

# Technology

Pak J Sci Ind Res 1999 42 (3) 156-160

## DEVELOPMENT OF CATALYST FROM NATURAL CLAYS FOR FRIEDEL CRAFTS ALKYLATION AND NEW SYNTHESIS OF 9,10 DIHYDROANTHRACENE

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(Received 8 September 1997; accepted 17 May 1998)

Catalytic activity of the natural kaolinitic clays of Pakistan containing transition metals (Fe and Ti) has been examined for the synthesis of 9, 10 dihydroanthracene [I]. The chemical composition of these clays has been determined with and without activation and XRF analysis has been carried out. Catalytic activity of these clays has also been evaluated for the synthesis of 9, 10 dihydroanthracene [I] of low temperature (60-100°C). This method has been standardised, which is a simple method as compared to the methods reported in the literature. The benzylation of phenol with benzyl chloride, resulting in the formation of ortho [II] and para [III] hydroxydiphenyl methane proceeds very smoothly in the water bath to yield 100% of the product. Clays containing (Ti) and (Fe) are most effective for the alkylation with benzyl chloride. Leaching of alkaline cations results in the generation of large amount of transition metal cations. This improves the catalytic effect of the acid treated clays.

**Key words:** Clay catalyst, Synthesis of 9, 10 dihydroanthracene.

### Introduction

The use of acid treated clays in catalysis is well studied especially for their use as cracking catalysts and their industrial use for alkylation of the phenols and dimerization and polymerisation of unsaturated hydrocarbons. Recently the acid treated clays have been used as catalyst in place of  $AlCl_3$  catalyst (Sabu *et al* 1993) for the benzylation of benzene. The Pakistani clays have also been evaluated with and without acid treatment as a catalyst for benzylation (Ahsan 1993). It is observed that some of the clays have very good catalytic activity for benzylation. Benzyl chloride on condensation in presence of a clay catalyst gives 9, 10 dihydroanthracene [I]. In the present study chemical and physical evaluation of the most effective clay has been studied which has industrial uses as a hydrogen donor, in heat treatment of coal, heat stabiliser and antioxidant in polymer and plastic. Keeping in view the industrial uses of this chemical, synthesis of 9, 10 dihydroanthracene has been thoroughly investigated. Benzylation of phenol using clays in place of  $AlCl_3$  has also been investigated.

### Experimental

**Analysis of clay.** Chemical analysis was carried out by standard method (Bennet and Hawley, 1965). XRD spectrographs were recorded by using Siemens D 5000 X-ray diffractometer; XRF analysis was carried out with Jeol X-ray spectrometer.

**Activation of clay.** Finely ground clay (about 10g) was treated with conc. HCl (200 ml) which was added slowly with constant stirring, the mixture was allowed to stand overnight with occasional stirring. The clay was washed 4-5 times with distilled water till the washings became neutral, then dried and calcinated at 500°C.

**Synthesis of 9, 10 dihydroanthracene.**

**Method 1 (Scheme I).** A mixture of benzyl chloride (11.0 g-0.087 mole), hexane (100 ml, b.p. 69°C) and a clay sample (MPG 98-99) (5.0 g) was refluxed in a round bottom flask for twenty minutes on a boiling water bath. Reaction proceeded with the evolution of HCl. After the evolution of HCl stopped, the solvent was removed by decantation and washed with hexane. Chloroform was added to the residue to dissolve the product and clay was filtered off. The filtrate was concentrated to get the crystalline product which was dried and weighed (7.5g) and its m.p. (106°C) was also taken. The I.R. spectrum of the product was found to be identical with that of 9, 10 dihydroanthracene [I] given in Stadler No.19205. The reaction was repeated using different clays under the same conditions. The results are depicted in the Table 1.

**Method 2.** A mixture of benzyl chloride (11.0 g) and clay sample (MPG 98) (5.0 g) was heated on a boiling water bath. The



Scheme 1

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reaction was over in 15-20 min when the evolution of HCl gas stopped. Chloroform was added to the mixture to dissolve the product. Clay was filtered and the filtrate was concentrated to get a crystalline product (7.4 g, m.p. 106°C). Its m.p. and IR were taken. The same reaction was carried out using different clays under the same conditions. The results are depicted in Table 2.

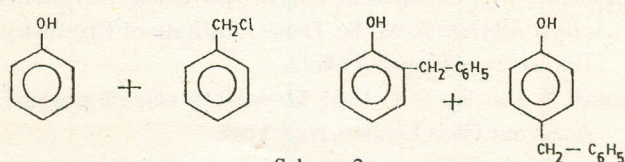
**Synthesis of hydroxy diphenyl methane (Scheme 2).** Phenol (10.0 g, 0.106 mole) and Benzyl chloride (12.0 g, 0.1 mole) were taken in a round bottom flask. Clay samples (5.0 g) were added and then the mixture was refluxed on the water bath. After completion of the reaction the mixture was identified by IR spectrum which indicated that the product is a mixture of two compounds, o-hydroxy diphenyl methane and p-hydroxy diphenyl methane.

**Table 1**

Sample No.	Reaction Time	Yields(%)
MPG 96	2 h	50
MPG 97	2 h	60
MPG 98	15-20 min	over 90
MPG 99	15-20 min	over 90

**Table 2**

Sample No.	Reaction Time(min)	Yield (%)
MPG 96	After 20	48
MPG 97	20	50
MPG 98	15-20	over 90
MPG 99	5-10	over 90



Scheme 2

## Results and Discussion

Pakistan possesses large resource of high aluminous clays, fire clays, kaolins and bentonites which are still undeveloped and under exploited. Most of the clays produced in the country are consumed by the refractory bricks and ceramic industry. Kaolin is utilised by ceramic industries after elutriation, bentonites are activated and utilised for edible oil clarification and by the petroleum and chemical industries. These clays have never been evaluated as an absorbent of various toxic gases or as an industrial catalyst. It is a well-established fact that clays containing transition metals, Iron (Fe) Titanium (Ti) and Aluminium (Al) show catalytic activity for alkylation in place of  $AlCl_3$  (Ahsan 1993; Sabu *et al* 1993).

XRD pattern of the clay before and after activation indicated that both are disordered kaolinite  $Al_2Si_2O_5(OH)_4$  and illite trioctahedral  $KO_5(Al, Fe, Mg)3(Si, Al)_4O_{10}$ . After acid treatment a change is observed in the proportion of transition metals (Fe, Ti) and Al. The treatment with cold HCl conc. has little effect on the composition of the host layer and results in an acid treated clay. The acid attack on the clay structure progresses inward from the edge of the clay platelets leaching alkaline cations, particularly Mg, Ca, K and to some extent Fe. Acid activation causes little damage to the silicate layer and the structure in the centre of the platelets remains unaffected. XRD studies of the sample confirm the results of XRF evaluation (Table 3) as well as chemical analysis (Table 4). The d-spacing of the clays were observed at  $d=7.1506, 3.5700$  and  $4.3462$ .

Two samples (MPG 96, MPG 98) of clay contain the transition metals such as Fe, Ti, Al., etc. The quantity of Fe slightly differs in both the samples but Ti is almost 2.5 times and Al is about 5 times more in MPG 98 as compared to MPG 96. Sample MPG 96 shows very little activity in the raw and dried form. It is only active at a higher temperature but sample MPG 98 is

**Table 3**  
Elemental analysis by X-ray fluorescence spectrometer

Element	MPG 96 (inactivated clay)	MPG 97 (activated clay)	MPG 98 (inactivated clay)	MPG 99 (activated clay)
Sr	1.52	-	-	1.71
Fe	39.00	44.33	45.38	17.19
Ti	6.50	11.10	16.69	28.55
Ca	30.30	1.20	1.54	-
Al	1.52	2.17	7.69	16.07
Mg	4.24	-	-	-
P	0.06	-	-	-
S	3.94	6.67	16.92	32.86
Cd	2.12	-	-	-
Sn or K	-	23.30	7.69	2.01

**Table 4**  
Chemical analysis of clay catalysts

Sample clay	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	CaO	Loss on ignition
MPG 96	47.26	21.12	4.50	0.375	1.17	1.72	3.54	8.40	11.84
MPG 97	63.78	20.2	4.00	0.75	0.58	0.17	1.51	4.20	4.40
MPG 98	11.84	29.53	37.50	4.75	0.90	0.45	1.51	3.50	10.12
MPG 99	20.16	41.12	16.00	4.75	0.40	0.32	0.01	3.50	12.14

quite active in raw form too. After the activation and calcination, both the samples exhibit increased catalytic activity for the conversion of benzyl chloride into 9, 10 dihydroanthracene.

In sample MPG 96, after activation and calcination the improvement in composition of Fe is very small but Ti and Al is improved almost twice as much. But in sample MPG 98 the quantity of Fe is reasonably less and quantity of Ti is increased almost 2 times more than the original clay. Similarly MPG 99 is a good catalyst in the alkylation of hydrocarbon with benzyl chloride. Benzyl chloride is easily converted into 9, 10 dihydroanthracene [1] on water bath with a yield of over 90%.

XRF analysis shows that Ca, Mg and K have been completely eliminated with acid treatment. Natural clays having transition metals in their lattices possess disordered structure and hence, on acid activation, result in the generation of larger amounts of transition metal cations. It is known that clay which has isomorphously substituted Fe (II) or Ti (II) has a higher degree of disorder (lower crystallinity) than an ideal clay. Hence the structure of this clay could be easily attacked and ruptured by the process of calcination and acid treatment resulting in the leaching of alkaline cations (K, Ca, Mg) and formation of relocatable cations Fe, Al of Ti of transition metal with respect to each other. The surface area and acidity of these clays increase with leaching of alkaline cations. The catalytic activity of activated clays is moderate as compared to AlCl<sub>3</sub> catalyst. Hence polysubstitution and polymerisation is not possible. This quality has enabled us to synthesise 9, 10 dihydroanthracene from benzyl chloride. The synthesis of this compound was not possible with AlCl<sub>3</sub> because dihydroanthracene is converted to anthracene with AlCl<sub>3</sub> and polymerisation of benzyl chloride also takes place. Thus while manufacturing diphenyl methane, the reaction is carried out with excessive quantity of benzene. These catalysts have given us a simple method of synthesis of dihydroanthracene which till now has been manufactured by the reduction of anthracene.

Acid treatment enhanced the activity of most of the clays to a very little extent whereas some of the clays like bauxite showed

no activity after treatment. The activity of these clays is most probably due to transition metals such as Fe and Ti.

The methods for the synthesis of 9, 10 dihydroanthracene are mostly based on the reduction of anthracene by physical or chemical methods. The simplicity and ease of formation of the dihydroanthracene alone by using these clay catalysts is the basis of this simple synthetic method.

The alkylation of phenol with benzyl chloride in the formation of ortho and para-substituted benzylphenol (Scheme 2) proceeds very smoothly in a water bath to yield 100% of the product. These catalysts are very useful for the alkylation of organic compounds and are a substitute for aluminium chloride. The reactions are less complicated. Moreover, the removal of these clay catalysts is easier as compared to aluminium chloride. However, these clay catalysts have proved to be ineffective for the synthesis of triphenylmethane from chloroform, benzene, and anthraquinone from phthalic anhydride and benzene.

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