

## Utilization of Metal-Pillared Montmorillonite as a Remarkable Solid Acid Catalyst for the Synthesis of Linear Monoalkylbenzenes

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### Abstract

Alkylation of benzene with 1-dodecene catalyzed by metal-pillared montmorillonite (M-PILC, M = Al, Cr, Fe, Al-Fe, Fe-Cr) was successfully carried out. The formation of linear monoalkylbenzenes in 98% yield in the presence of Fe-PILC during two hours is remarkable. The 2-phenyldodecane obtained with 30% concentration within the other 3-, 4-, 5-, and 6-monosubstituted products is similar to that obtained in Universal Oil Products Detal catalysis process.

**Keywords:** Alkylation; Benzene; 1-Dodecene; Metal pillared; Motmorillonite

### 1. Introduction

The nonlinear alkylbenzenesulfonate formed the basis for the heavy duty household washing powders of the 1950s and early 1960s with excellent cleaning ability. But rivers and lakes soon began foaming since enzymes present in bacteria could not degrade these "hard" detergents because of the highly branched side chain. Based on the investigation into the problem, it became apparent that detergents made of linear alkylbenzenesulfonate (LABS) are "soft" or biodegradable [1].

The HF alkylation technology which was originally developed by the Philips Petroleum Company in 1942 in producing aviation fuel was later used in the alkylation of benzene with tetrapropylene. Universal Oil Products (UOP) participated in the development of HF-catalyzed process for the manufacture of alkylbenzenes. The standard process used by industries for producing linear alkylbenzene (LAB) consists of linear olefins produced either by Shell Higher Olefin Process (SHOP), or

catalytic dehydrogenating linear paraffins to linear olefins (Pacol Process) and then alkylating benzene with the linear olefins in the presence of a catalyst such as HF or AlCl<sub>3</sub>. The HF-based process became more prevalent than that is based on AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and AlCl<sub>3</sub> have customarily been used as the Friedel-Crafts alkylation either in laboratory or in commercial scale during the past years. Reaction of olefin with acid generates the carbenium ion which reacts with the benzene molecule in a second step. Due to the greater stability of the secondary carbenium ions compared with the primary carbenium ions, practically no-1-phenylalkane is formed [2]. The use of these catalysts gives rise to many problems including handling, safety, corrosion and waste disposal and hence is not benign and environmentally friendly [2]. The search for the alternative solid acid catalysts has been under investigation due to the need of green-sustainable technology. By knowing that about a major part of the 30 million tones of the world benzene production is alkylated by acid catalysts, the need for the substituted

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solid acids in order to eliminate the environmental hazardous materials can be envisaged [3]. Therefore, many efforts have been devoted to the search of solid acid catalysts having properties such as more selectivity, environmentally friendly, reusable and not to be destroyed after reaction. Among the solid acids considered as catalysts for benzene alkylation, various zeolites [4-6], clays [7-8], heteropolyacids [9-10], sulfated zirconia [11], and immobilized ionic liquids [12-13] were tested. However, they gave results, which have not industrially exploited so far [3]. The introduction of a solid catalyst system in 1991 by UOP, commercially known as the Detal process [2], led to a number of technical process advantages such as non-corrosive medium, complete regeneration of the catalyst, fewer demands on the plant materials, omission of neutralization streams, omission of fluoride removal, smaller technical safety costs and smaller apparatus costs [2,3]. The catalytic applications of clays modified by pillaring, cation exchange and isomorphous substitution in organic synthesis have been discussed previously [14]. Moreover, an exhaustive review on industrial applications of reactions catalyzed by various acid-treated clays has been published recently [15-16].

In this article, we are pleased to report the successful alkylation of benzene with 1-dodecene catalyzed by metal-pillared M-PILC (M = Al, Cr, Fe, Al-Fe, Fe-Cr).

## 2. Experimental

### 2.1 Chemicals

All chemicals used in this research were purchased from Merk Company and used without further purification. Montmorillonite was obtained from Sigma.

### 2.2. Physical Measurements

Powder XRD patterns of samples were recorded on a diffractometer type, SEIFERT XRD 3003 PTS, Cu  $K\alpha_1$  radiation ( $\lambda = 0.1540$  nm). Products were characterized by GC (Agilent series 6890) and GC-Mass system (complex mass selective detector Agilent 5973 net work and GC Agilent 6890 net work). FTIR spectra of the samples were collected on a Bruker (Tensor 27) instrument using KBr pellet technique in the range of 4000-400  $\text{cm}^{-1}$  (5 mg sample with 100 mg KBr). Quantitative analysis of M-PILC for determination of Fe, Cr and Al metals were carried out by atomic absorption method using the 109 model from GBC Company.

### 2.3. Alkylation of Benzene: General Procedure

The M-PILC (M= Al, Cr, Fe, Al-Fe, and Fe-Cr) were prepared according to the procedure previously reported in literature [17,18]. In a typical experiment, 25 mmol of benzene and 1mmol of 1-dodecene were mixed with 1gram of M-PILC in a Parr Instrument 50 mL stainless steel autoclave. The mixture was heated for two hours at 120°C. After cooling, the mixture was subjected to GC and GC-Mass analyses.

## 3. Results and Discussion

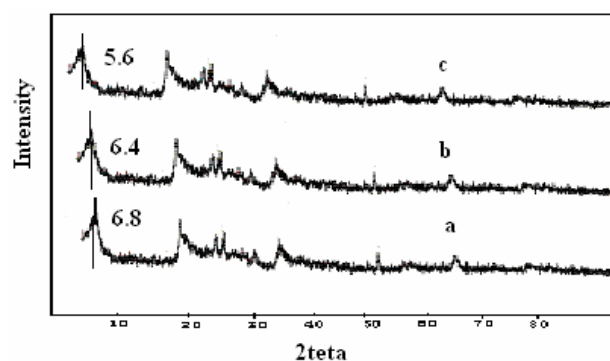
Montmorillonite is a clay mineral that can hold a variety of guest molecules between its layers. The cations can be replaced by hydroxyl metal lattice layers. Upon calcination, the clay is converted into a rigid microporous material with substantial surface area due to the formation of oxide pillars. Thus, the pillaring of clays enables the formation of layer pores that can adsorb bulky reactant molecules [19]. Different pillared clays such as Fe-PILC, Cr-PILC, Fe-PILC, Ca-PILC and Ti-PILC have been prepared [20].

Table 1 presents the basal spacing ( $d_{001}$ ) of montmorillonite and M-PILCs. The XRD patterns of natural montmorillonite,  $\text{Fe}^{3+}$ -montmorillonite and Fe-PILC are depicted in Figure 1. We have selected the Fe-PILC as the representative metal-pillard since this solid showed the highest alkylation catalytic activity (*vide infra*). As seen in Figure 1, the  $d_{001}$  position of Fe-PILC is 15.54Å in comparison to  $\text{Fe}^{3+}$ -montmorillonite which is 14.33Å. The increase in basal spacing is due to pillaring [17].

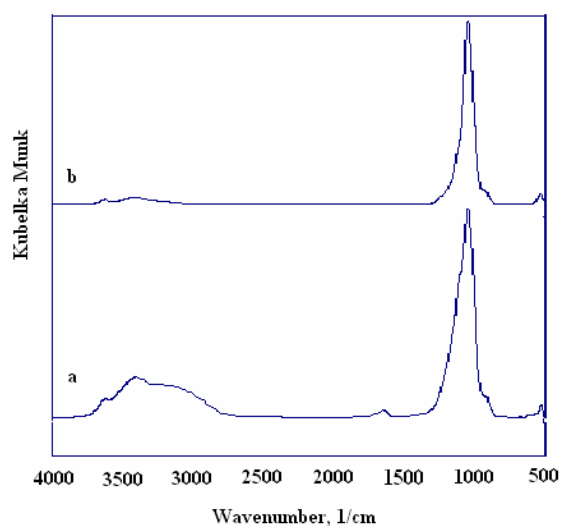
The Kubelka Munk (KM) of natural montmorillonite and Fe-PILC are shown in Figure 2. As it is seen, the intensity of silicate layers OH stretching in the region of 3600-3000  $\text{cm}^{-1}$  in Fe-PILC extensively decreases relative to the natural montmorillonite. This is due to the interaction of montmorillonite silicate layers OH with metal polycations. The presence of a sharp peak in all samples is attributed to the Si-O stretching.

**Table 1.** Basal spacing ( $d_{001}$ ) of montmorillonite and MPILs

Catalyst	2 $\theta$	$d_{001}$ (Å)	M-PILC (%M)
Montmorillonite	6.8	12.80	-
Fe-PILC	5.6	15.54	8.50
Cr-PILC	6.4	13.70	1.49
Fe-Cr-PILC	6.1	14.33	1.76, 1.30
Al-PILC	4.04	21.80	1.80
Al-Fe-PILC	4.8	18.09	4.26, 1.20



**Figure 1.** XRD patterns of (a) montmorillonite, (b) Fe<sup>3+</sup>-montmorillonite, (c) Fe-PILC.



**Figure 2.** The FT-IR Kubelka Munk spectra of (a) montmorillonite, (b) Fe-PILC.

In the beginning, we decided to run an experiment in order to obtain the best catalyst. We thought that benzene can be used as reactant as well as the reaction solvent. It was found that Fe-PILC among all pillared clays show the best catalytic effect on benzene alkylation with 1-dodecene during two hours at 120°C. Therefore, this solid acid was chosen as the representative catalyst in order to obtain the best reaction conditions.

Tables 2, 3 and 4 represent the effect of benzene to 1-dodecene molar ratio on 1-dodecene, temperature and time on 1-dodecene conversion and products distribution. As seen in these Tables, 98% of 1-dodecene is converted by using the molar ratio of 25 during two hours at 120°C in alkylation of benzene in the presence of Fe-PILC.

**Table 2.** Effect of benzene to 1-dodecene molar ratio on 1-dodecene total conversion and products distributions in alkylation with benzene in the presence of Fe-PILC

Molar ratio	Conversion (%)	Monoalkylbenzenes				
		a	b	c	d	e
5	89	11.5	12.5	12	15	24
10	54	5	6	9.5	17	26.5
25	98	14	17	17	20	30
35	81	10	14	14	16	27

Reaction conditions: temperature: 120°C, time: 2 h, catalyst: 0.5 g, a: 6-phenyldodecane, b: 5-phenyl-dodecane, c: 4-phenyldodecane, d: 3-phenyldodecane, e: 2-phenyldodecane.

**Table 3.** Effect of temperature on 1-dodecene conversion and products distributions in alkylation with benzene in the presence of Fe-PILC

Temperature (°C)	Conversion (%)	Monoalkylbenzenes				
		a	b	c	d	e
60	0	0	0	0	0	0
80	15	1	1.5	2	3	7
100	77	8	11	12	16	30
120	98	14	17	17	20	30

Reaction conditions: [benzene]/[1-dodecene]=25, time: 2 h, catalyst: 0.5 g, for a to e see Table 2 footnote.

**Table 4.** Effect of time on 1-dodecene conversion and product distributions in the alkylation with benzene in the presence of Fe-PILC

Time (h)	Conversion (%)	Monoalkylbenzenes				
		a	b	c	d	e
0.5	80	10.5	13	13.5	16	27
1	93	12	16	16	19	30
1.5	94.5	13	16	16	19.5	30
2	98	14	17	17	20	30

Reaction conditions: [benzene]/[1-dodecene]=25, temperature: 120°C, time: 2 h, catalyst: 0.5 g, for a to e see Table 2 footnote.

Figure 3 shows the results obtained from alkylation of benzene with 1-dodecene in the presence of M-pillared clays (M = Al, Cr, Fe, Al-Fe, Fe-Cr). It is evident that a range of 21.5 to 98% of 1-dodecene conversion is obtained under the effect of Al-Fe-PILC to Fe-PILC, respectively.

Among the solid acids considered as catalysts for benzene alkylation, an important breakthrough was achieved and patented by UOP in 1992 [21,22], which

jointly with CEPESA developed the new Detal process, a flourided silica-alumina, a non-corrosive catalyst to replace the liquid HF acid [3]. This catalyst is satisfactorily active with periodic mild rejuvenation [3]. The LAB produced in this way is phenylalkanes comprising a linear aliphatic alkyl group and a phenyl group in which the phenyl group is attached to any secondary carbon atom. In contrast to the LAB produced using HF catalyst in which only 14% of 2-phenylalkane is formed, 31% mol percent of this isomer is reported to be produced in Detal process [2]. It is worth noting that hand dishwashing liquid formulation based on LABS as the major detergent surfactant richer in 2-phenylalkane samples have lower cloud points but higher viscosities [2].

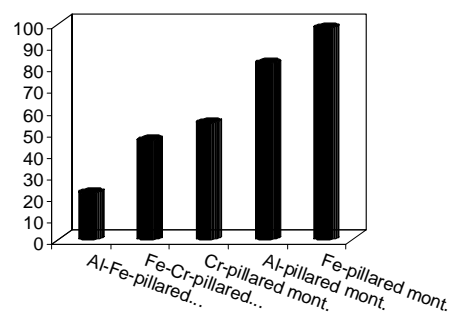
Catalytic activity of Zr-PILC has been reported in the alkylation of benzene with long chain  $\alpha$ -olefins. Although the olefin conversion was in the range of 80-91%, the method suffered from high temperature (150-180°C) and pressure (15 bar) that makes the system uneconomical at industrial scale [19].

Based on our results, the linear monoalkylbenzenes obtained in 98% yield at 120°C in the presence of Fe-PILC during two hours seems promising. More importantly is the formation of the valuable 2-phenyldodecane with 30% yield, comparable with that obtained in Detal process (*vide supra*).

Figueras and his co-workers have recently investigated the catalytic properties of pillareds containing Al, Fe, Ti, and Cr in the alkylation of aromatics with benzyl chloride [20]. They observed that in spite of their lower acidity, the most active clays were those containing Fe. The lack of correlation of activity for alkylation and acidity was attributed to the initiation by oxidation of benzylchloride by  $\text{Fe}^{3+}$  [20]. Although the highest activity in our system arises from Fe-PILC, it may not be the result of oxidation-reduction reactions due to the lower reducibility of 1-dodecene. Therefore, the higher activity of Fe-PILC in comparison to other pillared clays can not be envisaged easily.

### Conclusions

In this article, a simple method for alkylation of benzene with 1-dodecene catalyzed by a number of M-PILCs (M= Al, Cr, Fe, Al-Cr, Fe-Cr) was presented. It was found that the Fe-PILC efficiently catalyzes the alkylation of benzene with 1-dodecene. Due to the lower reaction time and almost quantitative yield percent of secondary linear monoalkyl benzene as well as obtaining 30% of the valuable 2-phenyldodecane makes this reaction merit for scaling up in industrial applications.



**Figure 3.** Benzene alkylation results with 1-dodecene in the presence of different M-PILCs.

### Acknowledgement

We acknowledge the financial support granted by the Research Council of the University of Alzahra for this project.

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