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Zinc-Containing Mesoporous Silicas as a Catalyst for the Benzylation of Benzene and Other Aromatics by Benzyl Chloride[1]

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Abstract—The benzylation of benzene and the substituted benzenes reaction employing benzyl chloride as the alkylating agent over a series of zinc-containing mesoporous silicas with different Zn contents have been investigated. These materials (Zn–HMS-*n*) have been characterized by chemical analysis, BET, and XRD. The mesoporous zinc-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. The kinetics of the benzene benzylation over these catalysts has also been investigated.

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1. INTRODUCTION

Friedel–Crafts alkylations comprise a very important class of reactions that are of common use in organic chemistry. These reactions are habitually catalyzed by Lewis acids in the 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 dielectries. In the homogeneous phase, this reaction is catalyzed on an industrial scale by $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, and H_2SO_4 [1–3].

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, 9] have already been proposed which are efficient catalysts. Cseri et al. [10] reported that zinc, iron, tin, and copper-exchanged zeolites are highly active and selective reagents for the catalysis of 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 [11, 12]. 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 adsorption and catalysis. Depending on the synthesis conditions, different phases could be obtained, like the hexagonal phase MCM-41 and the cubic phase MCM-48, as well as the lamellar compound MCM-50. Huo et al. [13] proposed four complementary synthesis pathways. The first pathway implicated the direct cocondensation of the cationic surfactant (S^+) with anionic inorganic species (I^-) to create assembled ion pairs (S^+I^-). In the second pathway, an anionic template (S^-) was used to direct the self-assembly of cationic species (I^+) through (S^-I^+) ion pairs. Pathways 3 and 4 involved counter ion–mediated assemblies of surfactants and inorganic species of similar charge. These counter ion–mediated pathways created assembled solution species of type $S^+X^-I^+$ or $S^-M^+I^-$ (with $X^- = Cl^-$, Br^- and $M^+ = Na^+$, K^+). Furthermore, another pathway was proposed by Tanev et al. [14] to prepare mesoporous silicas at room temperature by a neutral templating route (S^0I^0). In this case, the organic surfactant is not the 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 zinc and their testing as catalysts for the benzylation of benzene with

[1] This text was submitted by the authors in English.

benzyl chloride. The kinetics of the reaction over these catalysts has been investigated, and the reaction has been extended to other substrates like toluene, *p*-xylene, and anisole.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The catalysts Zn–HMS-*n* (where n is the Si/Zn ratio in the precursor gel = 60, 30, 15) were prepared following the pathway reported by Tanev et al. [14]. In a representative preparation, hexadecylamine (HDA (Aldrich)) was added to a solution containing water and ethanol (EtOH (Rhône—Poulenc)) and the mixture was stirred until homogeneous. Then tetraethyl orthosilicate (TEOS (Aldrich)) was added under vigorous stirring. The metal precursor $Zn(NO_3)_2 \cdot 4H_2O$ (Merck) 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 Zn(II) for Si(IV) [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.

2.2. Characterization of the Samples

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

2.3. 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 at different reaction temperatures = 343, 348, and 353 K. A quantity of 100 mg of the solids was tested after activation consisting of a heat treatment under air (2 l 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 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 × 0.32 nm i.d.). The selectivity is expressed by the molar ratio of formed diphenylmethane to converted benzyl chloride.

Table 1. Chemical composition and characteristics of the catalysts

Sample	Chemical analysis		Surface area ($m^2\ g^{-1}$)
	Zn (wt %)	Si/Zn	
HMS	0.00	0.00	1170.0
Zn–HMS-60	0.78	80.0	1143.0
Zn–HMS-30	3.51	29.6	1035.0
Zn–HMS-15	6.24	14.5	965.7

3. RESULTS AND DISCUSSION

3.1. Characterization

The results of the chemical composition and characteristics of the catalysts are given in Table 1. The zinc composition of the solids corresponded relatively well to those fixed for the synthesis except at low zinc content (Zn–HMS-60) where a loss of zinc 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 a mesoporous material [12, 22]. When the zinc content increased, they decreased slightly.

The x-ray powder diffraction patterns of the solids showed a broad peak at $(2\theta) = 2.1°$ (Fig. 1) characterizing a mesoporous material not well crystallized. The intensity of the peak decreased when the zinc content increased showing that the addition of zinc has a negative effect on the crystallinity.

3.2. Reaction Kinetics

The kinetic data for the benzene benzylation reaction in an excess of benzene (stoichiometric ratio Bz/BzCl = 15) over the Zn–HMS-30 catalyst could be fitted well to a pseudo-first-order rate law

$$\log[1/1 - x] = (k_{app}/2.303)(t - t_0),$$

where k_{app} is the apparent first-order rate constant, x is the fractional conversion of benzyl chloride, t is the reaction time, and t_0 is the induction period corresponding to the time required for reaching the equilibrium temperature. A plot of $\log[1/(1 - x)]$ as a function of

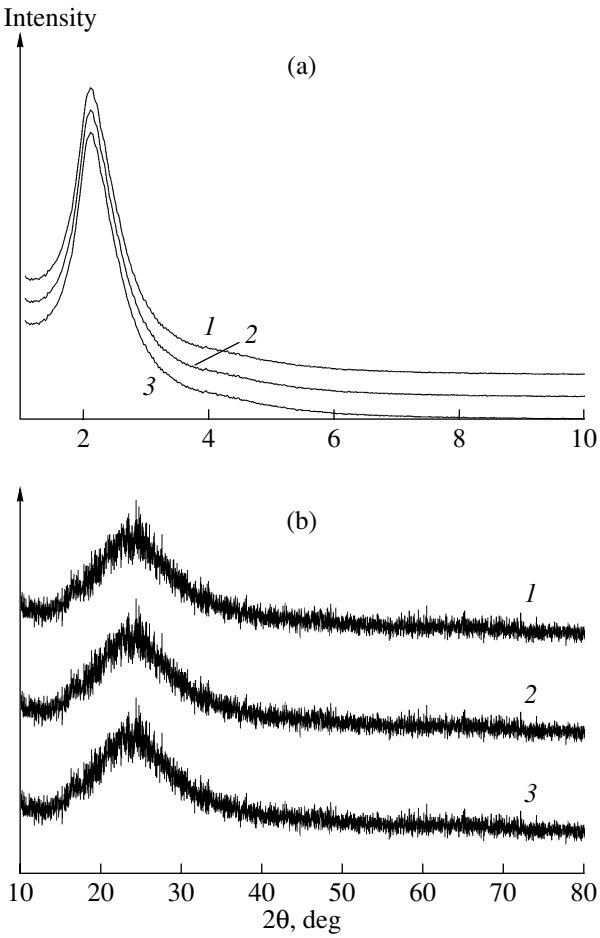

Fig. 1. DRX patterns of the Zn–HMS-*n* catalysts in the domain of 1–10°C (2θ). *n* = Si/Zn = (a) 60, (b) 30, (c) 15.

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 BzH/BzCl = 15 and 0.1 g catalyst). The results showed that the catalytic performances of the catalyst strongly increased with the reaction temperature (Table 2).

Table 2. Catalytic activities of Zn–HMS-30 at different temperatures: 343, 348, 353 K with ratio BzH/BzCl = 15 and 0.1 g catalyst

Temperature, K	Time[a], min	Diphenyl methane Selectivity, %	Apparent rate constant K_a ($\times 10^4$ min^{-1})
343	168.7	100	100.8
348	75	94	129.1
353	37.5	70.4	265.4

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

Indeed, the time for 50% conversion of benzyl chloride and the apparent rate constant K_a changed from 168.7 min and 100.8×10^{-4} min^{-1} at 343 K to, respectively, 37.5 min and 265.4×10^{-4} min^{-1} at 353 K.

By contrast, the selectivity to diphenylmethane decreased from 100 to 69.6%. The estimated activation energy thus obtained was 94.8 (kJ mol^{-1}).

Two BzH/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., $\log k_{app} = \log k_{app,0} + \sigma^+\rho$, in which $k_{app,0}$ is the rate constant for benzene, σ^+ is a coefficient representing the changes of reactivity due to the substituent, and ρ is a constant related to the charge on the intermediate complex [17].

In the present case, only a small change of k_{app} 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 homolytic rupture of the carbon–chlorine bond followed by the oxidation of the radical:

$$\phi\text{-}CH_2Cl \longrightarrow \phi\text{-}\dot{C}H_2 + Cl^{\bullet},$$

$$\phi\text{-}\dot{C}H_2 + Zn^{2+} \longrightarrow \phi\text{-}CH_2^+ + Zn^+,$$

$$Zn^+ + Cl^{\bullet} \longrightarrow Zn^{2+} + Cl^-.$$

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, 18–20].

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 size of the substituting group of the studied aromatic compounds. Using the E_s parameter tabulated by Charton [21], we have shown that such a relation did not exist.

It was interesting to compare the solids with Zn-exchanged clays investigated earlier under similar conditions (BzH/BzCl = 15, 353 K) [10]. Both systems reached a final conversion of 100% with complete

Table 3. Influence of the stoichiometric ratio between benzene and benzyl chloride for the benzylation of benzene over the Zn–HMS-30 catalyst at 348 K and 0.1 g catalyst

Benzene/benzyl chloride ratio	Time[a], min	Diphenyl methane selectivity, %
5	437.5	68.9
15	306.2	100

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

Table 4. Reaction rates for substituted benzenes at 353 K, BzH/BzCl = 15, and 0.1 g catalyst

Substituent	$K_a \times 10^4$, min^{-1}
Benzene	265.4
Toluene	242.5
p-Xylene	229.1
Anisole	185.0

Table 5. Catalytic properties of the catalysts in the benzylation of benzene with benzyl chloride at 348 K, BzH/BzCl = 15, and 0.1 g catalyst

Catalyst	Time[a], min	Diphenyl-methane selectivity, %	Apparent rate constant $K_a \times 10^4$ min^{-1}
HMS	–	–	–
Zn–HMS-60	–	–	–
Zn–HMS-30	306.2	100	129.1
Zn–HMS-15	216.2	90.5	275.3

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

selectivity to monoalkyl; the half reaction time was about 60 min for Zn/K10 and was here about 37.5 min, so that Zn–HMS-30 is more active than clays.

3.3. Catalytic Performances of Zn–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 zinc (Zn–HMS-60) were totally inactive. The other compounds showed an activity increasing with their zinc content. However, the selectivity to diphenylmethane at complete conversion of benzyl chloride decreased while the Zn content increased.

3.4. Effect of Water

Lewis acids are sensitive to water, and the effects of water on the catalytic activity were investigated using Zn–HMS–30 at 353 K with a ratio BzH/BzCl = 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 [20], indium oxides [22], 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 (Zn–HMS-30) 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 benzy-

Table 6. Effect of water on the catalytic properties of Zn–HMS-30 at 353 K, BzH/BzCl = 15, and 0.1 g catalyst

Water content, vol %	Time, min	Benzyl chloride conversion, %	Diphenyl methane selectivity, %	Apparent rate constant, $\times 10^4$ min^{-1}
–	510	100	78.8	264.5
0.1	530	100	75.9	248.3
0.2	620	98.5	75.6	182.5
0.3	703	86.7	68.1	115.8
0.5	800	69	67.5	89.8
0.6	818	57.2	64.3	56.5

Table 7. Effect of recycling of Zn–HMS-30 in the benzylation of benzene with benzyl chloride at 353K, Bz/BnCl = 15, and 0.1 g catalyst

	Time[a], min	Diphenylmethane selectivity, %	Apparent rate constant $K_a \times 10^4$ min^{-1}
Fresh	510	78.8	264.5
First reuse	525	80.9	257.0
Second reuse	532	79.3	259.5

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

lation process without a significant change in its catalytic activity.

4. CONCLUSIONS

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

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