

Study of the benzylation of benzene and other aromatics by benzyl chloride over transition metal chloride supported mesoporous SBA-15 catalysts

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Received 13 May 2006; received in revised form 17 June 2006; accepted 23 June 2006

Available online 8 August 2006

Abstract

The benzylation of benzene by benzyl chloride to diphenylmethane over FeCl₃, InCl₃, GaCl₃, ZnCl₂, CuCl₂ and NiCl₂ supported on mesoporous SBA-15 at 353 K has been investigated. The redox property due to the impregnation of the SBA-15 by transition metal chloride seems to play a very important role in the benzene benzylation process. Among the catalysts, the FeCl₃/SBA-15 showed both high conversion and high selectivity for the 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 have also been investigated.

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Keywords: Catalytic benzylation; Benzyl chloride; Benzenic compounds; Naphthenic compounds; (Iron, indium, gallium, zinc, copper, nickel)-supported on mesoporous SBA-15; Hammett relationship

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 FeCl₃ [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]. 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 proposed which are efficient catalysts such as: Fe-modified ZSM-5 and H-β zeolites; Fe₂O₃ or FeCl₃ deposited on micro-, meso and macro-porous [4]; Fe-

containing mesoporous molecular sieves materials [5,6]; Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts [7]; Ga- and Mg-oxides and chlorides derived from Ga–Mg-hydrotalcite [8]; Ga-SBA-15 [9]; Ga-HMS [10]; InCl₃, GaCl₃, FeCl₃ and ZnCl₂ supported on clays and Si-MCM-41 [11]; supported thallium oxide catalysts [12]; Sb supporting K10 [13]; solid superacid and silica-supported polytrifluoro-methanesulfonil oxane [14]; Si-MCM-41-supported Ga₂O₃ and In₂O₃ [15]; H₂SO₄, HNO₃ and HClO₄/metakaolinite [16]; alkali metal salts and ammonium salts of keggin-type heteropolyacids [17]; ion-exchanged clays [18]; clayzic [19]; solid superacids based on sulfated ZrO₂ [20]; HY [21]; H-ZSM-5 [22] and FeCl₃, MnCl₂, CoCl₂, NiCl₂, CuCl₂, ZnCl₂ supported on acidic alumina [23] for the benzylation of benzene and other aromatic compounds.

Furthermore, mesoporous silica materials, MCM-41 and SBA-15, have received increasing scientific interest owing to their narrow pore size distribution, high surface area and pore volume which make them promising candidates for use as catalyst support in catalysis field [24–30]. SBA-15 material was synthesized in acidic medium with poly(alkylene oxide) triblock copolymers under relatively mild synthesis conditions [31]. The pore size can be varied on a relatively large range

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between 5 and 20 nm depending on the synthesis conditions. The SBA-15 material also exhibits a higher stability due to the greater wall thickness compared to the MCM-41 material [32] which render it more suitable for use as catalyst support in catalytic processes where thermal treatments and repeated regeneration were frequently encountered.

In the present work, we report the benzylation of benzene reaction with benzyl chloride using FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 supported on mesoporous silicas SBA-15. The kinetics of the reaction over these catalysts have been investigated and the reaction has been extended to other substrates like toluene, *p*-xylene, anisole and naphthalenic compounds.

2. Experimental

2.1. Materials

Samples were synthesized with tetraethyl orthosilicate (TEOS, Merck), tri-block copolymer poly(ethylene glycol)-block poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO20PO70EO20, Aldrich), Transition metal chloride (FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 , Merck).

2.2. Catalysts preparation

SBA-15 sample was synthesized using tri-block copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) as a structure directing agent with the following molar gel composition: TEOS:0.016P123:0.46HCl:127H₂O. In a typical synthesis, 4 g of Pluronic P123 was added to 30 ml of water. After stirring for a few hours, a clear solution was obtained. The 70 g of 0.28 M hydrochloric acid was added to it and the solution was stirred for another 2 h. Then, 9 g of tetraethyl orthosilicate was added and the resulting mixture was stirred for 24 h at 313 K. The solid product was recovered by filtration, washed with water for several times, and dried overnight at 373 K. Finally, the product was calcined at 813 K to remove the template.

Supported transition metal chloride (FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 , NiCl_2) catalysts (loading of metal chloride = 1.15 mmol g⁻¹) were prepared by impregnating SBA-15 with anhydrous metal chloride from their acetonitrile solution by incipient wetness technique and evaporating the solvent in vacuum oven at 393 K for 12 h.

2.3. Catalytic testing

The benzylation reactions over the supported transition metal chloride catalysts were carried out in a magnetically stirred glass reactor (25 cm³) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture 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 reaction mixture, containing catalyst and aromatic compound with or without solvent. Measuring quantitatively the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by N₂ in a 0.1 M NaOH solution containing phenolphthalein indicator) followed the course of the reaction. The polybenzyl chloride (which is formed by the condensation of benzyl chloride) was isolated from the reaction mixture by the procedure given by Choudhary et al. [32]. In all the cases, the major product formed was mainly mono-benzylated compound along with polybenzyl chloride as side product depending upon the condition used.

Samples were analyzed periodically on a gas chromatograph (HP-6890) equipped with a FID detector and a capillary column RTX-1 (30 m × 0.32 mm i.d.). The products were also identified by GC–MS (HP-5973) analysis.

3. Results and discussion

3.1. Comparison of the mesoporous SBA-15-supported metal chloride catalysts for benzene benzylation

The FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 supported metal chloride catalysts are compared for their performance in the benzylation of benzene 353 K in Table 1.

From comparison of results in this table, the following important observations can be made:

- The catalyst support itself (SBA-15) shows no activity in the benzylation of benzene; however, its catalytic activity is increased drastically because of the impregnation of FeCl_3 , InCl_3 , GaCl_3 , ZnCl_2 , CuCl_2 and NiCl_2 .
- Among the supported metal chloride catalysts, the FeCl_3 /SBA-15 catalyst showed both high conversion and high selectivity in the benzylation. The conversion for the mesoporous SBA-15-supported transition metal chloride catalyst is much higher than that for the transition metal chloride with-

Table 1
Results of the benzylation of benzene by benzyl chloride over different transition metal chloride supported on mesoporous SBA-15 at 353 K

Catalyst	Time (min) ^a	Selectivity (%)		Apparent rate constant, k_a ($\times 10^3$ min ⁻¹)
		Diphenyl methane	Polybenzyl chloride	
FeCl_3 /SBA-15	11.2	98.8	1.2	254.0
InCl_3 /SBA-15	12.7	98.5	1.5	221.5
GaCl_3 /SBA-15	14.2	97.8	2.2	202.0
CuCl_2 /SBA-15	18.7	95.6	4.4	171.3
ZnCl_2 /SBA-15	20.3	87.1	12.9	140.1
NiCl_2 /SBA-15	30.8	83.4	16.6	97.9
FeCl_3	30.5	52.3	47.7	98.2
InCl_3	36.2	45.0	55	75.7
GaCl_3	42.4	49.2	50.8	69.4
CuCl_2	51.7	43.8	56.2	63.7
ZnCl_2	57.7	53.6	46.4	55.2
NiCl_2	85.6	50.7	49.3	37.8
SBA-15	–	–	–	–

^a Time required for 90% conversion of benzyl chloride.

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