# Benzylation of Benzene and Toluene with Benzylchloride over Clay-Based Acid Catalysts

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The pillared clay catalysts were calcined after in corporation of metal polycation ions with exchangeable cations and water. Friedel-Crafts alkylations of aromatic hydrocarbons were carried out in the presence of clay catalysts originating from bentonite. In these reactions, it has been found that pillared clays have excellent catalytic activity. It was found that iron pillared clay (Fe-PILC) was the more efficient catalyst producing quantitative conversion with greatly reduced amounts of catalysts in short reaction period. Their efficiency is attributed to the higher $Fe^{3+}$, $Cr^{3+}$ and $Al^{3+}$ contents in the catalysts and pillaring effect. The clays have both Bronsted and Lewis acidities which were determined by pyridine adsorption-desorption and *in situ* FTIR technique.

Key words:   Friedel-Crafts alkylation, Bentonite, Pillared clays, Surface acidity

## INTRODUCTION

Acid-treated clays were used as catalyst in petroleum refining[1] in early 1930. The use of montmorillonites as heterogenous catalyst has been reported by Ballantine[2]. An extensive review by Adams[3] describes the use of pillared, acid-treated and cation exchanged clays in synthetic organic chemistry. The catalytic applications of clays have been reviewed by Laszlo[4]. The applications of clays, modified by pillaring, cation exchange and isomorphous substitution in organic synthesis have been discussed by Izumi *et al.*[5] An exhaustive review on industrial applications of various acid-treated clay catalyzed reactions has been published by Chitnis and Sharma[6].

Among the Lewis acids, anhydrous aluminium chloride was the more widely employed reagent to trigger the Friedel-Crafts reaction in the liquid phase in the laboratory as well as in industry[7]. The major disadvantages encountered in the use of anhydrous aluminium chloride include corrosion, unfriendliness to environment, heavy expense due to requirement of large excess of reagent and waste by products induced by isomerization in the reaction. In view of these reasons, there was a long-felt need and demand to substitute these reagents by less corrosive and environment friendly materials in the Friedel-Crafts reactions. Intensive research in this direction revealed the materials in the form of solid acids developed from natural clays[8, 9]. Solid acids derived from montmorillonite (bentonite) by the

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process of exchange with different metal ions[10, 11] and impregnation with the salts of the metals were explored as catalysts in the alkylation of aromatic hydrocarbon. The report of Cseri *et al.*[11] have showed that metal ion-exchanged bentonites in the alkylations of aromatic hydrocarbons indicated that the catalyst containing reducible cations ($Fe^{3+}$, $Cr^{3+}$, $Sn^{4+}$) exhibited high activities in spite of their low number of Lewis acid sites when benzylchloride was used as alkylation agent. Olah *et al.*[12] has surveyed the Lewis acids as catalysts in the Friedel-Crafts reaction and also provided a scale for their efficiency.

The result of the Friedel-Crafts alkylations of aromatic hydrocarbons catalyzed by various metal supported bentonite catalysts including both the metal hydroxyl-oxy oligomers intercalated in the interlayers of bentonite has been reported in the present work. The study correlating the iron, chromium and aluminium contents and activities of pillared clays in alkylation of benzene and toluene with benzyl chloride is presented.

## EXPERIMENTAL

Bentonite was used as clay in this study and obtained from the town of Resadiye in Tokat, Turkey[13]. Bentonite: 58.3% $SiO_2$, 2.5% MgO, 16.0% $Al_2O_3$, 1.1% $K_2O$, 3.5% CaO, 0.6% $TiO_2$, 2.0% $Na_2O$, 0.1% $P_2O_5$, 3.1% (FeO + $Fe_2O_3$), 13.0% loss on ignition. The IR spectrum of natural bentonite indicated a moderate $Fe^{3+}$ content (885 $cm^{-1}$) with the presence of detectable quartz 697 $cm^{-1}$ and silica phase 797 $cm^{-1}$ impurities.

The aromatic subtances were obtained from commerical sources. Infrared spectra were recorded with Mattson FTIR-1000 under vacuum without using KBr in the range 4000–400 $cm^{-1}$. The diffractogram of X-ray powder diffraction patterns were recorded on a PTS-3000 with Ni-filtered $CuK_\alpha$ radiation.

FTIR spectra of pyridine adsorbed on the pillared-clay catalysts were recorded on a Mattson-100 FTIR spectrometer. The specific surface area of the samples was determined by BET method and the samples were degassed at 110°C under vacuum ($10^{-5}$ torr). The Sorpmatic 1990-Fission instrument (Protec GmBh) was used in order to calculate $N_2$ adsorption. The activity-time correlation of catalysts and the conversions of the acylation were followed by analyzing the samples of the reaction mixture collected at regular intervals by Shimadzu GC-14A model gas chromatography.

### Preparation of the catalysts

Solutions of 0.1 M ferric chloride, chromium chloride and aluminium chloride were prepared by dissolving equivalent amount of salt in deionized and distilled water. The solution of 0.1 M NaOH was slowly added to alter the pH of the mixture. The hydrolysis of $FeCl_3$, $CrCl_3$ and $AlCl_3$ was carried out at 25°C by using 0.1 M NaOH solution and 24 h were allowed for aging. The values of $OH^-/Fe^{3+}$, $OH^-/Cr^{3+}$ and $OH^-/Al^{3+}$ were found to be 2, 1 and 2, respectively. The pH of these solutions were measured as 2.5, 1.46 and 4.3, respectively. The clay suspensions (10 g clay in 500 $cm^3$ of water) were added to the 500 $cm^3$ hydrolyzed ferric and chromium solutions. The clay suspensions and the pillaring agent were intermixed for 8 h before being filtered, washed and dried at 300, 240 and 400°C in the oven for 4 h.

### Alkylation

Benzylchloride and benzene or toluene in the ratio 1 : 2 were mixed and the mixture was heated in a reactor at 25°C under $N_2$ atmosphere, every 60 min for 5 h.

The reaction mixture was stirred at the same temperature for 5 h. The reaction was monitored by GC. The products were seperated from the reaction mixture by fractional vacuum distillation. The pure compounds were characterized using IR spectroscopy and comparison of their boiling points with authentic samples.

## RESULTS AND DISCUSSION

The physcochemical characterization of the catalysts was carried out by $N_2$ adsorption techniques. The XRD patterns of natural montmorillonite and metal polycation-treated montmorillonite were recorded and increase in the basal spacings was observed. The expansion in the basal spacing of the montmorillonite due to the intercalation of metal-polycations was calculated as $\Delta d = d - 9.6$ Å, where d is the basal spacing of the pillared clays. The basal spacings and the surface area of the samples are given in Table-1.

TABLE-1
BASAL SPACING ($d_{001}$), SPECIFIC SURFACE AREAS (S.A.) AND
MICROPORE VOLUMES (V) OF THE PILCs

| Sample | $d_{001}$ (Å) | S.A. (m2/g) | V (cm³/g) |
|--------|---------------|-------------|-----------|
| Bentonite | 8.95 | 53 | 0.181 |
| Fe-PILC | 7.59 | 87 | 0.133 |
| Cr-PILC | 8.95 | 92 | 0.099 |
| Al-PILC | 5.30 | 60 | 0.089 |

In view of the above statments, the presence of acid sites was also confirmed by pyridine adsorption studies under vacuum. Fig. 1 shows the FTIR spectra
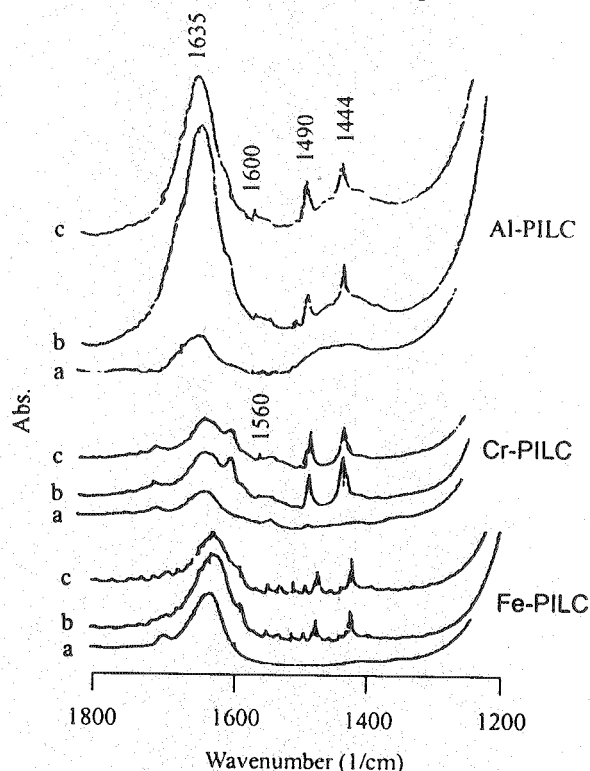


Fig. 1.  FTIR spectra of pyridine adsorbed on the pillared clays: (a) Reference  (b) 60 min adsorption, (c) 298 K desorption

obtained from pyridine adsorbed on the pillared clays. The surface acidity was evaluated by FTIR spectroscopy of adsorbed pyridine[14, 15]. A general decrease of FTIR bands intensity in the 1800–1400 cm$^{-1}$ region was observed, in particular of 1560, 1540 cm$^{-1}$ and 1490, 1450 cm$^{-1}$ bands typical of the pyridine banded to the Bronsted and Lewis acid sites, respectively[16]. It seems that the low catalytic activity of the $Al^{3+} > Cr^{3+} > Fe^{3+}$ clay is probably due to the relative weakness of the surface Lewis acid sites on this catalyst. In contrast, the $Cr^{3+}$, $Fe^{3+}$ exchanged clays both exhibit stronger Lewis acidity and significantly higher catalytic activities.

The reaction was monitored by GC, until all starting benzylchloride was consumed. As can be seen from Table-2, it has been found that all catalysts have been examined. These catalysts have very effective alkylation activity of benzene and toluene. The conversion as a function of the reaction time for alkylation of benzene and toluene with benzylchloride is given in Fig. 2.
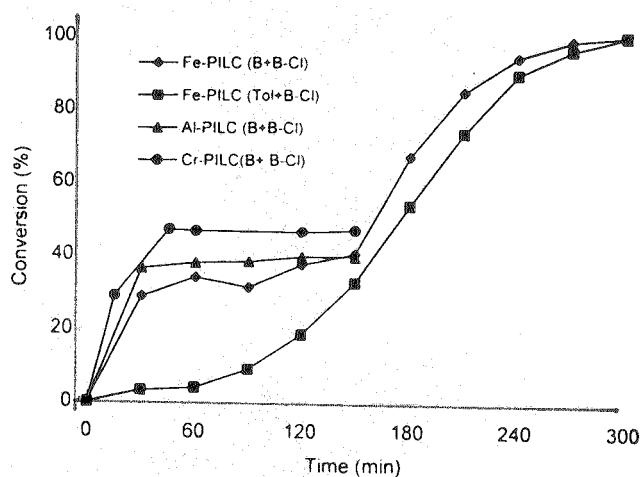


Fig. 2. Conversion as a function of the reaction time for alkylation of benzene and toluene with benzyl chloride taking amounts of pillared clays

TABLE-2
BENZYLATION OF BENZENE AND TOLUENE WITH BENZYL CHLORIDE
USING DIFFERENT CATALYSTS (100 mg) AT 25°C

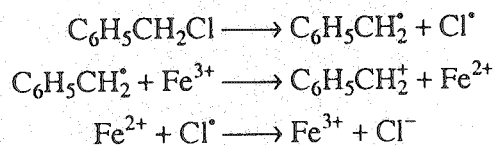| Catalysts | Substrate | Time (h) | Conversion[a] (%) | Monoalkylated product (%) | Other product (%) |
|-----------|-----------|----------|-------------------|---------------------------|-------------------|
| Fe-PILC | Benzene | 5 | 100 | 95 | 5 |
| Fe-PILC | Toluene | 5 | 100 | 95 | 5 |
| Cr-PILC | Benzene | 3 | 52 | 5 | 47 |
| Al-PILC | Benzene | 3 | 31 | 24 | 7 |

[a]Conversion of benzylchloride determined by GC.

## Conclusion

The determination of acid properties of the pillared clays shows great difference in acidities among the samples dried at 393 K. The samples calcinated at 513, 573 and 673 K are converted to rather Lewis acids and the number of sites varies in a certain range, as evidenced from the intensities of the FTIR bands of pyridine.

Calcination of sample has also a strong influence on the activity when benzyl chloride is used as alkylation agent.

These results suggest that the slow step of the reaction is different in the case of benzylchloride, and that some particular mechanism occurs in the case of reducible cations. The $FeCl_3$ in clay can be reduced at room temperature and can produce radicals by interaction with anisole. It is well known that Friedel-Craft's reaction proceeds through carbocations[7] and that radicals are powerful redundants, which should readily be oxidized to cations in presence of reducible metallic ions such as $Fe^{3+}$ as shown in **Scheme-1.**

$$C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2^{\bullet} + Cl^{\bullet}$$

$$C_6H_5CH_2^{\bullet} + Fe^{3+} \longrightarrow C_6H_5CH_2^{+} + Fe^{2+}$$

$$Fe^{2+} + Cl^{\bullet} \longrightarrow Fe^{3+} + Cl^{-}$$

**Scheme-1.**    The oxidation of alkylhalogenes by $Fe^{3+}$

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