



## Room temperature solvent free aza-Michael reactions over nano-cage mesoporous materials



Pranjal Kalita<sup>a,\*</sup>, Choitayna Dev Pegu<sup>b</sup>, Prantu Dutta<sup>b</sup>, Pranjal K. Baruah<sup>b,\*</sup>

<sup>a</sup> The Energy and Resources Institute, Energy Environment Technology Division, Darbari Seth Block, India Habitat Centre, Lodhi Road, New Delhi 110 003, India

<sup>b</sup> Gauhati University, Department of Chemical Science, Guwahati 781014, Assam, India

### ARTICLE INFO

#### Article history:

Received 9 April 2014

Received in revised form 16 June 2014

Accepted 17 June 2014

Available online 11 July 2014

#### Keywords:

Aza-Michael

Amines

$\alpha,\beta$ -Unsaturated carbonyl compounds

Mesoporous materials

Aluminosilicate

### ABSTRACT

An efficient highly acidic three dimensional mesoporous aluminosilicate nano-cage material Al-KIT5, exhibited excellent catalytic activity in solvent free room temperature aza-Michael reactions of amines with  $\alpha,\beta$ -unsaturated carbonyl compounds to produce  $\beta$ -amino carbonyl compounds with 100% product selectivity in a short reaction time. The high acidity, 3D pores, and a huge space in the nano-cages materials make them attractive candidate for carrying out important organic reactions. The catalyst provide a simple, easy to handle method, and could be used to solve the problems of corrosion, toxicity, waste production, and a high cost that are being currently encountered by the conventional homogeneous catalysts.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

The aza-Michael reaction is prominent reaction for forming carbon–nitrogen (C–N) bond and is widely used in modern synthetic organic chemistry. Conjugate addition of amine nucleophiles to electron deficient  $\alpha,\beta$ -unsaturated carbonyl compounds generate  $\beta$ -amino carbonyl compounds, which have been widely used as key intermediates of anticancer agents, antibiotics and several other drugs [1]. The utility of aza-Michael reaction is well explored in the synthesis of various natural products like colchicine, podophylotoxin and combretastatine A-4 and others. 6,7,2',3',4'-substituted-1,2,3,4-tetrahydro-2-phenylquinolone have potential application for cytotoxic and antitubuline effects which could be synthesized through aza-Michael addition [2,3]. When strong acids or bases are used to catalyze aza-Michael addition reactions side products are observed. Alternately aza-Michael reaction of amine with  $\alpha,\beta$ -unsaturated carbonyl compounds catalysed by Lewis acid catalysts such as  $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$  [4],  $\text{Cu}(\text{OTf})_2$  [5],  $\text{InCl}_3$  [6],  $\text{Yb}(\text{OTf})_3$  [7],  $\text{LiClO}_4$  [8],  $\text{Bi}(\text{NO}_3)_3$  [9],  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  [10],  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  [11],  $\text{ZnO}$  [12] are known. The homogeneous organometallic complexes like Pd (II), Rh (II) Ru (III), Ir (III) and ferrocenyl Ni (II) complexes

were also found to be very effective catalyst for the formation of C–N bond [13]. Moisture and air sensitive mild Lewis acid zirconium oxychloride [14] and sulfated zirconia [15] were also used as a catalyst for conjugate addition of amines to  $\alpha,\beta$ -unsaturated ketones under solvent-free condition. For zirconium oxychloride the reaction occurred at elevated temperature and for zirconia catalyst high yield of about 95% obtained with longer reaction time of 90 min. Bronsted acid like heteropoly acid [16] and silica supported perchloric acid, sulfuric acid and aluminium chloride promoted aza-Michael reactions were also reported [17]. Several researchers were interested for Michael addition of amines with  $\alpha,\beta$ -unsaturated carbonyl compounds over ionic liquid functionalized mesoporous material. The major drawback of using this catalyst is that, it requires several steps for preparation with precaution. Moreover, some researchers have also investigated aza-Michael reactions with or without supported ionic liquids [32]. Very recently, Phan et al. reported a promising heterogeneous catalyst metal-organic framework for the aza-Michael reactions of benzyl amine with ethyl acrylate [18]. They observed that the desired product was obtained with 80% and 96% yields using 2.5 mol% of catalysts and reactant ratio 1:1.5, respectively. In addition, metal organic framework materials could be used as a solid catalyst and has a potential application for different types of organic reactions [19]. The aza-Michael reaction of benzyl carbamates with  $\alpha,\beta$ -unsaturated carbonyl compounds was also reported by Phukan et al. over iodine as a suitable catalyst with moderate yield of

\* Corresponding authors. Tel.: +91 1124682100; fax: +91 1124682144.

E-mail addresses: [Pranjal.Kalita@teri.res.in](mailto:Pranjal.Kalita@teri.res.in), [amipranjal@gmail.com](mailto:amipranjal@gmail.com) (P. Kalita), [pranjal@gauhati.ac.in](mailto:pranjal@gauhati.ac.in) (P.K. Baruah).

70–80% [20]. Besides, Choudhury et al. developed a methodology for aza-Michael reaction using boric acid as a novel and safe catalyst with longer reaction time and yield 70–90% [21]. The acceleration of aza-Michael reaction of aniline/substituted anilines with different enones was examined over aqueous sodium carbonate solution by Wang et al. [22]. This reaction has a main drawback where reaction needs extended time (72 h) at room temperature.

Mesoporous silica materials with tunable pore size in the range of 2–50 nm have recently been studied extensively due to their unique structures with organized porosity, high specific surface area, and specific pore volume, which make them available to a wide range of applications in the areas of adsorption, separation, sensing, fuel cells and catalysis [23,24]. Among the various mesoporous materials, materials that consist of interconnected large-pore cage-type mesoporous systems with three-dimensional (3D) porous networks are highly interesting and promising supports for heterogeneous catalysis. In addition, they are considered to be more advantageous than porous materials that have a hexagonal pore structure with a one-dimensional array of pores because they allow for a faster diffusion of reactants, avoid pore blockage, provide more adsorption sites, and can be used for processing large-sized molecules. SBA-16, SBA-1, and KIT-5 are a few examples of porous materials that possess a 3D cage type porous structure [23c,22]. Among them, KIT-5, discovered by Kleitz et al., is very interesting as it possesses a highly ordered cage-type mesoporous structure with a cubic  $Fm\bar{3}m$  closely packed symmetry, a high surface area, a large cage-type tunable pore, and a high specific pore volume [25]. These exciting properties made it an excellent adsorbent for capturing large biomolecules as well as an ideal replica for the fabrication of cage-type carbon material [26]. Recently, Vinu et al. reported the three-dimensional mesoporous silica framework with cage type structure by controlling the amount of HCl in the synthesis mixture [23d,27]. They also studied the Al content, pore diameter and the morphology of the materials and these properties could be easily tuned by simply altering the amount of Al in the silica framework of KIT-5 [23d]. The same research group reported high surface area, large pore volume and cage diameter, and high acidity of Al-KIT5 catalyst. They observed high catalytic activity of KIT-5 towards liquid phase acetylation of aromatic compounds [23d,27c] and are superior to zeolites and AIMCM-41 catalysts. Several other organic reactions including three component one-pot reaction of synthesis of  $\alpha$ -aminophosphonates, ring opening of epoxides with indoles and primary amines over nano-cage mesoporous Al-KIT5 catalysts [28] were also studied by this research group. Moreover, Kalita et al. reported the functionalization of mesoporous KIT-5 and Zr-TMS materials over super acid like triflic acid and found very good catalytic activities for the synthesis of coumarin via Pechmann reaction of resorcinol and ethylacetoacetate under solvent free system [29]. In addition, immobilization of super base like 1,5,7-triazabicyclo [4.4.0] dec-5-ene over mesoporous materials was also reported as an efficient catalyst for Michael-addition reactions under solvent-free condition [31b]. Besides, Kalita et al. investigated incorporation of different metals over mesoporous materials for different types of organic reactions like Pictet-Spengler, Mukaiyama-aldol, Mukaiyama-Michael, and Friedel-Craft alkylation [30].

Many of the above methods suffered from drawbacks, such as they need large excess of reagents, long reaction time, and environmental pollution. Here, we report a synthetic methodology for preparation of  $\beta$ -carbonyl compounds through aza-Michael reactions of amines with  $\alpha,\beta$ -unsaturated carbonyl compounds by utilization of the highly acidic Al-incorporated KIT-5 catalysts addressing many of these issues. The catalyst was found to be highly active with 100% of product selectivity and affording excellent yield in a very short reaction time.

## 2. Experimental

### 2.1. Synthesis of Al-KIT5 catalyst and characterization

Al-incorporated highly ordered mesoporous KIT-5 catalyst was synthesized using pluronic F127 (EO<sub>97</sub>PO<sub>60</sub>EO<sub>97</sub>, molecular weight 12,500), and tetraethyl orthosilicate and aluminium isopropoxide as a structure directing agent, and the sources of silica and aluminium, respectively. They have been obtained from Sigma-Aldrich chemicals, Bangalore, India and used without further purification. The detailed synthesis procedure and characterization of the textural properties of the materials is available in the recent literature [22d,26c]. Al-KIT5 (10) where the number in the parenthesis denotes the Si/Al ratio was used for the synthesis of  $\alpha$ -aminophosphonates [27a]. In a typical synthesis, 5.0 g of F127 is dissolved in the required amount of HCl (35 wt%) and 240 g of distilled water. To this mixture, 24.0 g of TEOS and the required amount of the desired Al source were added, and the resulting mixture was stirred for 24 h at 100 °C. Subsequently, the reaction mixture was heated for 24 h at 100 °C under static condition for hydrothermal treatment. The solid product was filtered off and then dried at 100 °C without washing. The product was calcined at 540 °C for 10 h. Moreover, we also synthesized Si/Al ratio 28 and 44 for comparison studies.

Powder X-ray diffraction patterns were collected on a Rigaku diffractometer using Cu K $\alpha$  ( $\lambda = 0.15406$  nm) radiation, operated at 40 kV and 40 mA. The diffractograms were recorded in the  $2\theta$  range of 0.7–10° with a  $2\theta$  step size of 0.01° and a step time of 6 s. The all calcined samples show well-ordered characteristic properties of mesoporous materials with well-ordered cage type three dimensional silica networks and it is shown in Fig. 1. From XRD pattern it is seen that the peaks are slightly shifted towards lower  $2\theta$  values with increasing Al-content in the Al-KIT5 samples which increases the unit cell constant parameters. This is due to the formation of Al–O bond in the silica network which is longer than Si–O bonds.

The nitrogen adsorption-desorption isotherms were measured at –196 °C on a Quantachrome Autosorb 1 volumetric adsorption analyser. The surface area of synthesized catalyst was determined by BET technique and surface areas of calcined Al-KIT5 (10), Al-KIT5 (28) and Al-KIT5 (44) catalysts were 989, 815 and 713 m<sup>2</sup> g<sup>-1</sup>, respectively [22d,27a]. The details of characterization of Al-KIT5 catalysts and their physicochemical data were reported by Vinu et al. [22d,27a] and are not shown here. The total acidity of the calcined Al-KIT5 samples were determined through temperature-programmed desorption (NH<sub>3</sub>-TPD) techniques using Micromeritics Autochem 2910 instrument. The total

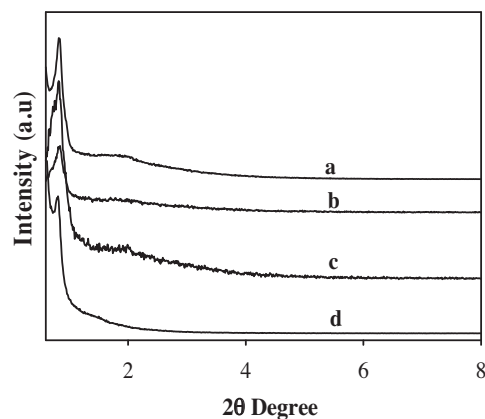


Fig. 1. The powder XRD patterns of the calcined AlKIT-5 samples of (a) Pure KIT-5, (b) Al-KIT5 (44), (c) Al-KIT5 (28) and (d) Al-KIT5 (10).

Download English Version:

<https://daneshyari.com/en/article/65421>

Download Persian Version:

<https://daneshyari.com/article/65421>

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