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Catalytic properties of Thallium-containing mesoporous silicas



A. Baradji ^{b,*}, K. Bachari ^a, J. Amari ^b

^a Centre de recherche scientifique et technique en analyses physico-chimiques (C.R.A.P.C), BP 248, Alger RP 16004, Alger, Algeria

^b Laboratoire valorisation matériaux, Université Ibn Badis, BP 273, Mostaganem, Algeria

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Abstract The benzylation of benzene by benzyl chloride over a series of Thallium-containing mesoporous silicas with different Tl contents has been investigated. These materials (Tl-HMS-n) have been characterized by chemical analysis, N₂ adsorption/desorption isotherm and X-ray diffraction (XRD). The mesoporous Thallium-containing materials showed both high activity and high selectivity for the benzylation of benzene. More interesting is the observation that these catalysts are always active and selective for large molecules like naphthenic compounds such as methoxynaphthalene.

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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 (Olah, 1973), 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 AlCl₃, FeCl₃, BF₃, ZnCl₂, and H₂SO₄ (Olah, 1973; Olah et al., 1985; Commandeur et al., 1991).

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 (Clark et al., 1994; Cao et al., 1998). Indeed, some solid acid catalysts (Tahir et al., 2008; Benadji et al., 2010; Bachari et al., 2010; Merabti et al., 2010) have already been proposed which are efficient catalysts for Friedel–Crafts alkylations.

The discovery of a 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 (Kresge et al., 1992; Beck et al., 1992). 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 (Huo et al., 1994). Furthermore, another pathway was proposed by Tanev et al. (1994) to prepare mesoporous

* Corresponding author. Tel./fax: +213 21247406.

E-mail address: baradji_ali@yahoo.fr (A. Baradji).

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silicas at room temperature by a neutral templating route (S^{0I^0}). In this case, the organic surfactant is not a 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 HMS (hexagonal mesoporous silica), reveal excellent catalytic capacity for macro molecular reactions and suggest new opportunities for transition metal incorporation into silica frameworks. In the present work, we report the synthesis and characterization of such materials incorporating Thallium and their test as catalysts for the benzylation of benzene with benzyl chloride. The kinetics of the reaction over these catalysts has been investigated and the reaction has been extended to other substrates like toluène, *p*-xylene, anisole, naphthalene, methylnaphthalene and methoxynaphthalene.

2. Experimental

2.1. Catalysts preparation

The catalysts TI-HMS-*n* (where *n* is the Si/Tl ratio in the precursor gel = 55, 35, 15) have been prepared following the pathway reported by Tanev et al. (1994). In a representative preparation, hexadecylamine (HDA) was added to a solution containing water and ethanol (EtOH) and the mixture was stirred until homogeneous. Then tetraethyl orthosilicate (TEOS) was added under vigorous stirring. The metal precursor $Tl(NO_3)_3$ 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_4Cl (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 In^{III} for Si^{IV} (Tuel et al., 1998; Echchahed et al., 1997). 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.

2.2. Characterization of the samples

Powder X-ray diffraction patterns were recorded on SIEMENS D500 diffractometer with Cu-K α radiation. The chemical compositions of the samples were determined by atomic absorption. The N_2 adsorption/desorption isotherms were measured on samples that were preliminarily outgassed at 523 K overnight using a Catasorb apparatus.

2.3. Catalytic testing

The benzylation of benzene by benzyl chloride has been used as a model reaction for Friedel–Craft alkylation catalytic properties. To avoid diffusional limitations, the solids were crushed below 50 μm and 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. 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 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 m \times 0.32 mm 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 the Table 1. The Thallium compositions of the solids corresponded relatively well to those fixed for the synthesis except at low Thallium content (TI-HSM-55) where a loss of Thallium was observed.

Most of the values of the specific surface areas of the solids were larger than 1000 ($m^2 g^{-1}$), which was typical of mesoporous materials (Beck et al., 1992; Huo et al., 1994). When the Thallium content increased, they decreased slightly. The N_2 adsorption/desorption isotherms show that the different solids contain regular pores of *ca.* 3.7 nm diameter.

The X-ray powder diffraction patterns of the solids showed a broad peak at $(2\theta) = 2$ (Fig. 1) characterizing a mesoporous material not well-crystallized. The intensity of the peak decreased very slightly when the Thallium content increased showing that the addition of Thallium has not a negative effect on the crystallinity. Furthermore, no peak is observed in the 10 to 80° (2θ) (Fig. 2). Indeed, no modification in the X-ray patterns or N_2 isotherms was observed throughout the series of samples, indicating that the materials do not lose their crystallinity with Tl incorporation.

3.2. Reaction kinetics

The kinetic data for the benzene benzylation reaction in excess of benzene (stoichiometric ratio Bz/BzCl = 15) over the TI-HMS-35 catalyst could be fitted well to a pseudo-first-order rate law:

$$\text{Log}[1/1 - x] = (k_a/2.303)(t - t_0)$$

Table 1 Chemical composition and characteristics of the catalysts.

Sample	Chemical analysis		Surface area ($m^2 \cdot g^{-1}$)	ϕ_p (\AA) ^a
	Tl (wt.%)	Si/Tl		
HMS	–	–	1170.0	38
TI-HMS-55	0.80	85.0	1137.0	33
TI-HMS-35	2.98	38.8	1082.0	35
TI-HMS-15	6.30	15.2	961.6	34

^a ϕ_p is the mean pore diameter obtained from N_2 adsorption isotherms.

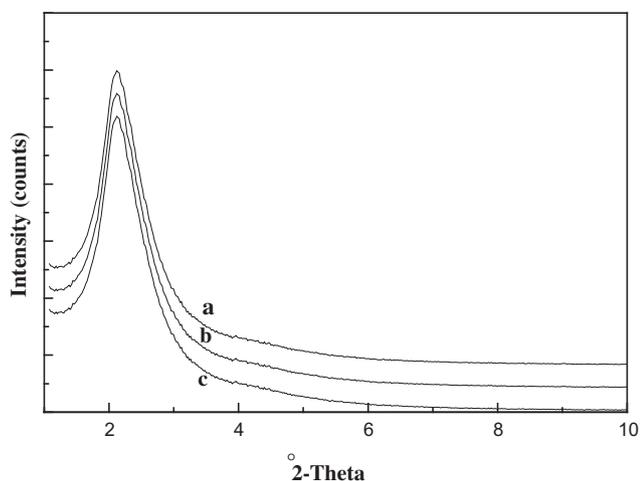


Figure 1 DRX patterns of the TI-HMS-*n* catalysts in the domain of 1–10° (2θ). *n* = Si/Tl = (a) 55, (b) 35, (c) 15.

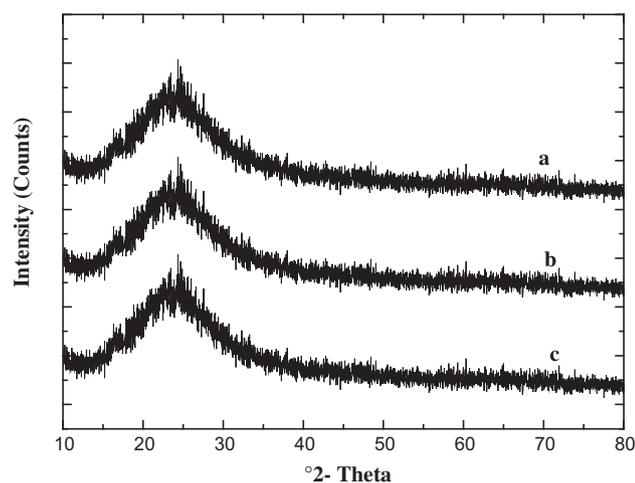


Figure 2 DRX patterns of the TI-HMS-*n* catalysts in the domain of 30–80° (2θ). *n* = Si/Tl = (a) 55, (b) 35, (c) 15.

where k_a is 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 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 120.6 min and $132 \times 10^{-4} \text{ min}^{-1}$ at 343 K to, respectively, 20.1 min and $338 \times 10^{-4} \text{ min}^{-1}$ at 353 K.

By contrast, the selectivity to diphenylmethane decreased from 100 to 73%. The activation energy estimated thus obtained was 98.5 kJ mol^{-1} .

Table 2 Catalytic activities of TI-HMS-35 at different temperatures: 343, 348 and 353 K.

Temperature (K)	Time ^a (min)	Diphenyl methane selectivity (%)	Apparent rate constant $K_a (\times 10^4 \text{ min}^{-1})$
343	120.6	100.0	132
348	50.5	100.0	165
353	20.1	73.0	338

^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 TI-HMS-35 catalyst.

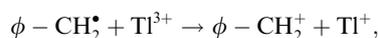
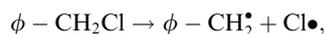
Benzene/benzyl chloride ratio	Time ^a (min)	Diphenyl methane selectivity (%)
5	339.2	63.7
15	231.4	100.0

^a Time required for the complete conversion of 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.

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 and σ^+ a coefficient representing the changes of reactivity due to the substituent, and ρ a constant related to the charge in the intermediate complex (March, 1985).

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



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 (Choudhary and Jana, 2001; Bachari et al., 2010, 2011; Hentit et al., 2007; Tahir et al., 2008; Benadji et al., 2010; Merabti et al., 2010; Briio et al., 2001; Choudhary and Jana, 2002).

In order to rule out the influence of a steric effect on the rate of reaction, we have applied the Taft relation (March, 1985). 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

Table 4 Reaction rates for substituted benzenes over TI-HMS-35 catalyst at 353 K.

Substituent	Benzene	Toluene	<i>p</i> -Xylene	Anisole	Naphthalene	Methylnaphthalene	Methoxynaphthalene
$K_a \times 10^4 (\text{min}^{-1})$	338	311.2	295.0	242.5	170.8	158.1	127.7

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 ($\times 10^4 \text{ min}^{-1}$)
HMS	–	–	–
TI-HMS-55	–	–	–
TI-HMS-35	231.4	100.0	165.0
TI-HMS-15	137.3	89.7	326.2

^a Time required for the complete conversion of benzyl chloride.

of the substituting group of the studied aromatic compounds. Using the E_s parameter tabulated by Charton (Charton, 1975) we have shown that such a relation did not exist.

It was interesting to compare the solids with $\text{TiO}_x/\text{zirconia}$ (LS) Choudhary and Jana, 2001. Both systems reached a final conversion of 100% with complete selectivity to the monoalkyl group; the half reaction time was about 3.8 min for $\text{TiO}_x/\text{zirconia}$ (LS) and was here about 20 min, so that TI-HMS is less active probably due to the higher amount of Thallium in $\text{TiO}_x/\text{zirconia}$ (LS).

Furthermore, the catalyst TI-HMS-35 is always active and selective for larger molecules like naphthenic compounds such as methoxynaphthalene (Table 4). The large pores of the mesoporous support permit the conversion of these molecules that could not be done on other supports.

3.3. Catalytic performances of TI-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 Thallium (TI-HMS-55) were totally inactive. The other compounds showed an activity increasing with increase of their Thallium content. However, the selectivity to diphenylmethane at complete conversion of benzyl chloride decreased while the TI content increased.

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 $K_a (\times 10^4 \text{ min}^{-1})$
Fresh	347	78.5	338.0
First reuse	385	76.8	319.3
Second reuse	393	77.1	305.5

^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 TI-HMS-35 at 353 K with a ratio $\text{PhH}/\text{BnCl} = 15$, 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 Gallium oxides (Choudhary and Jana, 2002) and Iron-mesoporous materials (Tahir et al., 2008).

3.5. Recycling of the catalysts

The stability of the catalysts has been studied by running the reaction successively with the same catalyst (TI-HMS-35) under the same conditions without any regeneration between the 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.

Table 6 Effect of water on the catalytic properties of TI-HMS-35 at 353 K.

Water content (vol.%)	Time (min)	Benzyl chloride conversion (%)	Diphenyl methane selectivity (%)	Apparent rate constant ($\times 10^4 \text{ min}^{-1}$)
–	347	100.0	78.5	338.0
0.1	377	99.5	78.0	302.1
0.2	472	99.2	76.1	278.6
0.3	558	91.1	60.8	225.3
0.5	662	79.4	59.4	138.3
0.6	672	67.3	58.9	88.1

4. Conclusion

In conclusion, Tl-HMS mesoporous 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 low sensitivity to water. The effective catalysts should correspond to small Thallium oxide particles well dispersed and stabilized on the mesoporous support.

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