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Benzylation of aromatics on tin-containing mesoporous materials

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Abstract

The benzylation of benzene and substituted benzenes reaction employing benzyl chloride as the alkylating agent over a series of tin-containing mesoporous silicas with different Sn contents has been investigated. These materials (Sn-HMS-*n*) have been characterized by elemental analysis, DRX method, N_2 adsorption Measurements (BET and BJH theory), XPS, UV–vis, FTIR and Mössbauer spectroscopic methods. The mesoporous tin-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. 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 has also been investigated.

Keywords: Benzylation of aromatics; Benzyl chloride; Tin-mesoporous materials; Diphenylmethane

1. Introduction

Friedel–Crafts alkylations comprise a very important class of reactions which are of common use in organic chemistry. These reactions are habitually catalysed 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, several solid acid catalysts have already been proposed which are efficient catalysts such as: Fe-modified ZSM-5 and H-β zeolites; Fe_2O_3 or $FeCl_3$ deposited on micro-, meso and macro-porous [6]; Fe-containing mesoporous molecular sieves materials [7,8]; Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts [9]; Ga- and Mg-oxides and chlorides derived from Ga–Mg-hydrotalicite [10]; Ga-SBA-15 [11]; Ga-HMS [12]; $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported on clays and Si-MCM-41 [13]; transition metal chloride supported mesoporous SBA-15 [14]; supported thallium oxide catalysts [15]; Sb supporting K10 [16]; solid superacid and silica-supported polytrifluoro-methanesulfosil oxane [17]; Si-MCM-41-supported Ga_2O_3 and In_2O_3 [18]; H_2SO_4, HNO_3 and $HClO_4$/metakaolinite [19]; alkali metal salts and ammonium salts of keggin-type heteropolyacids [20]; ion-exchanged clays [21]; clayzic [22]; Cu-HMS [23]; solid superacids based on sulfated ZrO_2 [24]; HY [25]; Fe, Ce, W-modified H-β zeolites [26]; H-ZSM-5 [27] and $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ supported on acidic alumina [28] for the benzylation of benzene and other aromatic compounds.

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 [29,30]. 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

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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. [31] proposed four complementary synthesis pathways. The first pathway implicated the direct co condensation of 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. [32] 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 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 tin 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, anisole, naphthalene, methylnaphthalene and methoxynaphthalene.

2. Experimental

2.1. Materials

Samples were synthesized with Hexadecylamine (Aldrich), orthosilicate (TEOS, Aldrich), tin tetrachloride ($SnCl_4 \cdot 5H_2O$, Loba Chemie) and ethanol (Rhône-Poulenc).

2.2. Catalysts preparation

The catalysts Sn-HMS-*n* (where *n* is the Si/Sn ratio in the precursor gel = 70, 40, 20) have been prepared following the pathway reported by Tanev et al. [32]. 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. The metal precursor 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) and the mixture was refluxed under vigorous stirring for 2 h. 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

The chemical compositions of the samples were determined by a combination of wet chemical methods and atomic absorption spectrometry (HITACHI Z 800). Powder X-ray diffraction patterns were recorded on SIEMENS D500 diffractometer with Cu Kα radiation. They were recorded with 0.02° (2θ) steps and 1 s counting time per step over two angular domains from 1° to 10° (2θ) and from 10° to 80° (2θ). Adsorption/desorption experiments using N_2 were carried out at 77 K on a NOVA 2000 porosimeter (Quantachrome) instrument. Before each measurement the samples were first outgassed at 423 K for 12 h at 5×10^{-3} Torr and then at room temperature for 2 h at 3.9×10^{-9} Torr. The N_2 isotherms were used to determine the specific surface areas and pore diameter using the BET equation and BJH theory. XPS measurements were carried out using a V.G. Scientific ESCA-3-MK II X-ray photoelectron spectrometer with Al Kα X-ray source and a hemispherical analyser connected to a five-channel detector. All binding energy values (BE (eV)) were determined with respect to the C 1s line (285.0 eV) of the carbon overlayer and the standard deviation of the peak position was within ±0.1 eV. The XPS spectra have been fitted with VGS program fit routine. A Shirley background substraction was applied and Gauss–Lorentz curves were used. UV–vis diffuse reflectance spectra (UV–vis DRS) were collected on a Perkin-Elmer UV–vis spectrometer (Lambda 9) in the range from 250 to 500 nm with a resolution of 1 nm. FTIR spectra were collected at ambient conditions with a Perkin-Elmer 2000 spectrometer using the KBr method (1 g of sample to 100 g of KBr).

Liquid N_2 temperatures ^{119}Sn Mössbauer spectra were measured in constant acceleration mode and at ±6 mm/s velocity range. The source used was $Ca^{119m}SnO_3$ of 10^8 Bq activity. All isomer shift data are given relative to SnO_2 with the center of the spectrum defining zero velocity. The spectra were evaluated assuming a simple Lorentzian lineshape. A computerized nonlinear least-squares regression procedure was applied for obtaining the Mössbauer parameters, namely, isomer shifts (I.S.), quadrupole splittings (Q.S.) and area.

2.4. Catalytic testing

The benzylation reactions over a series of Tin-containing mesoporous silicas catalysts were carried out in a magnetically stirred glass reactor (25 cm^3) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture free nitrogen N_2 (flow rate = 30 $cm^3\ min^{-1}$) 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