

DIAMINO-FUNCTIONALIZED SBA-15 AS AN EFFICIENT CATALYST FOR THE KNOEVENAGEL REACTION OF BENZALDEHYDE AND MALONONITRILE

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ABSTRACT

Highly ordered mesoporous silica SBA-15 was synthesized and functionalized via silane chemistry with N-[3-(trimethoxysilyl)propyl]ethylenediamine to create surface base sites. The diamino-functionalized SBA-15 was characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), elemental analysis (EA), and nitrogen physisorption measurements. The modified SBA-15 was used as an efficient heterogeneous base catalyst for the Knoevenagel condensation of benzaldehyde with malononitrile to produce benzylidene malononitrile as the principal product. Quantitative reaction conversion (>99%) was achieved under very mild conditions. It was also observed that no contribution from homogeneous catalysis of active amine species leaching into reaction solution was detected, indicating evidence for a real heterogeneous catalysis.

I - INTRODUCTION

The Knoevenagel condensation of aldehydes with compounds containing activated methylene groups is one of the most useful and widely employed methods for carbon—carbon bond formation with numerous applications in the synthesis of fine chemicals as well as heterocyclic compounds of biological significance [1, 2]. Conventionally, this reaction is catalyzed by weak bases like primary, secondary and tertiary amines under homogeneous conditions, which often requires upwards of 40 mol% catalyst with the attendant difficulties in catalyst separation and product purification [3]. Over the last decades, various solid-supported catalysts have been applied to this reaction such as aminoalkylsilane functionalized silica, tetraalkylammonium hydroxide-immobilized MCM-41, guanidine-

immobilized MCM-41, ammonia-grafted FSM-16, MCM-48 with silicon oxynitride frameworks, and silicate-organic composite materials [4 - 10]. On the other hand, Knoevenagel reactions catalyzed by Lewis acids have also been reported [11, 12].

SBA-15 has emerged as one of the most common mesoporous silica catalyst supports. It is known to be a well-defined, hexagonal mesoporous silica material with straight mesopores that are connected through small micropores [13, 14]. Mesoporous silicas of this type are useful model supports, as they are highly ordered, hydrothermally stable, and have pores of low polydispersity [15, 16]. In particular, guanidine moiety-functionalized SBA-15 was previously found highly active towards the Knoevenagel reaction [7]. In Viet Nam, Fe-SBA-15 was successfully synthesized

and tested in catalytic oxidation of phenol and photocatalytic oxidation of chlorophenol by P. T. Dang and co-workers [17]. In this paper, we wish to report for *the first time in Viet Nam*, to our best knowledge, the immobilization of diamino moiety on SBA-15 *via* silane chemistry to create surface base sites. The modified SBA-15 was used as an efficient heterogeneous base catalyst for the Knoevenagel condensation of benzaldehyde with malonitrile to produce benzylidene malonitrile as the principal product under very mild conditions.

II - EXPERIMENTAL

1. Materials and instrumentation

Chemicals were purchased from Sigma-Aldrich, Fisher, and Acros and used as received without further purification unless otherwise noted. The synthesis of SBA-15 and diamino-functionalized SBA-15 was carried out at School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, USA.

Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Equinox 55 instrument with samples being dispersed on potassium bromide pellets, nitrogen physisorption measurements were conducted using a Micromeritics Chem BET 3000 system, X-ray powder diffraction (XRD) patterns were recorded using CuK α radiation source on a D8 Advance Bruker powder diffractometer at HCMC Institute of Chemical Technology, Vietnamese Academy of Science and Technology.

Transmission Electron Microscope (TEM) studies were performed using a JEOL JEM 1400, thermogravimetric analysis (TGA) was carried out on a Netzsch Thermoanalyzer TG 209 at Polymer Research Center, HCMC University of Technology. Scanning electron microscope (SEM) studies were conducted at National Laboratory for Nanotechnology, HCMC National University. Elemental analysis (EA) was carried out at HCMC Center of Analytical Services and Experimentation.

GC-MS analyses were performed using an Agilent GC-MS 6890 at Analytical Laboratory, HCMC Institute of Chemical Technology, Vietnam Academy of Science and Technology. GC analyses were performed using a Shimadzu GC-17A equipped with a FID detector and a 30 m x 0.25 mm x 0.25 μ m DB-5 column. The temperature program for GC analyses heated samples from 60°C to 140°C at 10°C/min, held at 140°C for 1 min, from 140°C to 300°C at 50°C/min, and held at 300°C for 3 min.

2. Synthesis of SBA-15 and amino-functionalized SBA-15

In a typical preparation, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO-PO-EO) (12.00 g), 1,3,5-trimethylbenzene (TMB) (1.50 g), deionized water (317.77 g), 38% aqueous HCl solution (86.60 g) were stirred at room temperature until the EO-PO-EO completely dissolved. Tetraethyl orthosilica (TEOS) (25.63 g) was then added to the solution, and the solution was stirred for 5 min. The mixture was distributed into 10 Parr Teflon-line autoclaves and agitated at 35°C for 20 h, and was then aged at 100 °C without stirring for 24 h. The solid product was recovered by filtration, washed with deionized water extensively, and air-dried at 50°C overnight. The as-prepared material was calcined using the following temperature program: (1) increasing the temperature (1.2°C/min) to 200°C, (2) heating at 200°C for 1 h, (3) increasing the temperature (1.2°C/min) to 550°C, and (4) holding at 550°C for 6 h. The solid product was dried under vacuum overnight, and stored in a nitrogen glove box (7.5 g).

Prior to functionalization, the SBA-15 was dried under vacuum at 200°C for 3h and stored in a dry box. Diamino-functionalized SBA-15 was synthesized by stirring a toluene (30 ml) suspension of SBA-15 (1 g) and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (1 g) at room temperature for 24 h under an argon atmosphere. The solid was then filtered and washed with copious amounts of toluene,

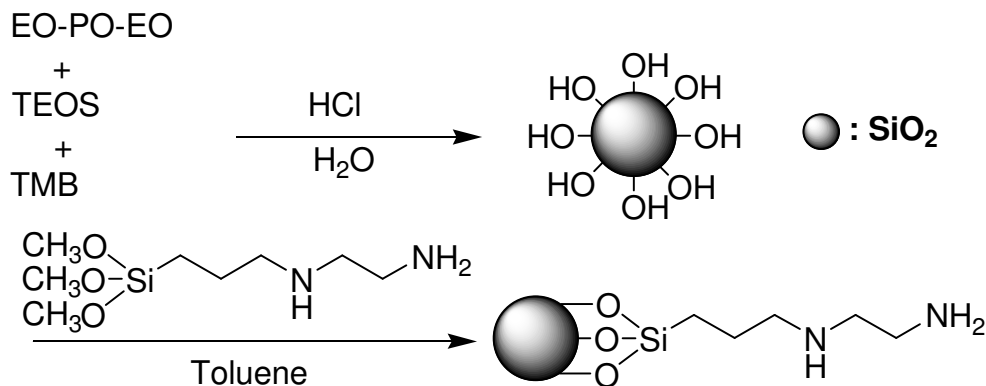
hexanes, methanol, ether in a dry nitrogen glove box and dried under vacuum at room temperature overnight, yielding approximately 1 g of diamino-functionalized SBA-15.

3. Catalytic studies

Unless otherwise stated, a mixture of benzaldehyde (40 mg, 0.38 mmol), and dodecane (21 mg) as the internal standard in toluene (4 ml) was introduced into a 50 ml glass vessel containing the diamino-functionalized SBA-15 catalyst (6 mg, 2.0 mol%). A solution of malonitrile (49 mg, 0.75 mmol) in toluene (1 ml) was then added, and the resulting mixture was stirred at room temperature. Reaction conversion was monitored by withdrawing aliquots (0.1 ml) from the reaction mixture at different time intervals, quenching with diethyl ether (2 ml), filtering through a short silica gel pad, drying over Na_2SO_4 , analyzing by GC with reference to dodecane, and further confirming product identity by GC-MS. Reactions were also carried out using different catalyst concentrations, different molar ratios, and different solvents.

III - RESULTS AND DISCUSSION

Mesoporous SBA-15 was synthesized by literature methods, utilizing the triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO-PO-EO) nonionic surfactant as the structure-directing agent and 1,3,5-trimethylbenzene (TMB) as a swelling cosolvent [18]. As with other silica, SBA-15 surface is covered with a large number of silanol (Si-OH) groups, facilitating the surface modification step. The as-synthesized silica was then functionalized *via* the reaction of these silanol groups with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine to create surface base sites (scheme 1). The so-called grafting method allowed the formation of covalent bonds between the diamine and the SBA-15 surfaces [19]. It was decided to immobilize diamine species on the SBA-15 surface as the diamine previously exhibited high activity in the Knoevenagel condensation under mild conditions, either in sol-gel entrapped form or MCM-41-supported form [20].



Scheme 1: Synthesis of SBA-15 and amino-functionalized SBA-15

The diamino-functionalized SBA-15 was characterized using a variety of different techniques. Low angle X-ray powder diffraction (XRD) profiles of the functionalized SBA-15 exhibited reflections in the 2θ range of $0.7 - 2^\circ$ attributable to 2D hexagonal symmetry. The patterns were consistent with the literature with no impurity peak being observed in the XRD

diffraction [21] (Figure 1). Being in good agreement with the literature, the TEM micrograph of the modified SBA-15 showed the honey-comb like structure, typical of an hexagonal array with highly regular parallel layers [22] (figure 2). The SEM micrograph revealed that the diamino-functionalized SBA-15 consisted of several rod-like domains with

relatively uniform sizes of 2 - 3 μm , which were aggregated into wheat-like macrostructures (figure 3).

Nitrogen physisorption measurements of the diamino-functionalized SBA-15 showed BET surface areas of $449.26\text{ m}^2/\text{g}$. The TGA analysis of the functionalized SBA-15 exhibited an organic loading of 12.88%, corresponding to approximately 1.3 mmol/ of the diamine being immobilized onto the silica support (figure 4). This result was also supported by the elemental analysis results, indicating a diamine loading of

1.36 mmol/g. FT-IR spectra showed an O-H stretching vibration due to physisorbed water and potentially surface hydroxyls near 3453 cm^{-1} , an O-H deformation vibration near 1639 cm^{-1} , and an Si-O stretching vibration near 1070 cm^{-1} , respectively. The significant feature observed for the functionalized SBA-15 was the appearance of the peaks near 2950 cm^{-1} due to the $-\text{CH}_2$ stretching vibration. There also existed the contribution of the $-\text{NH}_2$ group for the band near 3300 cm^{-1} , which was overlapped by the O-H stretching vibration [23] (figure 5).

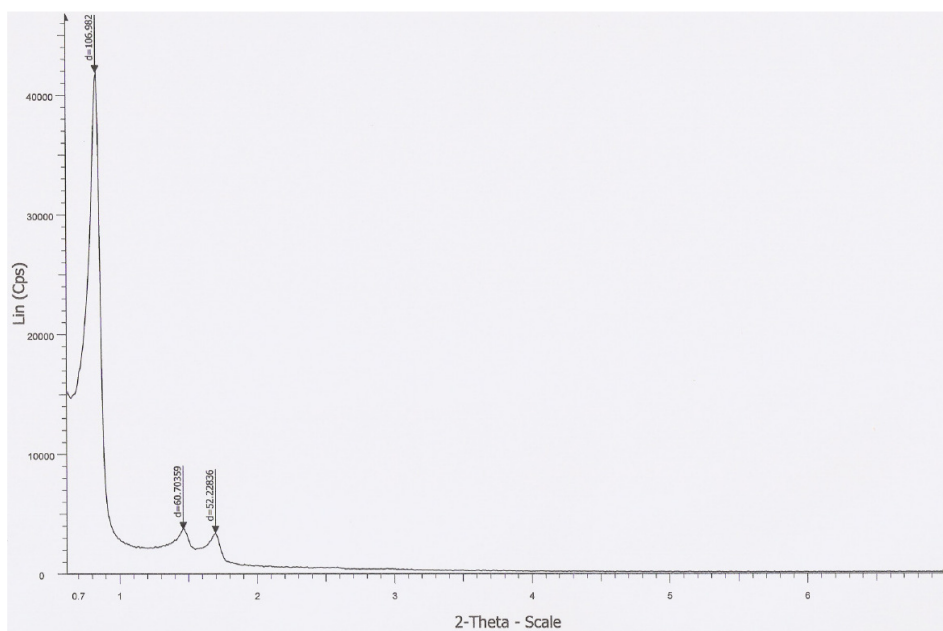


Figure 1: X-ray powder diffractogram of the diamino-functionalized SBA-15

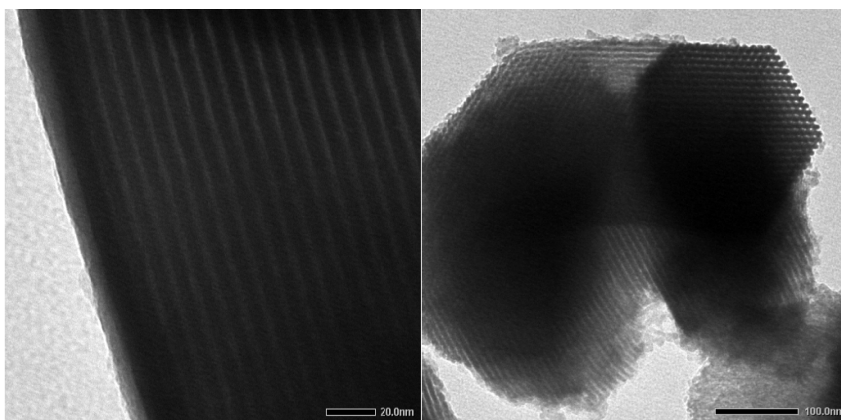


Figure 2: TEM micrographs of the diamino-functionalized SBA-15

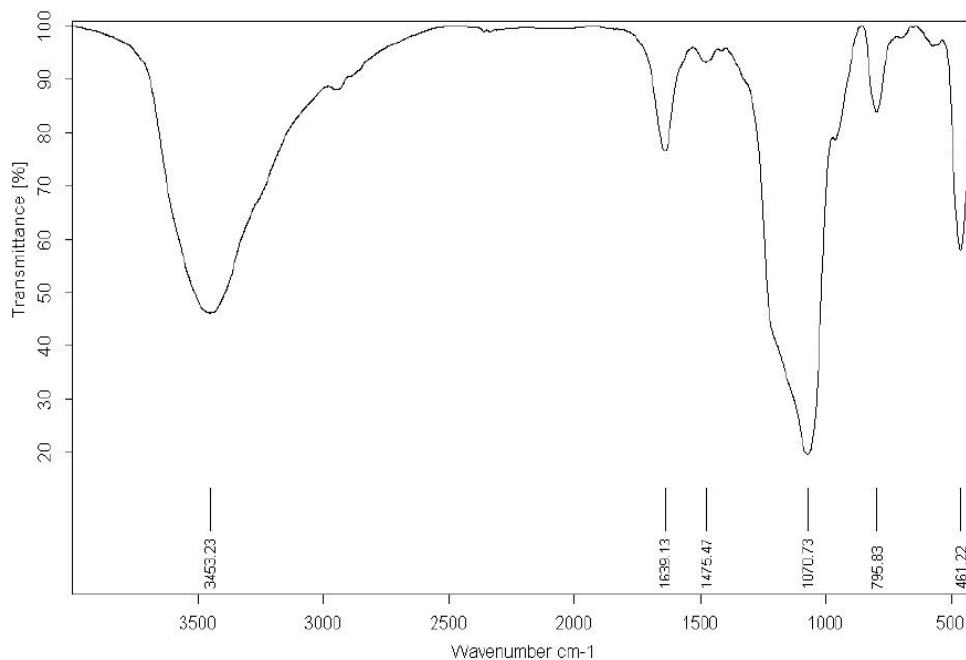


Figure 5: FT-IR spectra of the diamino-functionalized SBA-15

The diamino-functionalized SBA-15 was assessed for its activity in the Knoevenagel reaction by studying the condensation of benzaldehyde with malononitrile to form benzylidene malononitrile as the principal product (scheme 2). The initial reaction was carried out using 2.5 mol% diamine relative to benzaldehyde in toluene at reflux temperature. Complete conversion was achieved within just 5 min with no trace amount of benzaldehyde being detected by GC. It was therefore decided to carry out the reaction under milder conditions (*i.e.* at room temperature). The catalyst concentration, with respect to the diamine moiety immobilized on the SBA-15, was studied in the range of 1 - 2.5 mol% corresponding to the benzaldehyde at room temperature. More than 99% conversion of benzaldehyde was achieved within 60 min at 2.5 mol% catalyst concentration. As expected, decreasing the catalyst concentration resulted in a drop in reaction rate, with 99% conversion being observed within 180 min at 2 mol% catalyst (figure 6). The results indicated that the diamine-functionalized SBA-15 was quite active

in the Knoevenagel reaction. Furthermore, the reaction rate observed for the SBA-15 catalyst was higher than some previously reported catalysts, where longer reaction time or/and higher catalyst concentration were required for the same reaction [24, 25].

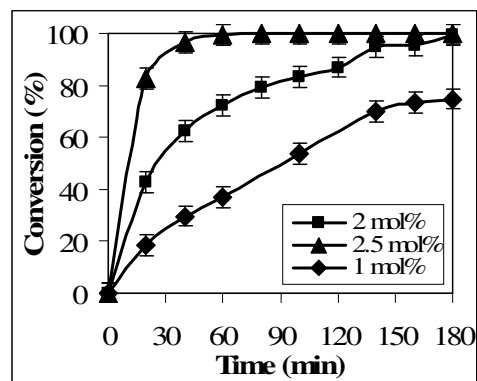


Figure 6: Effect of catalyst concentration on reaction conversions

The sensitivity of a heterogeneously catalyzed reaction to different solvents can

usually be of extreme importance, depending on the nature of the catalyst support material [26,27]. Macquarrie previously reported that the Knoevenagel condensation using functionalized MCM-41 catalysts had a very limited range of effective solvents, and gave the best reaction rate in nonpolar solvents [28]. We therefore decided to investigate the solvent effect in reaction using 2 mol% of the diamino-functionalized SBA-15 catalyst. A combination of toluene and the basic SBA-15 afforded an excellent conversion for the reaction. The reaction carried out in dichloromethane (DCM), a relatively more polar solvent than toluene, also gave a similar reaction rate with almost of the benzaldehyde being converted to the desired product within 180 min. Different from other basic catalysts, the reaction in tetrahydrofuran (THF) proceeded with slower rate, affording 83% conversion after 180 min (figure 7). It was previously proposed that the rate of the Knoevenagel reaction using silica-based catalysts might be influenced by the partitioning of the reactants (polar) between the catalyst pores and/or surface (polar) and the bulk reaction media [26,28]. However, the behavior of the diamino-functionalized SBA-15 catalyst in different solvents still needs further studies and these are underway.

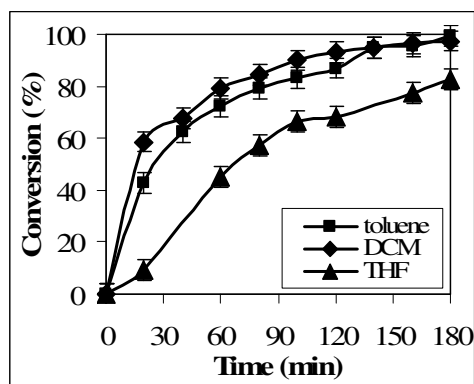


Figure 7: Effect of solvent on reaction conversions

When using a supported catalyst, a crucial issue is the possibility that some of active sites could migrate from the solid support to the liquid phase and that these leached species

could become responsible for a significant part of the catalytic activity. In order to determine if leaching was a significant problem for the Knoevenagel reaction using the modified SBA-15 catalyst, an experiment was performed to estimate the contribution of leached active species to the catalytic activity [19]. The reaction using 2 mol% diamine catalyst in toluene was carried out for 80 min at room temperature. The functionalized SBA-15 catalyst was then removed from the reaction mixture by centrifugation, and the reaction solution was transferred to a new reactor vessel. The solution without the solid catalyst was stirred for another 80 min with aliquots being sampled at different time intervals, and analyzed by GC. The data from GC determinations gave quantitative information about residual, catalytically active amine in solution. Within experimental error, no further reaction was observed after the solid catalyst was removed, proving there to be no contribution from leached active species (Figure 8). It was therefore inferred that the active diamine moiety was retained on the solid support during the course of the reaction. It should also be noted that the unfunctionalized SBA-15 was only very weakly active in the Knoevenagel condensation, with less than 5% conversion observed after 180 min. This indicated the necessity of the diamine coating on the surface of the SBA-15 particles to create basic sites.

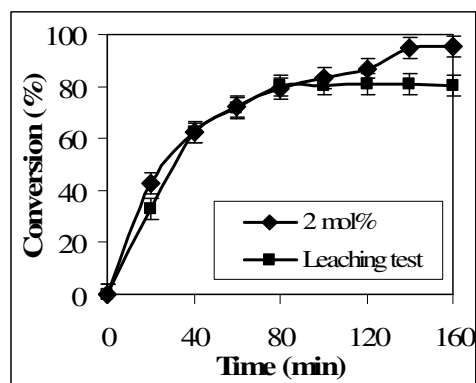


Figure 8: Leaching test result indicated that no further reaction was observed after the solid catalyst was removed

IV - CONCLUSIONS

In conclusion, highly ordered mesoporous silica SBA-15 was synthesized and functionalized *via* the reaction between silanol groups with *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine to create surface base sites. This immobilization method allowed the formation of covalent bonds between the diamine and the SBA-15 surfaces. The functionalized SBA-15 was used as an efficient heterogeneous base catalyst for the Knoevenagel condensation of benzaldehyde with malononitrile to produce benzylidene malononitrile as the principal product. Quantitative reaction conversion (> 99%) was achieved under very mild conditions. Leaching test result indicated that active diamine moiety was retained on the solid SBA-15 during the course of the reaction, and there was no contribution from leached active species into the reaction solution. Our results here demonstrated the feasibility of applying the SBA-15 as an efficient catalyst support for immobilizing homogeneous catalysts *via* covalent bonds. Current research in our laboratory has been directed to the design and immobilization of several homogeneous catalysts on SBA-15 for a wide range of organic transformations, and results will be published in due course.

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**NGHIÊN CỨU SỬ DỤNG DIAMINE CÓ ĐỊNH TRÊN SBA-15 LÀM XÚC TÁC CHO
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