Short Communication

CATALYTIC ACTIVITY OF PAKISTANI CLAY MINERALS FOR FRIEDEL-CRAFTS ALKYLATION OF BENZENE AND NAPHTHALENE

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Majority of the catalysts used by organic chemist are based on naturally occurring clays and minerals. These catalysts are prepared from the clays and minerals and are marketed by various chemical companies. The natural clays or minerals also find utility as a catalyst support and also suitable catalyst for the conversion of larger molecules. The clays supported reagents are known as pillared clays.

It has been observed that montmorillonites exchanged with the Fe (III) ions are effective for variety of Diels Alder reactions and for chlorination (Groggins, 1958). The transition metal atom present in natural clays is thought to be the seat of impressive and varied catalytic activity. Recently, the activity of natural clays as catalysts for Friedel Craft alkylation has been investigated by Ehsan et al 1999. 9, 10 Dihydroanthracene has been synthesized by using L-99 clay catalyst from benzyl chloride. The clay composition and structure changes with the change of source and number two clays are identical in all respect.

The activity of a Pakistani clays and minerals as a catalyst in an organic synthesis have not so far been investigated. The use of alumino silicate as catalyst in various organic synthesis is most environmentally sound because of ease of handling, work up, non-corrosiveness and low cost. In this study the catalytic activity of various Pakistani clays and minerals have been investigatd with a view to substitute them for aluminium chloride ($AlCl_3$) in the Friedel Craft reaction. Benzylation of benzene & naphthalene have been carried out using activated clays (L-99) [MPG 99, Ehsan et al 1999] as catalysts. Simple Benzylation of naphthalene has not been reported by friedel crafts reaction (Nurullah et al 1995 and Walter et al 1941). The yield and specificity of the reaction have been investigated. The clay catalysts (L-99) are better than $AlCl_3$ for benzylation of benzene and naphthalene.

Various minerals and clays (Table 1), which differ in their chemical composition, have been used for the purpose.

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Microprocessor contolled double beam Hitachi infrared Spectrophotometer Model 270-30, Hitachi Ltd., Tokyo, Japan was used for analysis.

A Siemens Diffractometer model D 5000 was employed for X-ray diffractometry.

Analysis of clay and minerals. Clay particles separated from the coarse material were dried at 125°C. Standard analytical/digestion procedures were adopted (Bennet et al 1965) for the determination of major oxides in the clay samples (Table 1).

Activation of catalyst. Clay samples were treated with HCl (1:2 parts by Wt.). Acid was removed and clay was washed with absolute alcohol. Alcohol dried samples were calcinated at 500°C.

Determination of catalytic activity of mineral clay. A mixture of benzyl chloride, Hexane and clay sample was refluxed on a round bottom flask for twenty minutes on a boiling water bath. Reaction proceeds 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 dissolve the product and the clay was filtered off. The filtrate was concentrated and yield of the 9, 10 dihydroanthracene was recorded (Ehsan et al 1999).

(i) Mixture of benzyl chloride and clay was refluxed on a round bottom flask for twenty minutes.

(ii) A mixture of benzyl chloride and the catalyst was heated above 100°C. After the evolution HCl was stopped yield was recorded.

Synthesis of diphenyl methane (Fig 1). Catalyst L-99 (2 g) was added to the mixture of benzene (50 ml, 0.64 mole) and benzyl chloride (12.6 ml, 0.1 moLe) and heated up to 60°C on water bath. Conversion of benzyle chloride to biphenyl methane took place at this temperature. Unreacted benzene was distilled under vacuum. Biphenyl methane (10 gm, yield 60%) was distilled at 262°C. It was confirmed with I. R. Stadler spectrum No.3389 against pure biphenyl methane.

Synthesis of benzyl naphthalene (Fig 2). A mixture naphthalene (12.8 gm, 0.1 mole) and catalyst L-99 (5.0 gm) were taken in a round bottom flask fitted with a condenser and heated on boiling water bath. The naphthalene and catalyst were thoroughly mixed and benzyl chloride (12.6 gm, 0.1 mole) was added to the mixture. The reaction proceeds on boiling water bath with the evolution of HCl. After the evolution of HCl stopped the mixture was cooled. The final pro-duct was washed with absolute alcohol (50 ml) twice. Residue was dissolved in hexane (100 ml) and filtered to remove the catalyst and solvent was evaporated to get benzyl naphthalene (11.50 gm, 52%) crystallized out in

Table 1
Catalytic Activity of Pakistani Clays for Alkylation (Friedal Craft Reaction)

Clay and Minerals	Ferrogenous Clay	Bauxite	Bauxite	Bauxite	Bauxite (high-grade)	Ferrogenous Clay	Ferrogenous Clay
Loss of ignition	15.20	13.26	13.96	13.79	13.52	11.84	12.14
SiO_2	12.10	44.41	40.64	36.50	42.56	47.26	20.16
Al_2O_3	30.80	37.17	39.51	45.01	38.23	21.12	41.12
Fe_2O_3	35.20	0.15	0.23	0.30	2.14	4.50	16.00
Na_2O	-	2.00	1.80	1.50	0.63	1.17	0.40
K_2O	-	0.11	0.18	0.13	0.18	1.72	0.32
TiO_2	5.5	0.59	0.64	1.11	1.57	0.375	4.75
CaO+MgO	-	1.53	1.78	0.96	-	11.94	3.51

Illmunite ($FeTiO3$), Rutile (TiO_2) and Kaolinite were collected from the market. All showds negative activity with or without acid treatment.

hexane. mp. 54.56°C. IR (KBr) 3020, 2904, 1590, 1490, 1432, 1388 cm^{-1}.

X-ray Diffraction of Clay Samples. Clay samples were collected from various parts of Pakistan and X-ray diffraction of clays was recorded as such and after activation. XRD patterns of clay samples indicate that the major component is Kaolinite [$Al_2Si_2O_5(OH)_4$]. A wide variation in the crystal structure of the clay sample has been observed after the treatment. it has been converted partially to disordered kaolinite, the crystalline index being about 0.89. The non-clay impurities have been detected which include quartz and gibbsite. These impurities were not present in a considerable amount but they were sufficient for detection by XRD. No change in the crystal structure of quartz and gibbsite was observed. Kaolinite clay structure had been partially destroyed after heating at 500°C. The peaks for calcium carbonate as calcite/aragonite are also absent after activation due to the complete removal of carbonate.

$AlCl_3$ is an industrial catalyst, which is employed for the manufacture of a number of industrial chemicals that are commonly

(Fig 1)

(Fig 2)

used in everyday life. Handling of $AlCl_3$ causes many problems like the construction of plant with specific material and size. The plant should be such that a known amount of catalyst packing may be emptied directly into the reactor. Workers also have to wear special clothes. These problems make the synthesis difficult and the product very expensive.

A simple and non-corrosive catalyst, has to be develop Chemicals like H_3PO_4, HCl, HF, $FeCl_3$, BF_3 are since long known to replace $AlCl_3$ as catalyst. But these are again difficult to handle and moreover, are carcinogenic in nature. It may be stated that recently a tragic incident of abnormal lung cancer was reported in Permutit plant where chloromethyl either was being prepared, using $AlCl_3$ as a catalyst (Leslie *et al* 1993) in the preparation of an ion-exchange resin a plant chemist, production worker and a fitter died of lung cancer.

To overcome such hazards, clays were tried to substitute $AlCl_3$ in the synthesis chemicals. It was observed that with clay catalysts, synthesis of biphenyl-methane becomes simple and synthesis of α and β benzyl naphthlene simple and possible. One has just to distil out only the unreacted benzene to get biphenyl methane directly. In the original method (Vogel *et al* 1989) the reaction was to be carried out under strictly controlled conditions. Presently no ice is to be added into the reaction vessel to decompose the aluminium complex and biphenyl is only distilled from the reaction flask. Biphenyl methane was checked by infrared spectrum. During alkylation with $AlCl_3$ a number of side reactions like polymerisation, isomerization, dehydrogenation start, destroying alkylation. All these are not produced if the reaction is carried out by clay catalyst. It is because the catalytic activity of the clay catalyst L-99 is moderate and side reactions do take place.

A possible convenient method for the synthesis of benzyl naphthalene would have been benzylation of naphthalene in
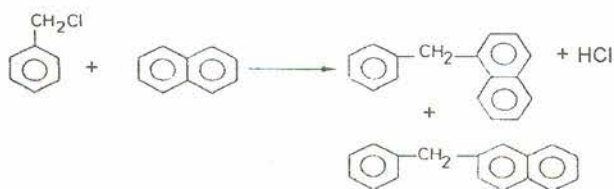
presence of Fridel Crafts catalysts such as $AlCl_3$, $FeCl_3$, $TiCl_4$ and $ZnCl_4$. Literature survey (Nurullah *et al* 1995; Rife Chambers *et al* 1985; James Smith *et al* 1980; Evans *et al* 1957; Orchin *et al* 1949; Lean Bradlow *et al* 1947 and Walter *et al* 1941) revealed the absence of any reported method of synthesis of benzyl naphthalene with benzyl chloride. Recently Albar (Albar *et al* 1996) reported method of synthesis of mixture of α and β benzyl naphthalene with benzyl alcohol using K-10 montmorillonite as catalyst. Melting point and IR of α and β bezyl naphthalene are almost the same as reported in literature. All the known methods of the synthesis of these compounds are not easy and economical so Benzyl Naphthalene is not available commercially. The present study demonstrates the simple method for the synthesis of benzyl naphthalene. The reaction is carried out on water bath and the product is thoroughly washed with ethanol to remove the reactants. Residue is dissolved in hexane and filtered. Hexane is removed on the water bath to get the final product. The yield of benzyl naphthalene is 52%. Sublimed naphthalene is recovered from washings.

Transition metals are known to behave as catalyst in many reactions. Perhaps the activities of these clays are due to the transition metal present in the alumino-silicate system. All Pakistan clays showed catatytic activity for alkylation before calciation but after calcination only ferrogeous clay showed activity in Table 1. Some of the minerals become inactive after leaching with strong acid. The leaching of clay with strong HCl perhaps has removed any such transition metal present in the mineral. Moreover, the clays which contain more ferroginous matter and TiO_2, show more catalytic activity.

It has been reported that normal clays have almost no activity (Attapollagite, Montmorillonite), but it is relatively easy to convert them into useful catalysts by either acid activation or cation exchange with polyvalent ions such as Al^{+3} or Cr^{+3}. Treatment of clays with strong mineral acid causes considerable delamination of structure, producing an increase in surface area, particularly at the sheet edges, as well as adsorption of quantities of acid on both internal and external surfaces. The swelling properties have been employed to manufacture "pillard clays". The ready-made catalysts can be purchased from variety of commercial resources. It is observed that crystalline minerals such as Illmunite ($FeTiO_3$), Rutile (TiO_2), Bauxite (Al_2O_3) that cannot be affected by acid does not show any catalytic activity for benzylation reaction. The clays having transition metals show chemical activity. The catalyst L-99 shows activity with or without acid treatment.

It has been reported that heating the acid treated clay to higher temperature (500°C) results in collapse of clay interlayer structure as water is driven out resulting in decrease in Bronsted acidity but increase in Lewis acidity. The catalytic activity of L-99 is due to Lewis acidity. Heating up to 500°C results eventually in complete dehydroxylation of alumino silicate lattice, producing completely amorphous L-99 that retains Lewis acidity.

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