



# Organic amine grafting on mesoporous silica as a hybrid catalyst for heterogeneous three-component one-pot reaction

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## ABSTRACT

The organic–inorganic hybrid catalyst was prepared by immobilizing 3-methylaminopropyl moiety onto mesoporous silica, MCM-41, and applied for solid base catalyst of three-component one-pot reaction, i.e. Knoevenagel condensation of aldehyde with the active methylene compound to yield an electron deficient alkene which is subjective to be reacted with nitromethane by Michael addition to form tri-substituted primary nitro compound. The catalyst was characterized by powder-XRD, TG–DTA, FT-IR, nitrogen adsorption–desorption measurement and solid-state cross polarization magic angle spinning (CP/MAS) NMR, and exhibited high catalytic activity in three-component one-pot reaction; however, with poor reusability.

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## 1. Introduction

The carbon–carbon forming reaction catalyzed by base is a pivotal tool in organic synthesis, and vast efforts have been attained so far. From the viewpoint of catalyst, homogeneous catalysts such as organic bases have been sufficiently investigated [1]; however, with increasing the demands for the environmental benign chemistry, much attention has been paid to the development for heterogeneous base catalyst that has advantages such as an ease for removal, recyclability and reusability [2]. Instead of typical solid base catalysts such as  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , the organic–inorganic hybrid mesoporous silica materials have become a promising candidate for heterogeneous base catalyst [3,4]. They are successfully applied in typical reactions such as Knoevenagel condensation [5–12], Claisen–Schmidt reaction [5], Henry reaction [13–17], Michael addition [7,18], and so on [19]. Recently, the multicomponent reactions (MCRs) involving base catalyzed C–C bond forming reaction have been designed by utilizing bifunctional mesoporous silica catalyst [20,21]. The MCRs are responsible for higher efficiency, not only because of intrinsic aspects of the reaction such as superior atom economy, atom utilization and selectivity, but also because of extrinsic aspects of the processing reaction such as simpler procedures and equipment, lower cost, time and energy [22]. However, the reports on heterogeneous catalyst in MCRs seem to be poor than those on homogeneous (including asymmetric) catalyst

system. Thus the development for heterogeneous MCRs should be a challenging task [23].

Our strategy in this study, three-component one-pot reaction, is based on the combination of typical base catalyzed reactions such as Knoevenagel condensation and Michael addition illustrated in Scheme 1, i.e. Knoevenagel condensation of aldehyde with active methylene compound bearing electron-withdrawing group (EWG) offers the formation of unsaturated and electron deficient product, this can be utilized as Michael acceptor followed by the addition of nucleophile ( $\text{Nu}^-$ ) as Michael donor, resulting in production of Michael adduct. It can be expected that the organic amine immobilized onto mesoporous silica would be responsible for base catalysis in both reactions, and that the formed product bearing multi-functional groups should serve as a versatile intermediate for pharmaceuticals, because they have acceptable substituents for further chemical transformations in their molecules.

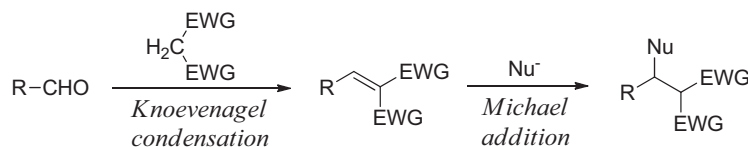
Here, we wish to report the heterogeneous three-component one-pot reaction over the organic–inorganic hybrid catalyst.

## 2. Experimental

### 2.1. Characterizations and materials

Powder X-ray diffraction (XRD) was measured by a Shimadzu XRD-6000 diffractometer with  $K\alpha$  radiation ( $\alpha = 1.5418 \text{ \AA}$ ). Nitrogen adsorption isotherm measurements were carried out on a Belsorp 28SA apparatus (Bel, Japan). Liquid  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements in  $\text{CDCl}_3$  containing tetramethylsilane as an internal standard and solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  cross polarization (CP) magic

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Scheme 1.

angle spinning (MAS) NMR spectra were recorded at ambient temperature by using 4 mm diameter zirconia rotor with a spinning rate of 6 kHz (ECA-500 NMR spectrometer, JEOL Ltd.). FT-IR measurement was performed by PerkinElmer 2000. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out by using a Shimadzu DTG-50 analyzer at a ramping rate of 10 K/min under an air stream. All of reagents were commercially available and used without purification.

## 2.2. Synthesis of MCM-41

Mesoporous silica MCM-41 was synthesized by according to the reported procedure [24,25]. A 25.1 g of hexadecyltrimethylammonium bromide (HDTMABr) was completely resolved in 77.0 g of distilled water at 50 °C (solution A). In a 300 mL beaker, a 28.1 g of sodium silicate (SiO<sub>2</sub>: 29.3%, Na<sub>2</sub>O: 9.3% in water) was added into an aqueous H<sub>2</sub>SO<sub>4</sub> solution (0.31 mmol g<sup>-1</sup>), then was added into the solution A. After stirring for 1 h at ambient temperature, the pH of the solution was adjusted to 9.98 by adding H<sub>2</sub>SO<sub>4</sub> solution. The resulting white suspension was transferred into a 500 mL of bottle (polypropylene), and stood at 100 °C for 9 days. The obtained white powder was washed with distilled water and EtOH thoroughly and dried at 50 °C for overnight. The calcination of as-synthesized MCM-41 was taken place at 550 °C for 6 h.

## 2.3. Immobilization of organic amine on MCM-41 (MAP-M41)

The heterogeneous dry toluene solution containing the calcined MCM-41 and the prescribed silylating agent, 3-aminopropyltrimethoxysilane, was refluxed for 6 h. After filtration, the resulting pale yellow solid was washed with toluene and EtOH thoroughly. Then the solid was dried at 50 °C for overnight.

## 2.4. Trimethylsilyl end capped MCM-41 (MAP-M41 (TMS))

The suspension of the well-dried MAP-M41 (0.80 g) in dry toluene (55 mL) was added 1,1,1,3,3,3-hexamethyldisilazane (1.5 mL) at room temperature. The resulting mixture was stirred for 4 h, and then, the obtained solid was washed with toluene and EtOH, respectively. This procedure was repeated three times to sufficiently substitute the trimethylsilyl moiety to the exposing silanol.

## 2.5. One-pot reaction

Into the mixture of benzaldehyde (0.50 mmol) and ethyl cyanoacetate (0.60 mmol) in toluene (1.0 mL) was added the catalyst (10 mol%; the supported amine base) and stirred for 1 h at 60 °C. The mixture was subjected to the addition of CH<sub>3</sub>NO<sub>2</sub> (1.0 mmol) at the same temperature and stirred for extended 4 h. The catalyst was removed by filtration, and the organic filtrate was concentrated in vacuo. The resulting crude product was purified by column chromatography using *n*-hexane/EtOAc (4/1) as an eluent to determine the isolated yield. The structural assignment was done by <sup>1</sup>H and <sup>13</sup>C NMR spectra comparing with the reported spectral data. The diastereomer ratios of all products are estimated at 50:50 by <sup>1</sup>H

NMR spectrum, thus all structural descriptions are ignored in this text.

## 3. Results and discussion

### 3.1. Characterization of MAP-M41 catalyst

Fig. 1 shows powder XRD charts of MCM-41 (a) and MAP-M41 (b), respectively. The peaks corresponding to MCM-41 were observed in the low-angle region indexed on a hexagonal unit cell with *p6mm* space group (a); however, the slight decrease in peak intensity associated with (1 1 0) and (2 0 0) reflections was observed after immobilization (b). It is clear that MAP-M41 has mesoporous alloy structure without collapse during modification.

The nitrogen adsorption–desorption isotherms of MCM-41 (a) and MAP-M41 (b) are given in Fig. 2. They show typical type-IV isothermal curves, and the significant decreasing of the adsorbed N<sub>2</sub> was observed in MAP-M41, resulting in the decreased surface area from 1048 to 784 m<sup>2</sup> g<sup>-1</sup> and pore volume from 1.00 to 0.48 cm<sup>3</sup> g<sup>-1</sup>, respectively.

Fig. 3 shows the FT-IR spectra of MCM-41 (a) and MAP-M41 (b) in the range of 1300–2000 cm<sup>-1</sup>. The characteristic band assignable to the stretching vibration of C–N bond was observed at 1465 cm<sup>-1</sup> in MAP-M41, indicating that *N*-methylaminopropyl moiety is effectively immobilized on mesoporous silica.

TG–DTA analysis of MAP-M41 revealed the clear weight loss at around 250 °C accompanying with exothermic reaction (see Supporting Information), and the amount of the supported amine based on the weight loss in TG is estimated as 1.21 mmol g<sup>-1</sup> [25].

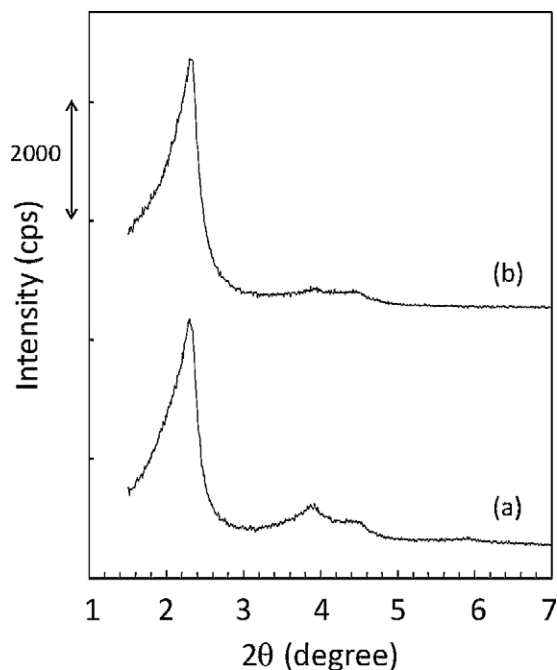


Fig. 1. Powder XRD charts of MCM-41 (a) and MAP-M41 (b).

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