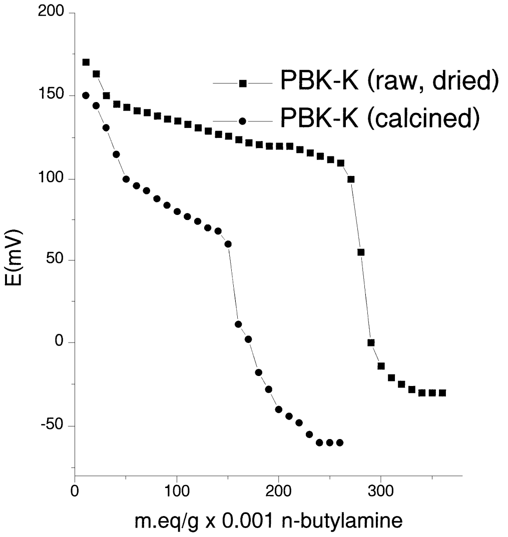

Fig. 1. Acidity distribution pattern of PBK-K and calcined PBK-K.

3.2. Acidity of activated metakaolinites

Fig. 1 shows that raw PBK-K sample contains larger number of stronger acid sites (higher *E* (mV)) compared to the metakaolinite, 550°C calcined PBK-K. This could be attributed to the presence of acidic components such as humic acid molecules strongly adsorbed on to the kaolinite surface which is removed during calcination. Moreover, metakaolinization converts partly the octahedral Al to tetrahedral Al. Al tetrahedra shows tendency to share edges rather than corners and become uncharged and hence they do not contribute to the acidity of the metakaolinite [22,23]. H_2SO_4 treatment of metakaolinite of PBK-K resulted in a considerable enhancement of stronger acid sites compared to the metakaolinite as shown in Figs. 1 and 2. In general, acid treatment of metakaolinite of PBK-K results in the process of exsolving of a large number of Al(III) cations and to a limited extent Fe(III) cations from the structure and their partial relocation in newly created pores. These relocated cations act as Bronsted acid centres in the presence of water molecules and as Lewis acid centres in anhydrous conditions. Activation of the metakaolinite with 3 and 4 M H_2SO_4 produced

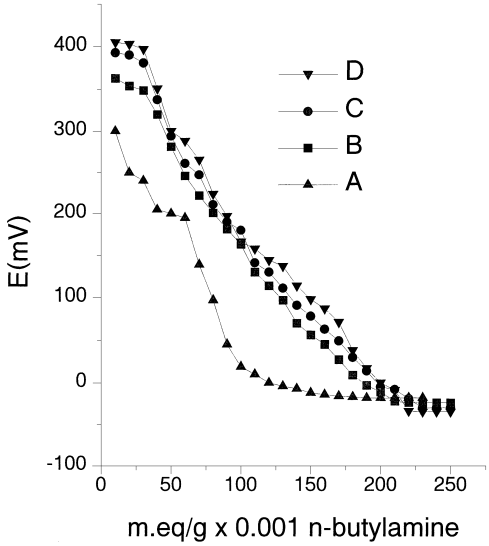

Fig. 2. Acidity distribution pattern of metakaolinite activated with H_2SO_4.

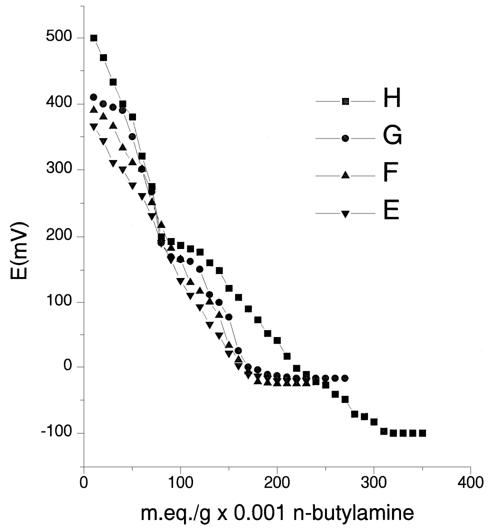

Fig. 3. Acidity distribution pattern of metakaolinite activated with HNO_3.

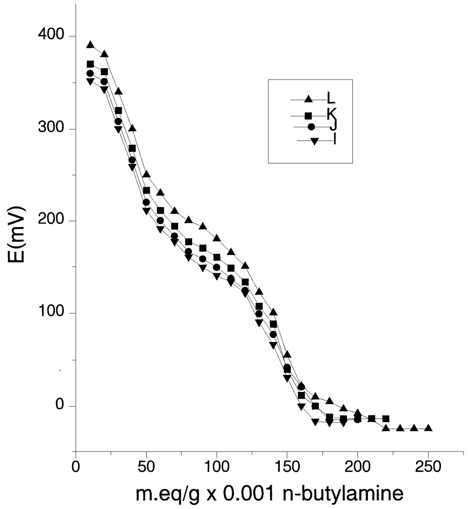

Fig. 4. Acidity distribution pattern of metakaolinite activated with $HClO_4$.

materials with more or less similar acidity distribution pattern. On further reducing the concentration of H_2SO_4 to 2 and 1 M, the highest acid strength corresponding to the highest *E* (mV) of the solid obtained decreased considerably eventhough the total acid amount remained more or less the same. In the case of HNO_3 activation (Fig. 3), increasing the concentration of acid solution from 1 to 3 M marginally increased the highest acid strength of the resulting solid acid. Refluxing the metakaolinite of PBK-K with 4 M HNO_3 produced a solid with the highest acid strength observed in the present study. Comparing Figs. 2–4, it can be noted that HNO_3 is slightly more effective as an activating agent for metakaolinite than H_2SO_4 or $HClO_4$. $HClO_4$ is comparable to H_2SO_4 of the same molarity (2–4 M) in its efficiency in producing metakaolinite based solid acids.

3.3. *Catalytic activity*

Table 3 shows the conversion and selective formation of diphenylmethane in the alkylation of benzene with benzyl chloride over the metakaolinite activated with H_2SO_4, HNO_3 and $HClO_4$ of different concentrations. The reaction time given in Table 3 corresponds to the time taken to cease the evolution of HCl vapour after attaining the reflux temperature. In the case of certain catalysts included in the present study, particularly those prepared by using $HClO_4$ solutions, the benzylation reaction proceeded slowly eventhough the experimental conditions remained the same. The longer reaction time observed may be attributed to the stronger adsorption and slow desorption (on the catalyst surface and from the catalyst surface,

Table 3
Catalytic activity of mineral acid treated metakaolinized PBK-K for alkylation of benzene

Catalyst sample	Reaction time (min)	Conversion of benzyl chloride (%)
A	40	74.16
B	45	76.55
C	30	81.33
D	45	86.12
E	45	81.30
F	40	83.70
G	90	86.10
H	30	87.00
I	105	82.26
J	90	83.00
K	270	85.62
L	240	86.50

respectively) of the product, diphenylmethane. Highest conversion to diphenylmethane in the shortest reaction time was observed in the case of metakaolinite activated with 4 M HNO_3. This may be due to the higher surface area and greater surface acidity of these samples. Even for activated metakaolinite with the lowest surface area, the conversion to diphenylmethane is above 75 mol%. Eventhough the catalytic activity of the presently studied samples differ, the selectivity to diphenylmethane obtained is 100% in all cases.

3.4. Mechanism of alkylation

Catalytic activity shown by cationic clays are due to their characteristic surface acidity. Alkylation reaction can be catalysed by both Bronsted and Lewis acid sites. In raw kaolinites, surface silanol or alanol, eventhough a few in number can catalyse the reaction. Thermal activation of kaolinite by heating above 300°C causes the removal of some of the structural hydroxyl groups in a pair-wise fashion giving rise to three coordinated Al with the loss of water molecules [15]. These Lewis acid sites can catalyse the alkylation reaction. However, in the case of acid activated metakaolinites, a significant quantity of acid sites capable of catalysing the alkylation reactions are created by the exsolved and relocated cations. The mechanism of alkylation reaction on a Bronsted acid site is analogous to that by a M^+–H species present on synthetic transition metal oxide – SiO_2–Al_2O_3 system [15,22]. Benzyl chloride interacts with the active species and forms the alkylating moiety M^+–CH_2–C_6H_5, which attacks the benzene molecule forming a Π complex. This is due to the partially filled p-orbitals of Al(III) and d-oribtals of Fe(III) [15,24–26]. The Π-complex on Π–σ rearrangement gives the product, diphenylmethane. Alkylation of benzene taking place on a Lewis acid site is initiated by the coordination of benzyl chloride giving the alkylating moiety. This alkylating moiety attacks the benzene molecule forming a Π-complex which rearranges to give the product, diphenylmethane.

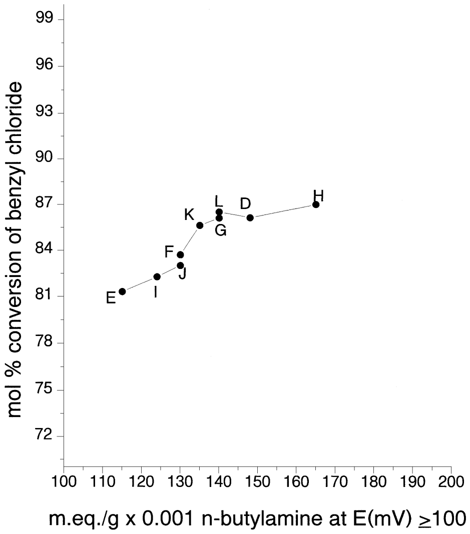

Fig. 5. Correlation of acidity with catalytic activity of different catalysts.

3.5. Correlation of acidity with alkylating activity

By comparing the acid amount values of all the acid treated metakaolinites with their alkylating activity, it is seen (Fig. 5) that acid sites with strength corresponding to an E (mV) value >100 are suitable for catalysing the benzylation of benzene. Thus, it is found that metakaolinite of PBK-K activated with 4 M HNO_3 has the highest acid amount value at E (mV)$\geq$100 and gave the maximum conversion (87 mol%) within 30 min of reaction time.

4. Conclusions

Solid acid catalysts of remarkable acidity values could be produced by the activation of metakaolinized Padappakkara black kaolinite (Kerala State, India) using HNO_3, H_2SO_4 and $HClO_4$ of concentrations 1–4 M. The metakaolinite thus activated served as extremely efficient Friedel–Crafts alkylation catalyst for the liquid phase benzylation of benzene.

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