

Study of the benzylation of benzene and other aromatics by benzyl chloride over transition metal chloride supported mesoporous SBA-15 catalysts

K. Bachari^{a,b,*}, O. Cherifi^b

^a Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques (CRAPC), BP 248, Alger RP 16004, Alger, Algérie

^b Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, BP 32, 16111, El Alia, USTHB, Bab Ezzouar, Alger, Algérie

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Abstract

The benzylation of benzene by benzyl chloride to diphenylmethane over FeCl₃, InCl₃, GaCl₃, ZnCl₂, CuCl₂ and NiCl₂ supported on mesoporous SBA-15 at 353 K has been investigated. The redox property due to the impregnation of the SBA-15 by transition metal chloride seems to play a very important role in the benzene benzylation process. Among the catalysts, the FeCl₃/SBA-15 showed both high conversion and high selectivity for the benzylation of benzene. The activity of these catalysts for the benzylation of different aromatic compounds is in the following order: benzene > toluene > *p*-xylene > anisole. More interesting is the observation that this catalyst is always active and selective for large molecules like naphthenic compounds such as methoxynaphthalene and he can also be reused in the benzylation of benzene for several times. Kinetics of the benzene benzylation over these catalysts have also been investigated.

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1. Introduction

Friedel–Crafts alkylations, which are usually catalyzed by Lewis acids in the liquid phase, constitute a very important class of reactions which are of common use in organic chemistry [1]. Among these reactions, the alkylation of benzene by benzyl chloride is interesting for the preparation of substitutes of polychlorobenzenes used as dielectrics. This reaction is presently catalyzed in the homogeneous phase at the industrial scale by FeCl₃ [2]. The new environmental legislation pushes for the replacement of all liquid acids by solid acid catalysts which are environmentally more friendly catalysts and which lead to minimal pollution and waste [3]. The substitution of liquid acid catalysts in the case of the Friedel–Crafts alkylation is an important challenge that is on the way to being successful. Indeed, several solid acid catalysts have already been proposed which are efficient catalysts such as: Fe-modified ZSM-5 and H-β zeolites; Fe₂O₃ or FeCl₃ deposited on micro-, meso and macro-porous [4]; Fe-

containing mesoporous molecular sieves materials [5,6]; Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts [7]; Ga- and Mg-oxides and chlorides derived from Ga–Mg-hydrotalcite [8]; Ga-SBA-15 [9]; Ga-HMS [10]; InCl₃, GaCl₃, FeCl₃ and ZnCl₂ supported on clays and Si-MCM-41 [11]; supported thallium oxide catalysts [12]; Sb supporting K10 [13]; solid superacid and silica-supported polytrifluoro-methanesulfonil oxane [14]; Si-MCM-41-supported Ga₂O₃ and In₂O₃ [15]; H₂SO₄, HNO₃ and HClO₄/metakaolinite [16]; alkali metal salts and ammonium salts of keggin-type heteropolyacids [17]; ion-exchanged clays [18]; clayzic [19]; solid superacids based on sulfated ZrO₂ [20]; HY [21]; H-ZSM-5 [22] and FeCl₃, MnCl₂, CoCl₂, NiCl₂, CuCl₂, ZnCl₂ supported on acidic alumina [23] for the benzylation of benzene and other aromatic compounds.

Furthermore, mesoporous silica materials, MCM-41 and SBA-15, have received increasing scientific interest owing to their narrow pore size distribution, high surface area and pore volume which make them promising candidates for use as catalyst support in catalysis field [24–30]. SBA-15 material was synthesized in acidic medium with poly(alkylene oxide) triblock copolymers under relatively mild synthesis conditions [31]. The pore size can be varied on a relatively large range

* Corresponding author. Tel.: +213 212 47406; fax: +213 212 47406.
E-mail address: bachari2000@yahoo.fr (K. Bachari).

between 5 and 20 nm depending on the synthesis conditions. The SBA-15 material also exhibits a higher stability due to the greater wall thickness compared to the MCM-41 material [32] which render it more suitable for use as catalyst support in catalytic processes where thermal treatments and repeated regeneration were frequently encountered.

In the present work, we report the benzylation of benzene reaction with benzyl chloride using FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 supported on mesoporous silicas SBA-15. The kinetics of the reaction over these catalysts have been investigated and the reaction has been extended to other substrats like toluene, *p*-xylene, anisole and naphthalenic compounds.

2. Experimental

2.1. Materials

Samples were synthesized with tetraethyl orthosilicate (TEOS, Merck), tri-block copolymer poly(ethylene glycol)-block poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO20PO70EO20, Aldrich), Transition metal chloride (FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 , Merck).

2.2. Catalysts preparation

SBA-15 sample was synthesized using tri-block copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) as a structure directing agent with the following molar gel composition: TEOS:0.016P123:0.46HCl:127H₂O. In a typical synthesis, 4 g of Pluronic P123 was added to 30 ml of water. After stirring for a few hours, a clear solution was obtained. The 70 g of 0.28 M hydrochloric acid was added to it and the solution was stirred for another 2 h. Then, 9 g of tetraethyl orthosilicate was added and the resulting mixture was stirred for 24 h at 313 K. The solid product was recovered by filtration, washed with water for several times, and dried overnight at 373 K. Finally, the product was calcined at 813 K to remove the template.

Supported transition metal chloride (FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 , NiCl_2) catalysts (loading of metal chloride = 1.15 mmol g⁻¹) were prepared by impregnating SBA-15 with anhydrous metal chloride from their acetonitrile solution by incipient wetness technique and evaporating the solvent in vacuum oven at 393 K for 12 h.

2.3. Catalytic testing

The benzylation reactions over the supported transition metal chloride catalysts were carried out in a magnetically stirred glass reactor (25 cm³) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture through the liquid reaction mixture, at the following reaction conditions: reaction mixture = 15 ml of moisture-free liquid aromatic compound (or 2.5 ml of moisture-free aromatic compound mixes with 12.5 ml of moisture-free solvent) + 1.0 ml of benzyl chloride, amount of catalyst = 0.1 g

and reaction temperature = 353 K. The reaction was started by injecting benzyl chloride in the reaction mixture, containing catalyst and aromatic compound with or without solvent. Measuring quantitatively the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by N₂ in a 0.1 M NaOH solution containing phenolphthalein indicator) followed the course of the reaction. The polybenzyl chloride (which is formed by the condensation of benzyl chloride) was isolated from the reaction mixture by the procedure given by Choudhary et al. [32]. In all the cases, the major product formed was mainly mono-benzylated compound along with polybenzyl chloride as side product depending upon the condition used.

Samples were analyzed periodically on a gas chromatograph (HP-6890) equipped with a FID detector and a capillary column RTX-1 (30 m × 0.32 mm i.d.). The products were also identified by GC–MS (HP-5973) analysis.

3. Results and discussion

3.1. Comparison of the mesoporous SBA-15-supported metal chloride catalysts for benzene benzylation

The FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 supported metal chloride catalysts are compared for their performance in the benzylation of benzene 353 K in Table 1.

From comparison of results in this table, the following important observations can be made:

- The catalyst support itself (SBA-15) shows no activity in the benzylation of benzene; however, its catalytic activity is increased drastically because of the impregnation of FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 .
- Among the supported metal chloride catalysts, the FeCl_3 /SBA-15 catalyst showed both high conversion and high selectivity in the benzylation. The conversion for the mesoporous SBA-15-supported transition metal chloride catalyst is much higher than that for the transition metal chloride with-

Table 1
Results of the benzylation of benzene by benzyl chloride over different transition metal chloride supported on mesoporous SBA-15 at 353 K

Catalyst	Time (min) ^a	Selectivity (%)		Apparent rate constant, k_a ($\times 10^3 \text{ min}^{-1}$)
		Diphenyl methane	Polybenzyl chloride	
FeCl_3 /SBA-15	11.2	98.8	1.2	254.0
InCl_3 /SBA-15	12.7	98.5	1.5	221.5
GaCl_3 /SBA-15	14.2	97.8	2.2	202.0
CuCl_2 /SBA-15	18.7	95.6	4.4	171.3
ZnCl_2 /SBA-15	20.3	87.1	12.9	140.1
NiCl_2 /SBA-15	30.8	83.4	16.6	97.9
FeCl_3	30.5	52.3	47.7	98.2
InCl_3	36.2	45.0	55	75.7
GaCl_3	42.4	49.2	50.8	69.4
CuCl_2	51.7	43.8	56.2	63.7
ZnCl_2	57.7	53.6	46.4	55.2
NiCl_2	85.6	50.7	49.3	37.8
SBA-15	–	–	–	–

^a Time required for 90% conversion of benzyl chloride.

out any support. This result can be probably due to synergetic effect.

- The benzylation activity of the mesoporous SBA-15-supported transition metal chloride catalysts is in the following order: $\text{FeCl}_3/\text{SBA-15} > \text{InCl}_3/\text{SBA-15} > \text{GaCl}_3/\text{SBA-15} > \text{CuCl}_2/\text{SBA-15} > \text{ZnCl}_2/\text{SBA-15} > \text{NiCl}_2/\text{SBA-15}$.
- It is interesting to note that this order for the benzylation of benzene activity is quite similar to that of the redox potential of the metal in the supported metal chloride catalysts. This indicates a close relationship between the redox potential and the catalytic activity of the supported metal chlorides.
- The kinetic data for the benzene benzylation reaction in excess of benzene over all the mesoporous SBA-15-supported transition metal chloride catalysts could be fitted well to a pseudo-first-order rate law:

$$\log \left[\frac{1}{1-x} \right] = \left(\frac{k_a}{2.303} \right) (t - t_0),$$

where k_a is the apparent first-order rate constant, x the fractional conversion of benzyl chloride, t the reaction time and t_0 is the induction period corresponding to the time required for reaching equilibrium temperature. A plot of $\log [1/(1-x)]$ as a function of the time gives a linear plot over a large range of benzyl chloride conversions. The values of the apparent rate constants for the reaction over the different catalysts have been included in Table 1.

3.2. Effect of temperature

The effect of temperature on the rate was studied by conducting the reaction at 343, 348 and 353 K under the standard reaction conditions (benzene = 15 ml, benzyl chloride = 1 ml) using $\text{FeCl}_3/\text{SBA-15}$ as catalyst (0.1 g). The results showed that the catalytic performances of the catalyst strongly increased with the reaction temperature but, the selectivity to diphenylmethane decreased (Table 2).

3.3. Effect of benzene/benzyl chloride

Two Bz/BzCl ratios have been investigated. The results obtained are reported in Table 3. It appears that the stoichiometric ratio between benzene and benzyl chloride has a strong influence on the selectivity to diphenyl methane. With a low ratio, the secondary reactions to dibenzylbenzenes and tribenzylbenzene were favored.

Table 2
Catalytic activities of $\text{FeCl}_3/\text{SBA-15}$ at different temperatures: 343, 348, 353 and 373 K

Temperature (K)	Time (min) ^a	Selectivity (%)		Apparent rate constant, k_a ($\times 10^3 \text{ min}^{-1}$)
		Diphenyl methane	Polybenzyl chloride	
343	19.7	100.0	–	146.3
348	14.5	100.0	–	199.5
353	11.2	98.8	1.2	254.0
373	7.5	73.2	26.8	320.0

^a Time required for 90% conversion of benzyl chloride.

Table 3

Influence of the stoichiometric ratio between benzene and benzyl chloride for the benzylation of benzene at 353 K over $\text{FeCl}_3/\text{SBA-15}$ catalyst

Benzene/benzyl chloride ratio	Time (min) ^a	Selectivity (%)	
		Diphenyl methane	Polybenzyl chloride
5	20.2	77.6	22.4
15	11.2	98.8	1.2

^a Time required for 90% conversion of benzyl chloride.

Table 4

Effect of solvent on the conversion of benzyl chloride at 353 K in the benzylation of benzene over $\text{FeCl}_3/\text{SBA-15}$

Solvent	Time (min) ^a	Apparent rate constant, k_a ($\times 10^3 \text{ min}^{-1}$)
Without solvent	11.2	254.0
Dichloroethane	12.3	234.3
<i>n</i> -Heptane	19.3	149.0

^a Time required for 90% conversion of benzyl chloride.

3.4. Effect of solvent

To understand the role of solvent in benzylation of benzene by mesoporous SBA-15-supported transition metal chloride with benzyl chloride, the reaction was carried out with different solvents, such as dichloroethane and *n*-heptane. The reaction conditions and the results of benzene benzylation with $\text{FeCl}_3/\text{SBA-15}$ catalyst are presented in Table 4. The reaction rate is highest in the absence of any solvent. It is decreased when the solvent (via dichloroethane and *n*-heptane) is used, the decrease is quite large when *n*-heptane is used as a solvent but it is small for dichloroethane as a solvent. The observed solvent effect on reaction rate is expected because of the competitive adsorption of both the reactants and the solvent on the catalyst. The results show that between the two solvents, dichloroethane is a better solvent for the benzylation reaction.

3.5. Effect of catalyst concentration

The reaction profile using different amount of $\text{FeCl}_3/\text{SBA-15}$ catalyst revealed that selectivity to diphenylmethane was higher at a lower concentration (Table 5). At the higher concentration, the formation of polymerised product was favored. Hence, an optimum of 0.1 g of catalyst in the reaction mixture was ideal

Table 5
Benzylation of benzene with benzyl chloride at different $\text{FeCl}_3/\text{SBA-15}$ concentration

Catalyst (g)	Time (min) ^a	Selectivity (%)		Apparent rate constant, k_a ($\times 10^3 \text{ min}^{-1}$)
		Diphenyl methane	Polybenzyl chloride	
0.1	11.2	98.8	1.2	254.0
0.3	8.5	78.3	21.7	300.3
0.4	5.3	55.2	44.8	439.7

^a Time required for 90% conversion of benzyl chloride.

Table 6
Effect of water on the catalytic properties of FeCl₃/SBA-15 at 353 K

Water content (vol.%)	Time (min)	Selectivity (%)		Apparent rate constant, k_a ($\times 10^3$ min ⁻¹)
		Diphenyl methane	Polybenzyl chloride	
–	11.2	98.8	1.2	254.0
0.1	12.0	98.0	2.0	241.1
0.2	14.8	93.1	6.9	185.3
0.3	17.3	82.7	17.3	157.4
0.5	20.4	78.6	21.4	138.7

Time required for 90% conversion of benzyl chloride.

for achieving better selectivity for diphenylmethane (98.8%) at 90% conversion of benzyl chloride.

3.6. Effect of water

Lewis acids are sensitive to water and the effects of water on the catalytic activity were investigated at 353 K under the standard reaction conditions (benzene = 15 ml, benzyl chloride = 1 ml) using FeCl₃/SBA-15 as catalyst (0.1 g) and adding different amounts of water. The results are reported in Table 6. A small addition of water had almost no effect on the catalytic properties of the compound whereas a larger addition had a drastic one with a decrease both of the activity and of the selectivity. This result can be probably due to competitive adsorption on active sites. Similar results have been obtained on supported thallium [12], indium oxides [15] and iron-mesoporous [6].

3.7. Recycling of the catalysts

The stability of the catalysts has been studied by running the reaction successively with the same catalyst using FeCl₃/SBA-15 under the same conditions without any regeneration between two runs. The reaction was first run under the standard conditions (benzene = 15 ml, benzyl chloride = 1 ml, 353 K) to the complete conversion of benzyl chloride. Then after a period of 8 min another quantity of benzyl chloride was introduced in the reaction mixture leading to the same benzene to benzyl chloride ratio. After the achievement of the second run, the same protocol was repeated a second time. The results, presented in Table 7, showed that the catalyst could be used several times in the benzene benzylation process without a significant change of its catalytic activity.

Table 7
Effect of recycling of the FeCl₃/SBA-15 catalyst in the benzylation of benzene with benzyl chloride at 353 K

Catalyst	Time (min) ^a	Selectivity (%)		Apparent rate constant, k_a ($\times 10^3$ min ⁻¹)
		Diphenyl methane	Polybenzyl chloride	
Fresh	11.2	98.8	1.2	254.0
First reuse	11.7	96.9	3.1	243.3
Second reuse	12.1	95.3	4.7	239.7

^a Time required for 90% conversion of benzyl chloride.

Table 8
Reaction rates for substituted benzenes

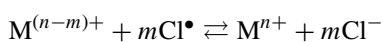
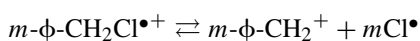
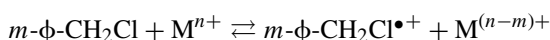
Substituent	k_a ($\times 10^3$ min ⁻¹)
Benzene	254.0
Toluene	243.0
<i>p</i> -Xylene	234.3
Anisole	185.8

3.8. Effect of substituents

Results showing the influence of different substituent groups attached to aromatic benzene nucleus on the conversion of benzyl chloride in the benzylation of corresponding substituted benzenes at 353 K over the FeCl₃/SBA-15 catalyst are presented in Table 8. According to the classical mechanism of the Friedel–Crafts type acid catalyzed benzylation reaction, the benzylation of an aromatic compound is easier if one or more electron donating groups are present in the aromatic ring [1]. Hence, the order for the rate of benzylation for the aromatic compound is expected as follows: anisole > *p*-xylene > toluene \gg benzene. But, what is observed in the present case is totally opposite to that expected according to the classical mechanism. The first-order rate constant for the benzylation of benzene and substituted benzenes is in the following order: benzene > toluene > *p*-xylene > anisole. This indicates that, for this catalyst, the reaction mechanism is different from that for the classical acid catalyzed benzylation reactions. Furthermore, in order to rule out the influence of a steric effect on the rate of reaction, we have applied the Taft relation [33]. According to this relation when a steric effect influences the reaction, there is a linear relation between the rate and the parameter E_s values considered to be representative of the size of the substituting group of the studied aromatic compounds. Using the E_s parameter tabulated by Charton [34] we have shown that such a relation did not exist.

3.9. Reaction mechanism

The mesoporous SBA-15-supported transition metal chloride species have redox properties, which are expected to play important role in the benzylation reaction. The probable redox mechanism for the activation of both benzyl chloride and benzene by the transition metal chloride species leading to the benzylation of benzene reaction is proposed:



where M = Ga, In, Fe, Zn, Cu, Ni; $n = 3$ (for In, Ga and Fe) or 2 (for Zn, Cu and Ni) and $m = 2$ (for In and Ga) and 1 (for Fe, Zn, Cu and Ni).

The redox mechanism is similar to that proposed earlier for the benzene benzylation [11] and alkylation or acylation reactions [12,18,35]. This mechanism is quite consistent with

Table 9
Reaction rates for substituted naphthalene

Substituent	k_a ($\times 10^3 \text{ min}^{-1}$)
Naphthalene	87.5
Methylnaphthalene	79.5
Methoxynaphthalene	47.5

the observations; the order for the benzene benzylation conversion of the mesoporous SBA-15-supported transition metal chloride ($\text{FeCl}_3/\text{SBA-15} > \text{InCl}_3/\text{SBA-15} > \text{GaCl}_3/\text{SBA-15} > \text{CuCl}_2/\text{SBA-15} > \text{ZnCl}_2/\text{SBA-15} > \text{NiCl}_2/\text{SBA-15}$) catalysts is almost same as that for the redox potential of the metal present in the catalysts.

3.10. Applications to other aromatic alkylations

The $\text{FeCl}_3/\text{SBA-15}$ catalyst has been used with success for the alkylation of benzenic compounds as illustrated in Table 8 and discussed above. More interesting is the observation that this catalyst is always active and selective for larger molecules like naphthenic compounds such as methoxynaphthalene (Table 9). The large pores of the mesoporous support permit the conversion of these molecules that could not be done on other supports.

4. Conclusions

From the present studies on the benzylation of benzene with benzyl chloride using mesoporous SBA-15-supported transition metal chloride catalysts has been investigated. Following important conclusions can be drawn:

- The mesoporous SBA-15 alone in the absence of transition metal chloride was no active.
- Comparing unsupported and SBA-15-supported transition metal chloride as catalyst shows that SBA-15-supported catalysts gave higher conversion than their corresponding unsupported catalysts.
- The benzylation activity of the supported transition metal chloride catalysts is in following order: $\text{FeCl}_3/\text{SBA-15} > \text{InCl}_3/\text{SBA-15} > \text{GaCl}_3/\text{SBA-15} > \text{CuCl}_2/\text{SBA-15} > \text{ZnCl}_2/\text{SBA-15} > \text{NiCl}_2/\text{SBA-15}$.
- The benzene benzylation is influenced by the solvent used in the process. Among dichloroethane and *n*-heptane, the former is a better solvent for the reaction.
- In contrast to usual Lewis acids, the $\text{FeCl}_3/\text{SBA-15}$ catalyst shows a low sensitivity to water and can be easily be reused many times. These properties are linked to the mechanism which involves a redox step at the reaction initiation. This gives a greater independence to the effect of substituents, and this catalyst can therefore be used with substrates of low reactivity. Furthermore, the large pores of the mesoporous catalyst do not limit the size of the molecules that could be reacted.

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