



Nicotinic acid functionalized organomodified silica as an efficient heterogeneous catalyst for the synthesis of benzoyl fumarate



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ABSTRACT

A new hybrid catalyst has been developed by incorporating nicotinic acid onto an organomodified silica. The catalyst was applied as a heterogeneous catalyst for the synthesis of benzoyl fumarate. The reactions work well in the presence of 20 wt % of the catalyst at room temperature to produce the desired products in high yield. The catalyst could be recovered and reused without appreciable change in activity.

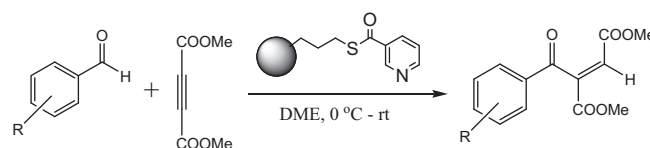
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The modification of silica and related materials by attachment of organic functionalities onto their surfaces is an important area of research in heterogeneous catalysis directed toward achieving green chemistry goals.¹ Surface functionalization of mesoporous silica has been widely practiced in recent years for generating active sites necessary for heterogeneous catalytic activity. Numerous strategies have been described for immobilizing inorganic and/or organic active species on or within the silica matrices.^{1a} Functionalization of mesoporous silica surface via tethering of an active group generally can be done in two different ways: through the so-called 'post-synthesis' method,² which involves grafting an organotrialkoxysilane onto the pore surfaces after mesoporous material synthesis, and through the 'direct synthesis' method,³ in which the functional groups are introduced during the synthesis of the mesoporous material. The pore functionalization is achieved through the co-condensation reaction occurring between the organotrialkoxysilane and the silica source in the presence of a structure-directing agent. The direct synthesis method is considered more predictable and hence valuable, because it can avoid several shortcomings of the post-grafting method, such as reduction in pore size, pore blocking at the aperture and difficulties in controlling the loadings as well as the distribution of active sites.⁴

Benzoyl fumarates and its corresponding acids are known to be an important precursor for the synthesis of many agrochemicals,⁵ drugs,⁶ and organic transformations.⁷ Nair et al. and later Shi et al. have prepared benzoyl fumarates by one pot reaction

between dimethyl acetylenedicarboxylate (DMAD) and aldehyde in presence of Lewis base as homogeneous catalyst.⁸ Bayat et al. have prepared this benzoyl fumarate by multicomponent reaction between DMAD, aldehyde, and PPh₃.⁹ We have also developed a ferrocene based pyridine catalyst for benzoyl fumarate synthesis under homogeneous condition.¹⁰ In addition, there are a few more examples for the synthesis of benzoyl fumarates from aldehyde and DMAD.¹¹ However, till date, heterogeneous approach has not been applied for this transformation. We have developed a new nicotinic acid functionalized organomodified mesoporous silica catalyst, for the first time, which acts as heterogeneous catalyst for the synthesis of benzoyl fumarates (Scheme 1). It has been observed that the organomodified silica, which has been characterized by various methods including spectroscopy and electron microscopy, is suitable as heterogeneous catalyst for the preparation of benzoyl fumarates from aldehydes and DMAD.

To realize our goal, we have developed a new organomodified mesoporous silica by incorporating nicotinic acid to the thiol group of mercaptopropyl silica (MPMS). Initially, MPMS was prepared by mixing tetraethylorthosilicate and mercaptopropyl (triethoxy) silane with a solution of *n*-dodecylamine in aqueous ethanol.^{3a,b}



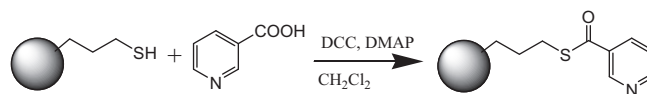
Scheme 1. Synthesis of benzoyl fumarates.

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The MPMS was characterized by powder X-ray diffraction, IR spectra, TGA, SEM, and EDX. The appearance of low-angle broad XRD peaks at $2\theta = 0.5$ – 2 degree is the characteristic of the mesoporous nature of MPMS (Fig. 1). The observed pattern does not show well resolved diffraction peaks. The broad peaks seen for this material suggest the lack of long-range order in the structure. In the IR spectrum (Fig. S1 of SI), the presence of bands at 2950 , 2560 cm^{-1} , and a broad peak at around 3300 – 3400 cm^{-1} confirms the presence of propyl, thiol (S-H stretching) and Si-OH groups in the MPMS. The TGA (Fig. S3 of SI) study indicates that loss in weight up to 100 $^{\circ}\text{C}$ is due to loss of water molecule from the surface and one main weight loss in the range 340 – 680 $^{\circ}\text{C}$ is due to loss of the organic group from the surface. Morphology of MPMS was also analyzed by using SEM (Fig. 2) and it is obvious from the picture that the major portion of the material is made up of aggregates of smaller roughly spherical particles. A second type of structure consists of single particles, again roughly spherical, but of a much larger size. Some of these are aggregated into groups of two or three, but not into larger aggregates. The spherical structures present are often seen in a range of mesostructured materials. EDX data (Fig. S2 of SI) confirm the presence of thiol moiety in the MPMS.

Nicotinic acid functionalized MPMS was prepared by simple esterification between MPMS and nicotinic acid in DCM (Scheme 2). Functionalization was carried out by stirring a mixture of MPMS,



Scheme 2. Synthesis of Nicotinic acid functionalized MPMS.

nicotinic acid, dicyclohexylcarbodiimide, and DMAP in dry DCM under N_2 atmosphere at room temperature for 48 h. The resulting white solid was separated by filtration, washed several times with DCM and dried in vacuum.

The X-ray diffraction patterns (Fig. 3) were also measured for nicotinic acid functionalized MPMS and as expected, these materials do not display the degree of a long range order associated with the MCM-41 class of silicates. Unlike MPMS, it shows a sharp peak at around $2\theta = 7^{\circ}$. The IR spectra of nicotinic acid functionalized MPMS show bands at around 1360 – 1310 cm^{-1} and 1725 – 1700 cm^{-1} which indicate the presence of aromatic C–N vibration of the pyridine ring and carbonyl group respectively. The SEM picture (Fig. 4) indicates no significant change in morphology after functionalization of MPMS with nicotinic acid.

Pore size distributions and surface areas were measured by N_2 adsorption studies for both the MPMS and nicotinic acid functionalized MPMS (Figs. S7–S10, SI). In both cases the materials

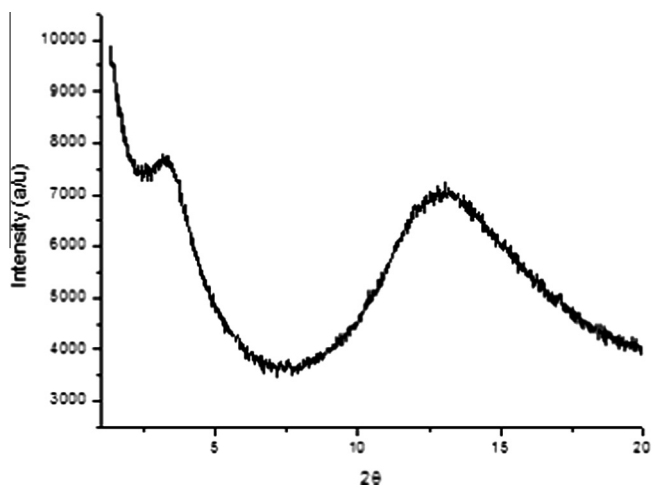


Figure 1. XRD pattern of MPMS.

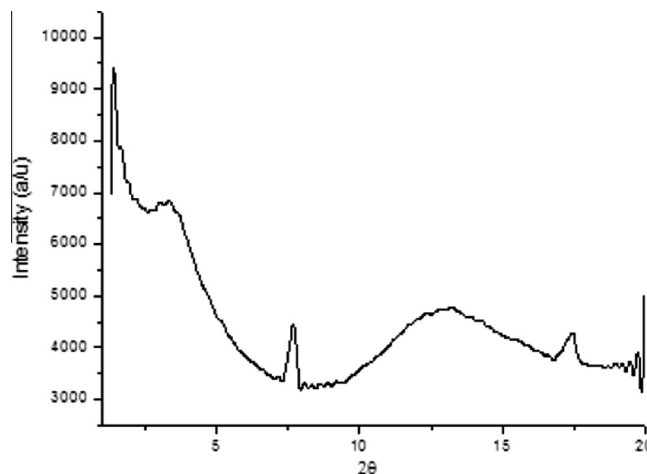


Figure 3. XRD pattern of nicotinic acid functionalized MPMS.

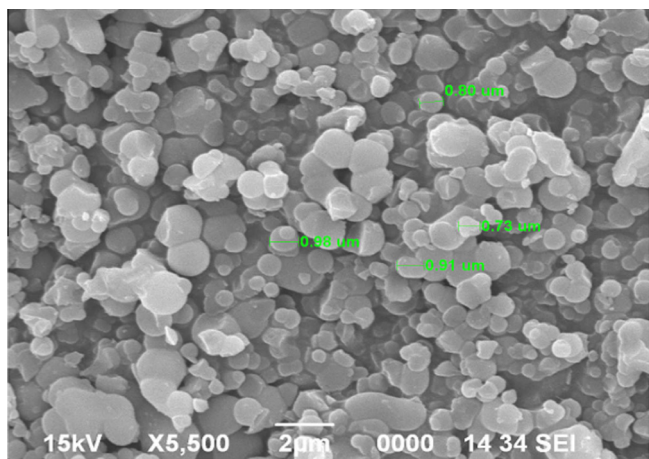


Figure 2. SEM image of MPMS.

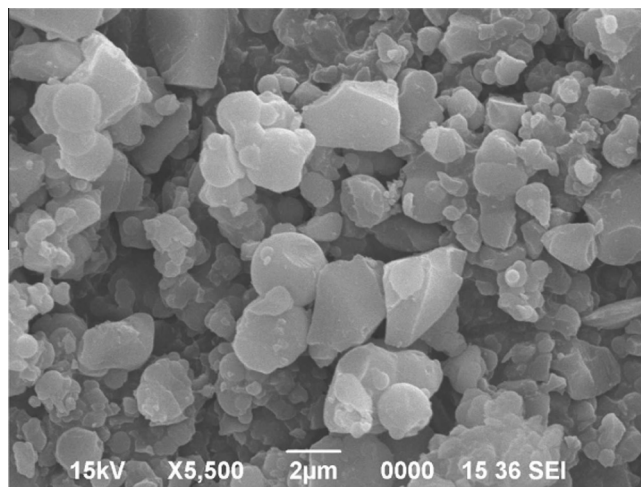


Figure 4. SEM image of nicotinic acid functionalized MPMS.

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