

# Solvent-free synthesis of flavanones over aminopropyl-functionalized SBA-15

Xueguang Wang, Soofin Cheng \*

*Department of Chemistry, National Taiwan University, No. 1, Roosevelt Road Section 4, Taipei 106, Taiwan*

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## Abstract

Flavanone was synthesized through the Claisen–Schmidt condensation between benzaldehyde and acetophenone and subsequent intramolecular Michael addition over aminopropyl-functionalized SBA-15 materials. The catalysts with well-ordered hexagonally arranged mesopores were synthesized by one-pot co-condensation of tetraethoxysilane and aminopropyltriethoxysilane using amphiphilic block copolymer as the template under acidic condition. The results showed that the catalysts had good activities and very high selectivities to flavanone in solvent-free condition, while the use of organic solvents decreased the catalytic activities and flavanone selectivities. The influence of substituents in the aromatic rings of benzaldehyde and 2'-hydroxyacetophenone was also investigated under the solvent-free condition.

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## 1. Introduction

The development of environmentally friendly solid catalysts for the synthesis of fine chemicals and pharmaceuticals is becoming an area of growing interest because the use of heterogeneous catalytic processes allows easier separation, recovery, and recycling of the catalysts from the reaction mixtures [1–3]. To maintain economic viability, a suitable heterogeneous system should also display activities and selectivities comparable or superior to the existing homogeneous route. Nevertheless, the number of available examples of successful transformation from homogeneous catalytic syntheses to heterogeneous ones is rather limited.

Flavonoids are polyphenolic compounds that are widely distributed in plants preserving the health of plants against infections and parasites. They have attracted increasing attention due to numerous pharmacological applications [4–10]. The synthesis of the flavonoids has been carried out through a variety of procedures, but the most common

one is performed via the Claisen–Schmidt condensation and subsequent intramolecular Michael addition between substituted benzaldehydes and substituted 2'-hydroxyacetophenones in basic or acidic media under homogeneous conditions [11–13]. It is widely accepted that there is a need to develop clean and economical processes, where the use of noxious substances and the generation of wastes can be avoided.

In the past decade, various solid catalysts have been applied to flavanoid synthesis, such as magnesium oxide [14], alumina [15], barium hydroxides [16,17], hydrotalcites [18–20], and natural phosphates modified with NaNO<sub>3</sub> or KF [21–23]. However, most of them require the use of expensive toxic solvents to facilitate the heat and mass transfer in the liquid phase reaction systems [14]. We have shown recently that amine-functionalized mesoporous SBA-15 silica was very effective for the synthesis of flavanone by Claisen–Schmidt condensation and subsequent isomerization reaction under solvent-free condition [24]. Herein a detailed study of the influence of solvents, amino group loadings, reaction conditions and substituting groups in the aromatic rings on the catalytic performance

\* Corresponding author. Tel.: +886 2 23638017; fax: +886 2 23636359.  
E-mail address: [chem1031@ntu.edu.tw](mailto:chem1031@ntu.edu.tw) (S. Cheng).

of amine-functionalized SBA-15 for the synthesis of flavanones was presented. Since elimination of organic solvents is a frequent goal in green chemistry, our catalyst represents a potentially valuable and clean route to prepare a large group of organic compounds useful for pharmaceuticals.

## 2. Experimental

### 2.1. Sample preparation

Surfactant P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ,  $M_{\text{av}} = 5800$ ) was purchased from Aldrich and other chemicals of reagent grade were from Acros. All chemicals were used as received.

The aminopropyl-functionalized SBA-15 materials were prepared by a one-pot co-condensation method according to the literature [24]. Four grams of Pluronic 123 was dissolved in 125 g of 2.0 M HCl solution at room temperature. After adding TEOS, the resultant solution was equilibrated at 40 °C for 1 h to pre-hydrolyze TEOS, and then APTES was slowly added into the solution. The molar composition of the mixture was  $(1-x)$  TEOS:  $x$  APTES: 6.1 HCl: 0.017 P123: 165  $\text{H}_2\text{O}$ , where  $x$  varied from 0 to 0.20, or the molar ratio of APTES/(TEOS + APTES) was 0–20%. The resulting mixture was stirred at 40 °C for 20 h and then transferred into a polypropylene bottle and reacted at 90 °C under static condition for 24 h. The solid product was recovered by filtration and dried at room temperature overnight. The template was removed from the as-synthesized material by refluxing in ethanol. Then the material was filtered, washed several times with water and ethanol and dried at 50 °C. The resultant samples are designated as SBA-NH<sub>2</sub>- $x$ -P, where P denotes “prehydrolysis of TEOS” and  $x$  is the molar percentage of the APTES/(TEOS + APTES). For comparison, a sample designated as SBA-NH<sub>2</sub>-10 was prepared by similar procedures except that TEOS and APTES were added to the acidic template solution at the same time without TEOS prehydrolysis. Another aminopropylated silica sample, denoted by SiO<sub>2</sub>-NH<sub>2</sub>-10, was synthesized without the addition of P123 template by the sol-gel process, where TEOS and APTES were added into an opening beaker with 125 g of 2.0 M HCl solution at 40 °C under stirring and the mixture was kept stirring at the same temperature until the water was dried out.

All the obtained dried solids were treated with 0.2 M methanol solution of tetramethylammonium hydroxide (TMAOH) for 20 min to remove the residue Cl<sup>-</sup> ions (1.0 g of the gel per 50 mL of solution). Finally, the materials were filtered, washed several times with methanol and dried at 120 °C.

### 2.2. Sample characterization

X-ray powder diffraction (XRD) data were obtained on a Panalytical X'Pert Pro diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 45 kV and 40 mA. N<sub>2</sub> adsorption–

desorption isotherms were carried out using a Micromeritics Tristar 3000 instrument at liquid nitrogen temperature. Before the measurements, the samples were degassed at 100 °C for 12 h. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the  $P/P_0$  range of 0.05–0.3. Pore size distribution curves were calculated using the desorption branch of the N<sub>2</sub> adsorption–desorption isotherms and the Barrett–Joyner–Halenda (BJH) method. Elemental analyses (EA) were performed on a Heraeus CHN elemental analyzer.

### 2.3. Catalytic reaction

The liquid phase base-catalyzed reactions were carried out under N<sub>2</sub> in a sealed flask immersed in a thermostat bath with a magnetic stirrer. In a typical experiment without the solvent, the reactants were mixed in the flask and heated to the set reaction temperature. Then, 0.15 g of the dried catalyst was rapidly added into the reactor. For the reactions in the presence of solvent, the mixture of the reactants in 5 ml of solvent was heated to the reaction temperature before the dried catalyst was added into the reactor. The liquid products were separated from the reaction mixture at appropriate reaction intervals with a filtering syringe and diluted with chlorobenzene for analysis. The products were identified by GC–Mass spectrometry (HP5971 mass spectrometer connected with a 30 × 0.25 mm RTX-50 capillary column) and analyzed by using a Chrompak CP 9000 gas chromatograph (GC) equipped with a 30 m × 0.32 mm RTX-50 capillary column and an FID detector, where dodecane was used as the internal standard. The overall organic mass balance based on the starting reactants was more than 95%.

## 3. Results and discussion

### 3.1. Textural characteristics and chemical composition of the catalysts

The TMAOH treated amino-functionalized materials with TEOS prehydrolysis showed one intense peak indexed to (100) reflection and two weak peaks of (110) and (200) reflections in their XRD patterns. The peak intensity weakens with the increase in the loading of amino groups in the samples from 5% to 20%. On the other hand, the materials containing 10% amino groups prepared without TEOS prehydrolysis (SBA-NH<sub>2</sub>-10) or without the addition of P123 template (SiO<sub>2</sub>-NH<sub>2</sub>-10) were X-ray amorphous. These results confirmed that the aminopropyl-functionalized materials synthesized with TEOS prehydrolysis had ordered pore structures and the TMAOH treatment had little influence on the ordering of mesoporous structure as reported previously [24].

The textural characteristics and chemical compositions of the modified materials after TMAOH treatment are summarized in Table 1. All the materials prepared with

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