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# Benzylation of benzene by benzyl chloride over iron mesoporous molecular sieves materials

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#### Abstract

The alkylation of benzene with benzyl chloride has been investigated over a series of iron-containing mesoporous silicas with different Fe contents. These materials (Fe-HMS-*n*) have been prepared at room temperature using a route based on hydrogen bonding and self-assembly between neutral primary amine micelles (S<sup>0</sup>) and neutral inorganic precursors (I<sup>0</sup>). They have been characterized by chemical analysis, BET, XRD, and UV–vis spectroscopy. The mesoporous Fe-containing materials were very active benzylation catalysts with almost 100% selectivity to monoalkylated product and showed excellent stability. The kinetics of the benzene benzylation over this catalyst have been thoroughly investigated. A mechanism in which the reaction could be initiated by an oxidation of benzyl chloride with formation of a charge transfer complex is proposed.

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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 FeCl<sub>3</sub> [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 [3,4].

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 poposed which are efficient catalysts. Arata and co-workers investigated the Friedel–Crafts ben-

\* Corresponding author. *E-mail address:* millet@catalyse.cnrs.fr (J.M.M. Millet). zylation and benzoylation of benzene with alkyl chlorides [5,6]. They found that calcined iron sulfate and iron oxide were excellent catalysts for the above reactions. Later, Cao et al. [4] reported that Fe-containing zeolites or HY were also good catalysts for the alkylation of benzene by benzyl chloride. Clark et al. [7] reported that montmorillonite-supported zinc and nickel chlorides are highly active and selective for the catalysis of Friedel–Crafts alkylations; in this last case the catalytic properties of the catalysts were high enough to warrant their commercialization [8].

In the 1990s, Mobil researchers reported the preparation of new class of silica and silica–alumina-based molecular sieves using supramolecular surfactant templates [9,10]. Originally, materials were synthesized at relatively high temperatures by a cooperative organization process between cationic surfactants (S<sup>+</sup>), namely alkyl trimethylammonium cations with C<sub>8</sub> to C<sub>16</sub> chains and anionic inorganic species (I<sup>-</sup>). Depending on the synthesis conditions, and on the surfactant/SiO<sub>2</sub> ratio, different phases could be obtained, like the hexagonal phase MCM-41, the cubic one MCM-48, and the lamellar compound MCM-50 [9,10]. Huo et al. [11] proposed four complementary synthesis pathways. The first

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pathway involved the direct cocondensation of cationic surfactant  $(S^+)$  with anionic inorganic species  $(I^-)$  to produce assembled ion pairs  $(S^+I)$ . The original synthesis of MCM-41 silicates is a prime example of this pathway. In the second pathway, an anionic template  $(S^{-})$  was used to direct the self-assembly of cationc species  $(I^+)$  through  $(S^-I^+)$ ion pairs. Pathways 3 and 4 involved counterion-mediated assemblies of surfactants and inorganic species of similar charge. These counterion-mediated pathways produced assembled solution species of type S<sup>+</sup>X<sup>-</sup>I<sup>+</sup> or S<sup>-</sup>M<sup>+</sup>I<sup>-</sup> (with  $X^{-} = Cl^{-}$  or  $Br^{-}$  and  $M^{+} = Na^{+}$  or  $K^{+}$ ). In 1994, a new pathway was proposed by Tanev et al. [12] to prepare mesoporous silicas at room temperature by a neutral templating route  $(S^0I^0)$ . In this case, the organic surfactant is not quarternary ammonium cation but a primary amine, and the assembly involves hydrogen-bonding interactions between neutral primary amines and neutral inorganic precursors. These materials, denoted HMS (hexagonal mesoporous silica), exhibit excellent catalytic ability for macromolecular reactions and offer new opportunities for transition metal incorporation into silica frameworks [13,14].

In the present paper, we report the synthesis and characterization of such materials incorporating iron and their test as catalysts for the benzylation of benzene with benzyl chloride. The kinetics of the reaction over these catalysts have been investigated and the reaction has been extended to other substrats like toluène, *p*-xylene, anisole, and naphthalenic compounds.

#### 2. Experimental

## 2.1. Materials

Samples were synthesized with hexadecyltrimethylammonium bromide (Aldrich Ref. 85,582-0), hexadecylamine (Aldrich Ref. 44,531-2), tetraethyl orthosilicate (Aldrich Ref. C13,190-3), ferric nitrate Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck Ref. 103883), and ethanol RP (Prolabo Ref. 20.821.296).

# 2.2. Catalyst preparation

The catalysts have been prepared using a protocol reported by Tanev et al. [12]. In a typical preparation, hexadecylamine (HDA) was added to a solution containing water and ethanol (EtOH). The mixture was stirred until it was homogeneous and then tetraethyl orthosilicate (TEOS) was added under vigorous stirring. Ferric nitrate was dissolved in an HDA/water/ethanol solution before addition of TEOS. After mixing, the resulting solution had the following composition [15]:

 $SiO_2$ -(1/2*n*)Fe<sub>2</sub>O<sub>3</sub>-0.3HDA-7EtOH-35H<sub>2</sub>O, with *n* = 100, 50, 44, 30, 15.

This solution was then stirred at room temperature for 24 h. The obtained solids were recovered by filtration,

washed with distilled water, and air-dried at 393 K. Organic molecules occluded in the mesopores were removed by solvent extraction. The dried precursor was dispersed in ethanol (5 g/100 ml) containing a small amount of NH<sub>4</sub>Cl (1 g/100 ml) and the mixture was refluxed under vigorous stirring for 2 h. The presence of NH<sub>4</sub><sup>+</sup> cations in EtOH was reported to be necessary to exchange protonated amines formed during the synthesis and balance the excess of negative charges resulting from the substitution of Fe<sup>III</sup> for Si<sup>IV</sup> [15,16]. The solid was then filtered and washed with cold ethanol. The extraction procedure was repeated twice before drying the samples at 393 K in an oven. Finally the samples were calcined at 823 K in air for 6 h. The sample were referred to as Fe-HMS-*n* where *n* was the Si/Fe ratio in the precursor gel.

#### 2.3. Characterization of the samples

The chemical compositions of the samples were determined by atomic absorption and their surface areas determined using the BET method. X-ray diffraction (XRD) patterns were obtained using a SIEMENS D500 diffractometer and Cu-K<sub> $\alpha$ </sub> radiation. They were recorded with 0.02° (2 $\theta$ ) steps and 1 s counting time per step over two angular domains from 1 to 10° (2 $\theta$ ) and from 10 to 80° (2 $\theta$ ). UV–vis spectra were collected on a Perkin-Elmer Lambda 9 spectrometer.

# 2.4. Catalytic testing

The alkylation of benzene by benzyl chloride has been used as a model reaction for Friedel-Craft alkylation catalytic properties. The reaction was carried out in a batch reactor between 333 and 363 K. The amount of 100 mg of the solids was tested after an activation consisting of a heat treatment under air (2 L h<sup>-1</sup>) up to 573 K with various heating rates. Immediately after cooling, the catalysts were contacted under stirring with a solution of 25 ml of benzene and 6.48 or 2.16 ml of benzyl chloride to obtain a benzene to benzyl chloride mole ratio of 5 or 15. The conversion of benzyl chloride was followed by analyzing samples of the reaction mixture collected at regular intervals by gas chromatography using a gas chromatograph equipped with a flame ionization detector FID and a capillary column RTX-1  $(30 \text{ m} \times 0.32 \text{ nm i.d.})$  The selectivity is expressed by the molar ratio of formed diphenylmethane to converted benzyl chloride.

#### 3. Results and discussion

#### 3.1. Characterization

The results of the chemical analysis and the BET surface area measurements of the catalysts are given in the Table 1. The iron contents of the solids corresponded relatively well

 Table 1

 Chemical analysis and BET surface area measurements data

Sample	Chemical	Surface area	
	Fe (wt%)	Si/Fe	$(m^2 g^{-1})$
HSM	0.0	0.0	1170
Fe-HMS-100	0.75	80.0	1162
Fe-HMS-50	1.66	54.6	1135
Fe-HMS-44	2.12	42.5	1106
Fe-HMS-30	3.7	23.8	935
Fe-HMS-15	6.08	14.0	698



Fig. 1. XRD patterns of the Fe-HMS-*n* catalysts in the domain of  $1-10^{\circ}$  (2 $\theta$ ). n = Si/Fe = (a) 15, (b) 30, (c) 44, (d) 50, (e) 100.

to those fixed for the synthesis except at low iron content (Fe-HMS-100) where a small excess of iron was observed. Most of the values of the specific surface areas of the solids were larger than 1000 m<sup>2</sup> g<sup>-1</sup>, which is typical of mesoporous materials [12,16]. When the iron content increased, they decreased slightly first and then more drastically at high iron loading (Fe-HMS-30 and -15).

The X-ray powder diffraction patterns of the solids showed a broad peak at d = 32 Å (Fig. 1) characterizing a mesoporous material not well crystallized. The intensity of the peak decreased when the iron content increased showing that the addition of iron has a negative effect on the crystallinity. At the same time, small peaks corresponding to  $\alpha Fe_2O_3$  (hematite form) appeared in the 10 to  $80^\circ$  ( $2\theta$ ) range and grew with the iron content (Fig. 2).

The UV-spectra of the samples Fe-HMS-100, -50 and -15 are reported in Fig. 3. The spectrum of Fe-HMS-100 catalyst showed two absorption bands at 230 and 245 nm corresponding to oxygen to metal charge transfers involving isolated tetrahedrally coordinated ferric cations. When the iron content of the solids increased, a very broad band



Fig. 2. XRD patterns of the Fe-HMS-*n* catalysts in the domain of  $10-80^{\circ}$  (2 $\theta$ ). n = Si/Fe = (a) 100, (b) 50, (c) 44, (d) 30, (e) 15.



Fig. 3. Diffuse reflectance UV-vis spectra of the Fe-HMS-*n* catalysts. n = Si/Fe = (a) 100, (b) 50, (c) 15.

appeared with a maximum around 350 nm. The presence of this band, which is characteristic of iron oxide, was in good agreement with the XRD data.

#### 3.2. Reaction kinetics

The kinetic data for the benzene benzylation reaction in excess of benzene (stoichiometric ratio PhH/BnCl = 15)

Table 2 Influence of the stoichiometric ratio between benzene and benzyl chloride for benzene benzylation reaction at 348 K over Fe-HMS-50 catalyst

Benzene to benzyl chloride ratio	Time <sup>a</sup> (min)	Diphenylmethane selectivity (%)
5	350	65.6
15	245	100

<sup>a</sup> Time required for the complete conversion of benzyl chloride.



Fig. 4. Effect of reaction temperature on the conversion of benzyl chloride in the benzene benzylation reaction over Fe-HMS-50 catalyst at 343 ( $\blacklozenge$ ), 348 ( $\blacksquare$ ), and 353 K ( $\blacktriangle$ ).

over the Fe-HMS-50 catalyst could be fitted well to a pseudo-first-order rate law,

 $\log[1/1 - x] = (k_a/2.303)(t - t_0),$ 

where  $k_a$  was the apparent first-order rate constant, x the fractional conversion of benzyl chloride, t the reaction time, and  $t_0$  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 gave a linear plot over a large range of benzyl chloride conversions.

Two PhH/BnCl ratios have been investigated. The results obtained are reported on Table 2. It appeared that the stoichiometric ratio between benzene and benzyl chloride has a strong influence on the selectivity to diphenylmethane. With a low ratio, the secondary reactions to dibenzylbenzenes and tribenzylbenzene were favored. A ratio of 15 between the two reactants, which corresponded to an excess of benzene, has thus been used to study the influence of the other parameters and particularly for the reaction kinetics study.

The effect of temperature on the rate was studied by conducting the reaction at 343, 348, and 353 K under the standard reaction conditions (stoichiometric ratio PhH/BnCl = 15 and 0.1 g catalyst). The kinetic curves are shown in Fig. 4 and the selectivities calculated in Table 3. The

Table 3	
Catalytic activitiy of Fe-HMS-50 at different temperatures	

Temperature (K)	Time <sup>a</sup> (min)	Diphenylmethane selectivity (%)	Apparent rate constant $K_{\rm a} \ (\times 10^4 \ {\rm min}^{-1})$
373	135	100	121
378	60	95	155
383	30	73.6	318

<sup>a</sup> Time required for 50% conversion of benzyl chloride.



Fig. 5. Arrhenius plot of  $\log K_a$  as a function of (1/T) for the benzene benzylation reaction over Fe-HMS-50 catalyst.

 Table 4

 Reaction rates for substituted benzenes

	Benzene	Toluene	p-Xylene	Anisole	Chlorobenzene
$K_{\rm a}\times 10^4~({\rm min}^{-1})$	318	291	275	222	247

results showed that the catalytic performances of the catalyst strongly increased with the reaction temperature. Indeed, the time for 50% conversion of benzylchloride and the apparent rate constant  $K_a$  changed from 135 min and  $121 \times 10^{-4}$  min<sup>-1</sup> at 343 K to, respectively, 30 min and  $318 \times 10^{-4}$  min<sup>-1</sup> at 353 K. By contrast, the selectivity to diphenylmethane decreased from 100 to 73.6%. The firstorder rate constants ( $K_a$ ) at the different temperatures calculated from these curves are reported in an Arrhenius plot in Fig. 5. The activation energy estimated thus obtained was 97 kJ mol<sup>-1</sup>.

The effect of substituents was investigated using different aromatic substrates. The results obtained are reported on Table 4. If the reaction was acid catalyzed a correlation of the Hammett type would have been expected, i.e.,  $\log K_a = \log K_{a_0} + \sigma^+ \rho$ , in which  $K_{a_0}$  is the rate constant for benzene and  $\sigma^+$  a coefficient representing the change of reactivity due to the substituent, and  $\rho$  a constant related to the charge on the intermediate complex [17]. For example, in acid-catalyzed reactions such as the alkylation of substituted benzenes with a tetramer of propylene (MeCH:CH<sub>2</sub>)<sub>4</sub> and anhydrous AlCl<sub>3</sub> giving C<sub>12</sub>H<sub>25</sub>, the reactivity of aromatics bearing various substituents was in the order OMe >

1





Fig. 6. log  $K_a$  for the benzene benzylation reaction over Fe-HMS-50 catalyst as a function of the ionization potential tabulated for the different substrates [21]. 1, Benzene; 2, toluene; 3, *p*-xylene; 4, mesithylene; 5, chlorobenzene; 6, anisole.

Me > H, while alkylation of a Cl-substituted ring proceeds only to a small extent [18].

In the present case, only a small change of  $K_a$  was observed and the rate constants remained in the same range within 20%. This suggested a mechanism different from the usual acid mechanism. It has been proposed earlier that the reaction could be initiated by an oxidation of benzyl chloride with formation of a charge transfer complex. This mechanism could be described as

$$\phi\text{-CH}_2\text{Cl} + \text{Fe}^{3+} \rightarrow \phi\text{-CH}_2^{\bullet^+} + \text{Cl}^{\bullet},$$
  
$$\phi\text{-CH}_2^{\bullet^+} \rightarrow \phi\text{-CH}_2^+ + \text{Fe}^{2+},$$
  
$$\text{Fe}^{2+} + \text{Cl}^{\bullet} \rightarrow \text{Fe}^{3+} + \text{Cl}^-.$$

This mechanism, which was first proposed to rationalize the catalytic properties of exchanged clays [19], has later been supported by the observation that thallium oxide, a solid base was an active alkylation catalyst [20]. Indeed the rate constant here was more directly related to the ionization potential of the substrates rather than to  $\sigma^+$  as shown in Fig. 6 [21]. The later figure shows a linear relation between the ionization potential and log  $K_a$  considered for all the substrates except chlorobenzene. In the case of chlorobenzene, the slow step was apparently not the the ionization of chlorobenzene but a subsequent step:

$$\phi$$
-CH<sub>2</sub><sup>+</sup> + ArH  $\rightarrow \phi$ -CH<sub>2</sub>-ArH<sup>+</sup>,  
 $\phi$ -CH<sub>2</sub>-ArH<sup>+</sup>  $\rightarrow \phi$ -CH<sub>2</sub>-Ar + H<sup>+</sup>.

In order to rule out the influence of a sterric effect on the rate of reaction, we have applied the Taft relation [17]. According to this relation when a sterric effect influences the reaction, there is a linear relation between the rate and the parameter  $E_s$  values considered to be representative of the

Table 5			
Effect of water on the catalytic	properties	of Fe-HMS-50	) at 353 K

Water content (vol%)	Time (min)	Benzyl chloride conversion (%)	Diphenyl- methane selectivity (%)	Apparent rate constant $(\times 10^4 \text{ min}^{-1})$
_	400	99	73.6	318
0.10	420	99	73.9	298
0.20	520	99	70.7	219
0.30	610	98.5	66	139
0.50	720	68	62.5	90
0.65	720	57.6	60	52
0.80	720	48.7	58.5	33



Fig. 7. Effect of moisture on the initial reaction rate (mol/L/min) at 353 K in the benzylation of benzene over Fe-HMS-50 catalyst.

size of the substituting group of the studied aromatic compounds. Using the  $E_s$  parameter tabulated by Charton [22] we have shown that such a relation did not exist.

It was interesting to compare the solids with Fe-exchanged clays investigated earlier under similar conditions (PhH/BnCl = 15, 353 K). Both systems reached a final conversion of 100% with complete selectivity to monoalkyl; the half reaction time was 10 min for Fe/K10 and was here about 20 min, so that Fe-MCM is less active than clays probably due to the higher amount of iron in the latter system. They are more active than dealuminated Y zeolites with a half reaction time 50 min against 112 for a PhH/BnCl ratio = 5. The final conversion reached here was 100% so that the final selectivity is lower, 65.6 against 94.2 for Y zeolites [23].

## 3.3. Effect of water

Lewis acids are sensitive to water and the effects of water on the catalytic activity were investigated using Fe-HMS-50 at 353 K with a ratio PhH/BnCl = 15, adding different amounts of water. The results are reported in Table 5 and in Fig. 7. A small addition of water had almost no effect on the catalytic properties of the compound whereas a larger

Table 6 Catalytic properties of the catalysts in the benzylation of benzene with benzyl chloride at 348 K

Catalyst	Time <sup>a</sup> (min)	Diphenylmethane selectivity (%)	Apparent rate constant $K_a (\times 10^4 \text{ min}^{-1})$
HSM	_	_	-
Fe-HMS-100	_	_	_
Fe-HMS-50	245	100	155
Fe-HMS-44	185	100	333
Fe-HMS-30	120	98.3	374
Fe-HMS-15	90	87.2	800

<sup>a</sup> Time required for the complete conversion of benzyl chloride.

Table 7

Influence of the pretreatment heating rate on the catalytic properties of the Fe-HMS-50 catalyst. The reaction temperature was 353 K and the ratio between benzene and benzyl chloride 15

Calcination	Time <sup>a</sup> (min)	Diphenylmethane selectivity (%)	Apparent rate constant $K_{\rm a} \ (\times 10^4 \ {\rm min}^{-1})$
Slow	620	74	130
Fast	400	73	318

<sup>a</sup> Time required for the complete conversion of benzyl chloride.

addition had a drastic one with a decrease both of the activity and of the selectivity. Similar results have been obtained on supported thallium [24] or indium oxides [25].

# 3.4. Catalytic performance of Fe-MCM materials in the Friedel–Crafts alkylation

A comparison of the catalytic properties of the solids tested are presented on Table 6. The pure silicic compound (HMS) and the compound containing less iron (Fe-HMS-100) were totally inactive. The other compounds showed an activity increasing with their iron content. However, the selectivity to diphenylmethane at complete conversion of benzyl chloride decreased while the Fe content increased. The best catalyst appears thus to be Fe-HMS-44.

The characterization of the compounds by UV–vis spectroscopy clearly showed that contrary to the other catalysts, Fe-HMS-100 contained only isolated iron species. These species should thus be inactive. This is in good agreement with previous results obtained on Fe-hydrotalcite showing that these species were inactive in the reduction of nitro aromatic compounds by hydrazine hydrate [26]. Furthermore, it was shown that these species could not have been reduced by hydrazine. The same observation had been made in the case of Fe-sulfated zirconia used in gas phase n-butane isomerization [27]. These results tend to confirm the proposed mechanism.

The effect of the pretreatment duration of the catalyst has been studied by varying the calcination time at 573 K of the Fe-HMS-50 compound from 50 to 180 min. It can be seen in Table 7 that a fast calcination time led to more active catalysts without affecting the selectivity to diphenylmethane. Fast calcination induces self steaming of the sample and the Table 8

Effect of recycling of the	e catalysts in the	benzylation of	benzene with	benzyl
chloride at 353 K				

Catalyst	Time <sup>a</sup> (min)	Diphenylmethane selectivity (%)	Apparent rate constant $K_a \; (\times 10^4 \; \text{min}^{-1})$
Fresh	400	98.9	318
First reuse	400	98.5	307
Second reuse	400	97.3	296

<sup>a</sup> Time required for the complete conversion of benzyl chloride.

 Table 9

 Reaction rates for substituted naphthalene

Substituent	Naphthalene	Methylnaphthalene	Methoxynaph thale ne
$K_{\rm a} \times 10^4 \; (\rm min^{-1})$	146	138	106

result confirms that the resulting Fe oxide is more active that isolated Fe cations.

# 3.5. Recycling of the catalysts

The stability of the catalysts has been studied by running the reaction successively with the same catalyst (Fe-HMS-50) under the same conditions without any regeneration between two runs. The reaction was first run under the standard conditions (benzene to benzyl chloride ratio of 15, 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 completion of the second run, the same protocol was repeated a second time. The results, presented in Table 8, showed that the catalyst could be used several times in the benzene benzylation process without a significant change of its catalytic activity.

#### 3.6. Applications to other aromatic alkylations

The Fe-HMS-50 catalyst has been used with success for the alkylation of benzenic compounds as illustrated in Fig. 6 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 and Fig. 8). The large pores of the mesoporous support permit the conversion of these molecules that could not be done on other supports.

# 4. Conclusion

In conclusion, Fe-MCM are active catalysts for alkylations. In contrast to usual Lewis acids they show a low sensitivity to water and can easily be regenerated by calcinations. 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 these catalysts can therefore be used with substrates of low reactivity. Furthermore, the large pores of the mesoporous catalyst do not



Fig. 8. Effect of substituents on the naphthalene ring on the conversion of benzyl chloride (at 383 K) in the benzylation over FeHMS-50 catalyst: naphthalene ( $\blacklozenge$ ), methylnaphthalene ( $\blacksquare$ ), and methoxynaphthalene ( $\blacktriangle$ ).

limit the size of the molecules that could be reacted. The effective catalysts should correspond to small iron oxide or oxi-hydroxide particles well dispersed and stabilized on the mesoporous support.

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