Catalysis Today 204 (2013) 140–147

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Flow-synthesis of mesoporous silicas and their use in the preparation of magnetic catalysts for Knoevenagel condensation reactions

Xinqing Chen[a], Manuel Arruebo[c], King Lun Yeung[a,b,*]

[a] Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
[b] Division of Environment, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
[c] Nanoscience Institute of Aragon (INA), Pedro Cerbuna 12, 50009 Zaragoza, Spain

ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 18 July 2012
Accepted 18 July 2012
Available online 27 August 2012

Keywords:
Catalyst
Mesoporous silica
Flow synthesis
Knoevenagel reaction
Magnetic

ABSTRACT

Mesoporous silica MCM-41 was successfully prepared by *flow synthesis* in a microreactor at shorter reaction times (i.e., minutes versus day) at high yield (i.e., 60% calcined sample) to give particles of more uniform size and shape compared to MCM-41 prepared by conventional batch synthesis. Magnetic iron oxide nanoparticles were incorporated and organic amines (i.e., propylamine and propyl diethylene amine) were grafted to obtain magnetic mesoporous catalysts for the Knoevenagel condensation reactions of benzaldehyde with ethyl cyanoacetate, ethyl acetoacetate and diethyl malonate. The incorporation of magnetic nanoparticles and large organic amines can hinder reactants access to the catalyst resulting in lower reactivity. NH_2-*mag*MCM-41 showed superb catalyst activity and selectivity for the all three Knoevenagel condensation reactions studied. The catalyst can be easily dispersed into solution and rapidly removed by a magnet for recovery and reuse.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Solid acid and base catalysts play a key role in green chemistry by providing a clean and sustainable route for the synthesis of fine chemicals and intermediates [1–8]. Solid catalysts often exhibit excellent selectivity and yield, and have an additional advantage that it can eliminate the need for solvents resulting in higher product purity and simpler downstream separation. Zeolites and molecular sieves are among the most commonly used solid base and acid catalysts [6–8]. Corma et al. [9] are the first to see the advantage of using zeolite base catalyst for solvent-free, Knoevenagel condensation reaction. The Knoevenagel condensation reaction involves carbon–carbon bond formation between an active methylene group compound with an aldehyde or ketone to form bulky unsaturated products, and is an important synthesis route for many fine chemicals and pharmaceuticals [10,11]. More recent advances saw large pore molecular sieves being increasingly used for Knoevenagel condensation reaction. They are often used as host for immobilizing homogeneous base catalysts and include MCM-41 supported alkylammonium hydroxide [12], MCM-41 and SBA-15 containing guanidine moieties [13,14], FSM-16 with surface grafted ammonia [15], MCM-41 containing silicon oxynitride framework [16] and ion-exchange resins [17].

Mesoporous materials are prepared mainly by batch synthesis under hydrothermal and solvothermal reaction conditions using either soft or hard templates [18–20]. There are a number of attempts to produce mesoporous silica in a continuous process. Schuth's group [21] synthesized MCM-41 in a tubular reactor in order to observe the early stages of their formation. Their in situ X-ray diffraction study shows that ordered hexagonal pores are formed even at a very short residence time of three minutes. More recently, Jammaer et al. [22] successfully prepared COK12 *P6m* mesoporous silica nanoplates in a flow process. The *"flow-synthesis"* of materials in microfluidic reactors has been shown not only to be feasible, but also economically attractive [23]. There are important advantages in the synthesis of nanomaterials in microreactors [24] that parallels works in organic synthesis [25–29]. These include the rapid heat and mass transport processes in microfluidic reactors, and the ability to control fluid flow and mixing as well as manipulate the reaction surfaces and interfaces within the confined reaction volume. Indeed, the rapid and controlled mixing in microfluidic reactors have been used to prepare metal and chalcogenide nanoparticles of narrow particle size and polydispersity [30,31]. Liu et al. [31,32] dramatically decreased the reaction time to prepare dendrimers from several hours and even days to just a few minutes using microfluidic reactor. The fast heat transfer in microreactors from its large interfacial surface area-to-volume ratio was used to manipulate the temperature gradient in the

* Corresponding author at: Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China. Tel.: +852 2358 7123; fax: +852 2358 0054.
E-mail address: kekyeung@ust.hk (K.L. Yeung).

0920-5861/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2012.07.017

microreactor, and thus obtained nanoparticles of exceptional quality [33].

This work investigates the preparation of mesoporous silicas (i.e., MCM-41) in a microfluidic reactor and their use as catalyst for Knoevenagel condensation reaction between benzaldehyde (BA) and ethyl cyanoacetate (ECA), ethyl acetoacetate (EAA) and diethyl malonate (DEM). The mesoporous silica prepared by *flow-synthesis* in the microfluidic reactor was characterized and compared to products from conventional batch synthesis. Base catalysts were obtained by grafting organic moieties containing amino groups on the pores of the mesoporous silica, while magnetic base catalysts were obtained with incorporation of magnetic iron oxide nanoparticles.

2. Experiments

2.1. Chemicals

The chemical reagents for the synthesis of mesoporous silica included cetyltrimethylammonium bromide (CTABr, 99%) and tetraethyl orthosilicate (TEOS, 99%) supplied by Sigma–Aldrich, NH_4OH (28–30%, General) and NH_4NO_3 (99%, Nacalai Tesque). The base catalysts were prepared by grafting MCM-41 with either 3-aminopropyltrimethoxysilane (APTMS, 97%) or N-[3-(trimethoxysilyl)propyl]-ethylenediamine (A_2PTMS, 97%) purchased from Sigma–Aldrich. Iron (III) chloride ($FeCl_3{\cdot}6H_2O$, 98%) and iron(II) chloride ($FeCl_2{\cdot}4H_2O$, 99%) from Sigma–Aldrich were used in the preparation of magnetic iron oxide nanoparticles for the magnetic base catalyst. BA (99%, Aldrich), ECA (99%, Aldrich), EAA (99%, Aldrich) and DEM (99%, Aldrich) were used for the Knoevenagel condensation reaction.

2.2. Flow-synthesis of mesoporous silica

Mesoporous MCM-41 silica was prepared by *flow-synthesis* and batch reaction. Flow-synthesis was carried out in a microfluidic reactor shown in Fig. 1. The microfluidic reactor was fabricated on silicon using conventional lithographic processes. The design of the reactor was based on computation fluid dynamic model calculations (COMSOL), and the reactor pattern was drawn using CAD/CAM and printed on a plastic mask. The reactor pattern was transferred on silicon by contact printing using a positive HPR504 photoresist and etched in hot KOH solution to obtain the microchannels. The microfluidic reactor was sealed by a glass wafer (Pyrex 7740) anodic bonded to the silicon using SUSS Microtec SB6 at a temperature of 380 °C and 800 V for 4 min. Fig. 1a shows the reactor consists of two inlets on each arms of the T-mixer. The two inlet channels as shown in Fig. 1b have a width of 250 ± 20 μm and depth of 200 ± 20 μm. Two reactant streams, one containing TEOS dissolved in ethanol and the other CTABr, NH_4OH and water were feed to the reactor and after mixing the reactant mixture containing 6.58 TEOS:1 CTABr:292 NH_4OH:755 EtOH:1460 H_2O was guided to a 2.5 m long, 500 ± 50 μm wide microchannels arranged in a spiral around the 10 cm diameter (4 in.) silicon wafer (Fig. 1b). The synthesis was done at 298 ± 2 K. Reactions, nucleation and crystallization of the mesoporous silicas occurred as the fluid travels down the microchannel to the outlet, where the solid products were separated and recovered by filtration. The MCM-41 was then dried

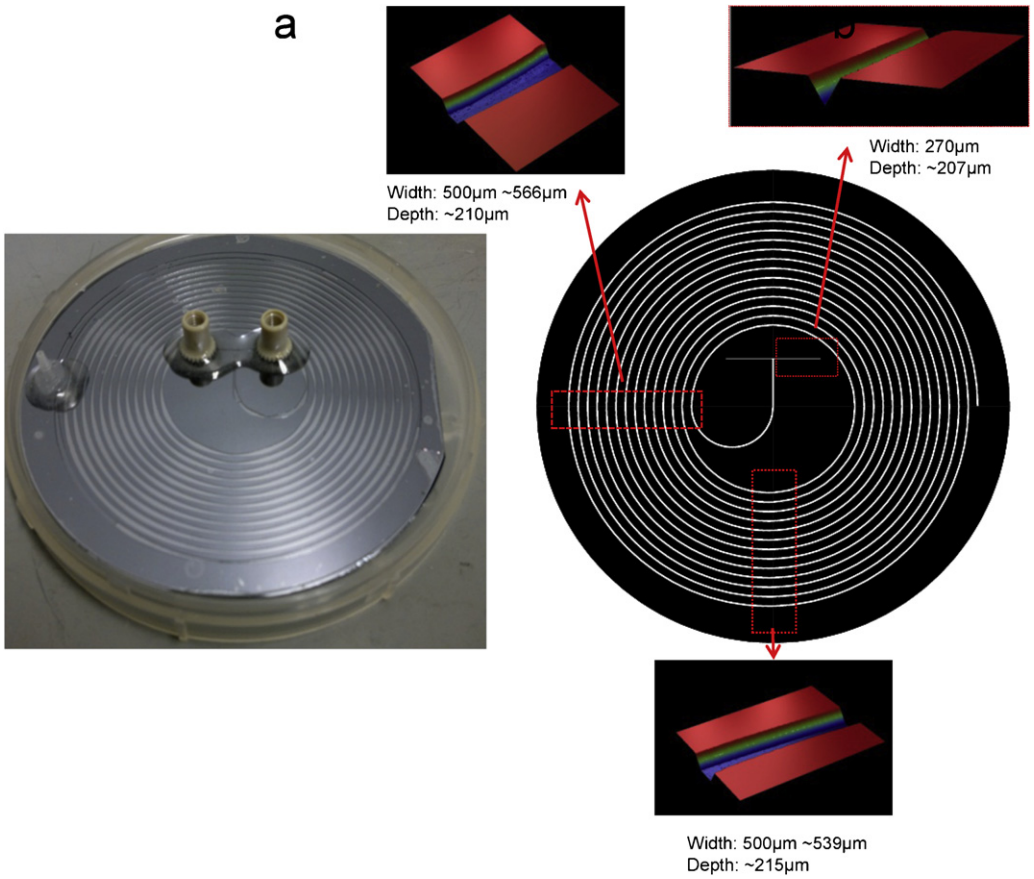

Fig. 1. (a) A picture of the microfluidic reactor for *flow-synthesis* of mesoporous MCM-41 and (b) a detailed drawing of the microfluidic reactor design pattern along with optical profiling images of the actual microchannel at various locations.

Download English Version:

https://daneshyari.com/en/article/54901

Download Persian Version:

https://daneshyari.com/article/54901

Daneshyari.com