Gallium-containing mesoporous silicas as a catalyst for alkylation of benzene and other aromatics by benzyl chloride

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Abstract

The benzylation of benzene and substituted benzenes reaction employing benzyl chloride as the alkylating agent over a series of gallium-containing mesoporous silicas with different Ga contents has been investigated. These materials (Ga-HMS-*n*) have been characterized by chemical analysis, BET and XRD. The mesoporous gallium-containing materials showed both high activity and high selectivity for 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. Kinetics of the benzene benzylation over these catalysts have also been investigated.
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1. Introduction

Friedel-Crafts alkylations comprise a very important class of reactions which are of common use in organic chemistry. These reactions are habitually catalyzed by Lewis acids in liquid phase [1], and the substitution of liquid acids by solid acid catalysts is a challenging task. The alkylation of benzene by benzyl chloride is interesting for the preparation of substitutes of polychlorobenzenes used as dielectrics. In homogeneous phase this reaction is catalyzed at the industrial scale by $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$ and H_2SO_4 [1–3].

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 [4,5]. Indeed, some solid acid catalysts such as: zeolites [6], Fe-MCM-41, Fe-HMS [5,7] and clays exchanged by metallic ions [8–10] have already been proposed which are efficient catalysts. Moreover, many papers concerning synthesis and catalytic applications of gallium-modified mesoporous materials have been reported.

Palomino et al. [11] presented in detail the synthesis and the characterization of gallium-containing mesoporous MCM-41 silica. Sakthivel and Selvam [12] reported that Ga-MCM-41 were good catalysts for the alkylation of phenol. Choudhary et al. investigated the Friedel-Crafts benzylation and acylation reactions in the presence and absence of moisture [13–16]. They found that Ga_2O_3 and $GaCl_3$ supported on montmorillonite-K10 and on mesoporous Si-MCM-41 were efficient catalysts for the above reactions. Narkhede and co-workers [17] reported that the $MgGa_2O_4$ (spinel)-MgO catalysts are highly active and selective for the catalysis of Friedel-Crafts alkylations. Recently, El Berrichi et al. [18] investigated the Friedel-Crafts liquid-phase acylation of anisole by benzoyl chloride. They reported that gallium-containing SBA-15 mesoporous were excellent catalysts.

The discovery of the new family of mesoporous silica molecular sieves with pore diameters in the 2.0–10 nm range, designated as M41S, is of considerable interest for heterogeneous catalysis and material science [19,20]. This family of materials is characterized by a regular array of pores with uniform diameter, high specific surface areas and pore volumes, which are advantageous for the adsorption and catalysis. Depending on the synthesis conditions, different phases could be obtained, like the hexagonal phase MCM-41, the cubic one MCM-48 as well as the lamellar compound MCM-50 [21]. Furthermore,

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another pathway was proposed by Tanev et al. [22] to prepare mesoporous silicas at room temperature by neutral templating route (S^0I^0). In this case, the organic surfactant is not quaternary ammonium cation but a primary amine, and the assembly involves hydrogen-bonding interactions between neutral primary amines and neutral inorganic precursors. These materials denoted hexagonal mesoporous silica (HMS), reveal excellent catalytic capacity for macro molecular reactions and suggest new opportunities for transition metal incorporation into silica frameworks [23–26]. In the present work, we report the synthesis and characterization of such materials incorporating gallium 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 substrates like toluène, p-xylene and anisole.

2. Experimental

2.1. Materials

Samples were synthesized with hexadecylamine (Aldrich), orthosilicate (TEOS, Aldrich), gallium-nitrate (Ga(NO$_3$)$_3$·8H$_2$O, Aldrich) and ethanol (Rhône, Poulenc).

2.2. Catalysts preparation

The catalysts Ga-HMS-n (where n is the Si/Ga ratio in the precursor gel = 70, 40, 20) have been prepared following the pathway reported by Tanev et al. [22]. In a representative preparation, hexadecylamine (HDA) (0.3 mol) was added to a solution containing water (36 mol) and ethanol (EtOH) (7 mol) and the mixture was stirred until homogeneous. Then 1 mol of tetraethyl orthosilicate (TEOS) was added under vigorous stirring. Gallium-nitrate was dissolved in TEOS itself.

This solution was then stirred at room temperature for 24 h to obtain the products. The 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$_4$Cl (1 g/100 ml) and the mixture was refluxed under vigorous stirring for 2 h. The presence of NH$_4^+$ 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 Ga^{III} for Si^{IV} [27]. 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.

2.3. Characterization of the samples

Powder X-ray diffraction patterns were recorded on SIEMENS D500 diffractometer with Cu Kα radiation. The chemical compositions of the samples were determined by atomic absorption and their surface areas determined using the BET method (NOVA 2000 porosimeter (Quantachrome)).

2.4. Catalytic testing

The benzylation 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 quantity of 100 mg of the solids was tested after an activation consisting of a heat treatment under air (21 h^{-1}) up to 573 K with diverse heating rates. Directly 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 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 m × 0.32 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 composition and characteristics of the catalysts are given in Table 1. The gallium compositions of the solids corresponded relatively well to those fixed for the synthesis except at low gallium content (Ga-HMS-70) where a loss of gallium was observed.

Most of the values of the specific surface areas of the solids were larger than 1000 (m^2 g^{-1}), which were typical mesoporous materials [22]. When the gallium content increased, they decreased slightly.

The X-ray powder diffraction patterns of the solids showed a broad peak at (2θ) = 2.1 (Fig. 1) characterizing a mesoporous material not well-crystallized. The intensity of the peak decreased slightly when the gallium content increased showing that the addition of gallium has not a negative effect on the crystallinity. Furthermore, no peak is observed in the 10–80° (2θ) (Fig. 2). This result proves probably that there are not any gallium extra-framework species in these materials.

3.2. Reaction kinetics

The kinetic data for the benzene benzylation reaction in excess of benzene (stoichiometric ratio PhH/BnCl = 15) over the Ga-HMS-40 catalyst could be fitted well to a pseudo-first-order

Table 1
Chemical composition and characteristics of the catalysts

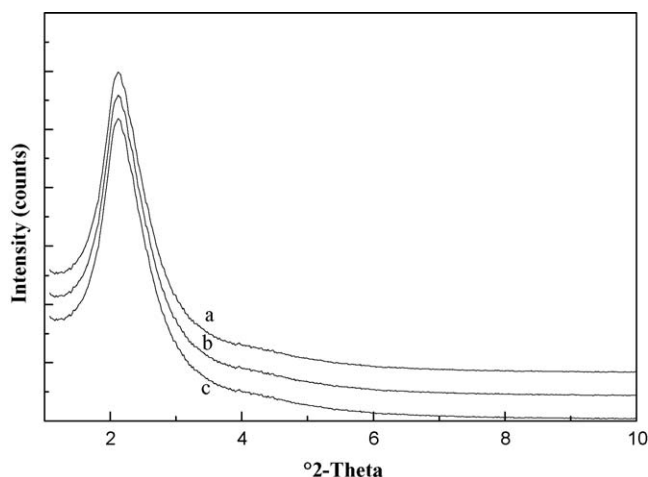| Sample	Chemical analysis		Surface area (m^2 g^{-1})
	Ga (wt.%)	Si/Ga	
HMS	0.00	0.00	1170.0
Ga-HMS-70	0.78	86.0	1153.0
Ga-HMS-40	2.81	39.6	1113.0
Ga-HMS-20	5.54	19.3	985.7

Fig. 1. DRX patterns of the Ga-HMS-*n* catalysts in the domain of 1–10° (2θ). *n*, Si/Ga: (a) 70, (b) 40 and (c) 20.

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 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 results showed that the catalytic performances of the catalyst strongly increased with the reaction temperature (Table 2). Indeed, the time for 50% conversion of benzyl chloride and the apparent rate constant k_a changed from 151.8 min and 110.9×10^{-4} min^{-1} to 33.7 min and 291.7×10^{-4} min^{-1} at 343, 353 K, respectively.
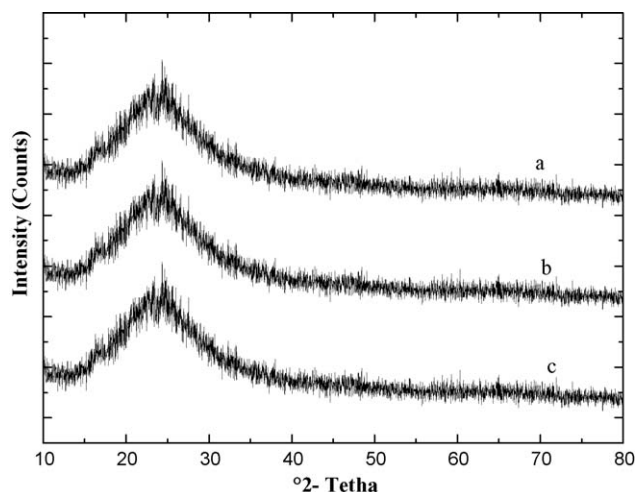

Fig. 2. DRX patterns of the Ga-HMS-*n* catalysts in the domain of 30–80° (2θ). *n*, Si/Ga: (a) 70, (b) 40 and (c) 20.

Table 2
Catalytic activities of Ga-HMS-40 at different temperatures: 343, 348 and 353 K

Temperature (K)	Time[a] (min)	Diphenylmethane selectivity (%)	Apparent rate constant k_a ($\times 10^4$ min^{-1})
343	151.8	100.0	110.9
348	67.5	94.5	142.0
353	33.7	72.0	291.7

[a] Time required for 50% conversion of benzyl chloride.

Table 3
Influence of the stoichiometric ratio between benzene and benzyl chloride for the benzylation of benzene at 348 K over Ga-HMS-40 catalyst

Benzene/benzyl chloride ratio	Time[a] (min)	Diphenylmethane selectivity (%)
5	393.7	67.2
15	275.6	100.0

[a] Time required for the complete conversion of benzyl chloride.

Table 4
Reaction rates for substituted benzenes

Substituent	Benzene	Toluene	*p*-Xylene	Anisole
$k_a \times 10^4$ (min^{-1})	291.7	266.7	252.0	203.5

By contrast, the selectivity to diphenylmethane decreased from 100 to 72%. The activation energy estimated thus obtained was 95.8 kJ mol^{-1}.

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 diphenylmethane. With a low ratio, the secondary reactions to dibenzylbenzenes and tribenzylbenzene were favored.

The effect of substituents was investigated using several aromatic substrates, with the results reported in Table 4. If the reaction was acid catalyzed a correlation of the Hammett type would have been expected, i.e. $\log k_a = \log k_{a0} + \sigma^+ \rho$, in which k_{a0} is the rate constant for benzene, σ^+ a coefficient representing the changes of reactivity due to the substituent and ρ a constant related to the charge on the intermediate complex [28].

In the present case, only a small change of k_a was observed. This suggested a mechanism different from the usual acid mechanism. The high activity observed with these catalysts could then

Table 5
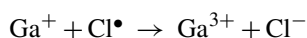Catalytic properties of the catalysts in the benzylation of benzene with benzyl chloride at 348 K

Catalyst	Time[a] (min)	Diphenylmethane selectivity (%)	Apparent rate constant k_a ($\times 10^4$ min^{-1})
HMS	–	–	–
Ga-HMS-70	–	–	–
Ga-HMS-40	275.6	100.0	142.0
Ga-HMS-20	185.6	90.3	305.3

[a] Time required for the complete conversion of benzyl chloride.

Table 6
Effect of water on the catalytic properties of Ga-HMS-40 at 353 K

Water content (vol%)	Time (min)	Benzyl chloride conversion (%)	Diphenylmethane selectivity (%)	Apparent rate constant ($\times 10^4$ min^{-1})
–	455	100.0	76.2	291.7
0.1	475	99.5	74.9	273.1
0.2	570	98.7	73.1	200.7
0.3	656	92.6	67.0	127.4
0.5	760	70.3	65.0	90.1
0.6	769	58.2	62.1	54.2

be ascribed to a different initiation of the reaction, for instance homolytic rupture of the carbon–chlorine bond followed by the oxidation of the radical:

$$\phi\text{-CH}_2\text{Cl} \rightarrow \phi\text{-CH}_2{}^\bullet + \text{Cl}^\bullet,$$

$$\phi\text{-CH}_2{}^\bullet + \text{Ga}^{3+} \rightarrow \phi\text{-CH}_2{}^+ + \text{Ga}^+,$$

$$\text{Ga}^+ + \text{Cl}^\bullet \rightarrow \text{Ga}^{3+} + \text{Cl}^-$$
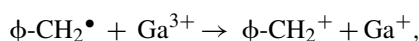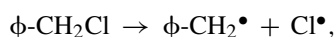
Indeed, this homolytic rupture of the carbon–chlorine bond should be the rate-determining step. This mechanism is similar to that proposed earlier for the alkylation and acylation reactions [7,10,16,29]

In order to rule out the influence of a sterric effect on the rate of reaction, we have applied the Taft relation [28]. 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 size of the substituting group of the studied aromatic compounds. Using the E_s parameter tabulated by Charton [30] we have shown that such a relation did not exist.

It was interesting to compare the solids with GaCl$_3$ supported on clays [13,16]. Both systems reached a final conversion of 100% with complete selectivity to monoalkyl; the half reaction time was about 5 min for GaCl$_3$/Mont-K10 and was here about 20 min, so that Ga-HMS is less active than clays probably due to the higher amount of gallium in the latter system.

3.3. Catalytic performances of Ga-HMS materials in the alkylation of benzene

A comparison of the catalytic properties of the solids tested is presented in Table 5. The pure silicic compound (HMS) and the compound containing less gallium (Ga-HMS-70) were totally inactive. The other compounds showed an activity increasing with their gallium content. However, the selectivity to diphenylmethane at complete conversion of benzyl chloride decreased while the Ga content increased. Indeed, the lower selectivity to diphenylmethane at high gallium content may be attributed to the residual Brønsted acid sites, which are mainly responsible for catalyzing the consecutive reactions in the benzylation of benzene.

Table 7
Effect of recycling of the catalysts in the benzylation of benzene with benzyl chloride at 353 K

	Time[a] (min)	Diphenylmethane selectivity (%)	Apparent rate constant k_a ($\times 10^4$ min^{-1})
Fresh	455	76.2	291.7
First reuse	525	78.9	282.3
Second reuse	532	75.3	275.5

[a] Time required for the complete conversion of benzyl chloride.

3.4. Effect of water

Lewis acids are sensitive to water and the effects of water on the catalytic activity were investigated using Ga-HMS-40 at 353 K with a ratio PhH/BnCl = 15, 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. Similar results have been obtained on supported thallium [29], indium oxides [14] and iron-mesoporous [7].

3.5. Recycling of the catalysts

The stability of the catalysts has been studied by running the reaction successively with the same catalyst (Ga-HMS-40) 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 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.

4. Conclusion

In conclusion, Ga-HMS catalysts show remarkable activities for the alkylation of aromatics. The mechanism involves a redox step at the reaction initiation. This gives a greater independence to the effect of substituents, and shows a low sensitivity to water.

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