



King Saud University  
Arabian Journal of Chemistry

www.ksu.edu.sa  
www.sciencedirect.com



## ORIGINAL ARTICLE

# Elaboration of nickel-impregnated over hexagonal mesoporous materials and their catalytic application

M. Laribi \*, K. Bachari, M. Touati

Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques (C.R.A.P.C), BP 248, Alger RP 16004, Alger, Algeria

Received 5 December 2011; accepted 13 March 2012

## KEYWORDS

Hexagonal mesoporous silicas;  
Characterization;  
Textural property

**Abstract** Hexagonal mesoporous silicas with different nickel contents have been synthesized and characterized by several techniques such as N<sub>2</sub> physical adsorption, elemental analysis, XRD, TEM and temperature programmed reduction (TPR). In fact, the nickel-impregnated over hexagonal mesoporous silicas showed both high activity and high selectivity for Friedel–Crafts alkylations 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 toluene, *p*-xylene, anisole, naphthalene and methylnaphthalene.

© 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

## 1. Introduction

Friedel–Crafts alkylations comprise a very important class of reactions which are of common use in organic chemistry.

*Abbreviations:* Bz, benzene; BzCl, benzyl chloride; TEOS, tetraethyl orthosilicate; EtOH, ethanol; MeO, methanol; HCl, chloride acid; NaOH, sodium hydroxide; XRD, X-ray diffraction; TEM, transmission electron microscopy; TPR, temperature programmed reduction; GC–MS, gas chromatography coupled with mass spectroscopy.

\* Corresponding author. Tel./fax: +213 21247406.  
E-mail address: mourad\_laribi@yahoo.fr (M. Laribi).

1878-5352 © 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

Peer review under responsibility of King Saud University.  
<http://dx.doi.org/10.1016/j.arabjc.2012.03.005>



Production and hosting by Elsevier

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 (Bz) by benzyl chloride (BzCl) 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<sub>3</sub>, FeCl<sub>3</sub>, BF<sub>3</sub>, ZnCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> (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, several solid acid catalysts have already been proposed which are efficient catalysts such as Fe-modified ZSM-5 and H-β zeolites; Fe<sub>2</sub>O<sub>3</sub> or FeCl<sub>3</sub> deposited on micro-, meso- and macro-porous (Choudhary et al., 2002a); Fe-containing mesoporous molecular sieves materials (He et al., 1998; Bachari et al., 2004); Ga- and Mg-oxides and chlorides derived from Ga–Mg-hydrotalcite (Choudhary et al., 2002b); Ga-SBA-15 (El Berrichi et al., 2006); Ga-HMS (Bachari and Cherifi, 2006a); transition metal chloride

supported mesoporous SBA-15 (Bachari and Cherifi, 2006b); supported thallium oxide catalysts (Choudhary and Jana, 2001); Sb supporting K10 (Deshpande et al., 2001); Si-MCM-41-supported  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  (Choudhary et al., 2000a); alkali metal salts and ammonium salts of keggin-type heteropolyacids (Izumi et al., 1995); ion-exchanged clays (Cseri et al., 1995); Cu-HMS (Bachari and Cherifi, 2006c); solid superacids based on sulfated  $\text{ZrO}_2$  (Koyande et al., 1998) 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 (Kresge et al., 1992; Beck et al., 1992). 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. Furthermore, another pathway was proposed by Tanev et al. (1994) to prepare mesoporous silicas at room temperature by neutral templating route ( $\text{S}^0\text{T}^0$ ). 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 as HMS (hexagonal mesoporous silica), reveal excellent catalytic capacity for macromolecular reactions and suggest new opportunities for transition metal incorporation into silica frameworks. In the present work, we report the elaboration of hexagonal mesoporous silicas with different nickel contents and their application as catalysts for Friedel–Crafts alkylations of benzene.

## 2. Experimental

### 2.1. Materials

Samples were synthesized with hexadecylamine (HDA, Aldrich), tetraethyl orthosilicate (TEOS, Aldrich), nickel–nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Merck), ethanol (EtOH, Rhône-Poulenc), methanol (MeOH, Aldrich), chloride acid (HCl, Aldrich), benzene (Bz, Aldrich), benzene chloride (Bz, Aldrich) and sodium hydroxide (NaOH, Aldrich).

### 2.2. Catalysts preparation

The HMS material was prepared following the pathway reported by Tanev et al. (1994). In a representative preparation, HDA (0.3 mol) was added to a solution containing water (36 mol) and EtOH (7 mol) and the mixture was stirred until homogeneous. Then 1 mol of TEOS was added under vigorous stirring. This solution was then stirred at room temperature for 24 h to obtain the product. The solid was recovered by filtration, washed with distilled water, and air-dried at 393 K for 24 h. Organic molecules occluded in the mesopores were removed by solvent extraction. The dried precursor was dispersed in EtOH (5 g/100 ml) and the mixture was refluxed under vigorous stirring for 2 h. The resultant 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. Impregnated mesoporous materials Ni (wt%)/HMS with Ni (%) = 2 and 8 are prepared as follows: the amount of nickel nitrate is added to 5 g of pure HMS and 50 g of MeOH. The

mixture is agitated at ambient temperature during 2 h, the solvent is then rapidly evaporated under vacuum and the solid is calcined under air at 723 K overnight at a heating rate of  $1 \text{ K min}^{-1}$ .

### 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). Adsorption/desorption experiments using  $\text{N}_2$  were carried out at 77 K on a NOVA 2000 porosimeter (Quantachrome) instrument. Powder X-ray diffraction patterns were recorded on SIEMENS D500 diffractometer with Cu-K $\alpha$  radiation. Transmission electron microscopy (TEM) measurements were performed with a Philips CM10 electron microscope operated at 100 kV. Temperature programmed reduction (TPR) experiments were performed with a TPDRO1100 apparatus from Thermo Quest CE Instruments. Temperature programmed reduction (TPR) experiments were performed with a TPDRO1100 apparatus from Thermo Quest CE Instruments. For the TPR measurements the calcined samples were pelletised, ground and sieved. Sieve fractions between 425 and 850  $\mu\text{m}$  were placed in a fixed bed reactor and used for analysis. A flow containing 5% hydrogen and 95% argon (Hoek Loos) was passed downward through the catalyst bed at a rate of  $20 \text{ ml min}^{-1}$ . After water removal from the outcoming flow (mol sieves) hydrogen consumption was measured using a tungsten thermal conductivity detector.

### 2.4. Catalytic testing

The benzylation reactions over a series of impregnated nickel over mesoporous silicas catalysts were carried out in a magnetically stirred glass reactor (25  $\text{cm}^3$ ) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture free nitrogen  $\text{N}_2$  (flow rate =  $30 \text{ cm}^3 \text{ min}^{-1}$ ) through the liquid reaction mixture, at the following reaction conditions: reaction mixture Bz/BzCl = 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 BzCl, amount of catalyst = 0.1 g and reaction temperature = 353 K. The reaction was started by injecting BzCl 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  $\text{N}_2$  in a 0.1 M NaOH solution containing phenolphthalein indicator) followed the course of the reaction (Choudhary et al., 2000b). Samples were analyzed periodically on a gas chromatograph (HP-6890) equipped with an FID detector and a capillary column RTX-1 (30 m  $\times$  0.32 mm i.d.). The products were also identified by GC–MS (HP-5973) analysis.

## 3. Results and discussion

### 3.1. Characterization

The results of the chemical composition and characteristics of the catalysts are given in Table 1. The nickel compositions of the solids corresponded relatively well to those fixed for the synthesis. Most of the values of the specific surface areas of

Download English Version:

<https://daneshyari.com/en/article/5142243>

Download Persian Version:

<https://daneshyari.com/article/5142243>

[Daneshyari.com](https://daneshyari.com)