

Benylation of benzene and other aromatics by benzyl chloride over copper-mesoporous molecular sieves materials

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Abstract

The benzylation of benzene and substituted benzene reactions employing benzyl chloride as the alkylating agent over a series of copper-containing mesoporous silicas with different Cu contents has been investigated. These materials (Cu-HMS-*n*) have been characterised by chemical analysis, BET and XRD. The mesoporous copper-containing materials showed both high activity 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. The kinetics of 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 usually catalysed by Lewis acids in liquid phase [1]. However, the commonly used liquid acid catalysts (e.g. AlCl₃, FeCl₃, BF₃, ZnCl₂ and H₂SO₄) [1–3] pose several problems including difficulty in separation and recovery, disposal of used catalyst, corrosion, high toxicity and the requirement of stoichiometric amounts of these catalysts [4,5].

The development of reusable acid catalysts (acidic solid catalysts) which can easily be separated from the reaction mixture, and also have high activity for the Friedel–Crafts reactions is, consequently, of large practical importance. Universal efforts have been made to achieve this goal, using different acidic solid catalysts, such as zeolites [6], Fe-MCM-41, Fe-HMS [5,7] and clays exchanged by metallic ions [8–10] for benzylation of benzene and toluene.

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 characterised 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 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 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. [14] to prepare mesoporous silicas

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at room temperature by neutral templating route (S^{0T^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 characterisation of such materials incorporating copper, and their assessment as catalysts for the benzylation of benzene with benzyl chloride. The kinetics of the reaction over these catalysts have been investigated and the reaction extended to other substrates like toluène, *p*-xylene and anisole.

2. Experimental (Materials and methods)

2.1. Materials

Samples were synthesized with Hexadecylamine (Aldrich), orthosilicate (TEOS, Aldrich), Copper-nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, Merck) and ethanol (Rhône-Poulenc).

2.2. Catalyst preparation

The catalysts Cu-HMS-*n* (where *n* is the Si/Cu ratio in the precursor gel = 50, 25, 15) were prepared as previously reported by Tanev et al. [14]. In a representative preparation, hexadecylamine (HDA) was added to a solution containing water and ethanol (EtOH) and the mixture was stirred to homogeneity. Tetraethyl orthosilicate (TEOS) was then added with vigorous stirring. The metal precursor dissolved in TEOS itself.

This solution was subsequently 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 with vigorous stirring for 2 h. The presence of NH_4^+ cations in EtOH was reported to be necessary to exchange the protonated amines formed during the synthesis, and to balance the excess negative charge resulting from the substitution of Cu^{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.

2.3. Characterisation of the samples

Powder X-ray diffraction patterns were recorded on SIEMENS D500 diffractometer with Cu $K\alpha$ radiation. The chemical composition of the samples was determined

by atomic absorption, and their surface areas were 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 (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 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 ($30 \text{ m} \times 0.32 \text{ mm i.d.}$). The selectivity is expressed by the molar ratio of formed diphenylmethane to converted benzyl chloride.

3. Results and discussion

3.1. Characterisation

The results of the chemical composition and characteristics of the catalysts are summarised in Table 1. The copper compositions of the solids corresponded relatively well to those fixed for the synthesis, except at low iron content (Cu-HSM-50) where a loss of copper was observed.

Most of the values of the specific surface areas of the solids were larger than $1000 \text{ m}^2 \text{ g}^{-1}$, which was typical of mesoporous materials [12,22]. When the copper content increased, they decreased slightly first and then more drastically at high copper loading (Cu-HSM-15).

The X-ray powder diffraction patterns of the solids showed a broad peak at $(2\theta) = 2.2$ (Fig. 1) characterising a mesoporous material not well crystallised. The intensity of the peak decreased as the copper content increased showing that the addition of copper has a negative effect on the crystallinity. At the same time very small peaks corresponding to CuO appeared in the $30\text{--}80^\circ$ (2θ) for Cu-HMS-15 (Fig. 2).

Table 1
Chemical composition and characteristics of the catalysts

Sample	Chemical analysis		Surface area ($\text{m}^2 \text{ g}^{-1}$)
	Cu (wt%)	Si/Cu	
HMS	–	–	1170
Cu-HMS-50	1.00	80.0	1162
Cu-HMS-25	3.25	27.5	1046
Cu-HMS-15	6.33	13.9	895

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