



Amino-Silane Functionalized MCM-22 Zeolite and Its Application on Nitroaldol Condensation

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Basic sites on microporous MCM-22 were introduced by post-synthesis grafting of aminosilane. The successful grafting of amino silane was evident from FT-IR, ²⁹Si MAS-NMR, and N₂ sorption studies. The basicity derived from organo-functionalized MCM-22 was utilized for liquid phase nitroaldol condensation of aldehydes using nitromethane under solvent free conditions. The organo functionalized MCM-22 showed better benzaldehyde conversion than the parent MCM-22 material and its catalytic activity remained intact upon reuse cycles.

Keywords: Zeolites, MCM-22, Functionalization, Aminosilane, Nitro Aldol Condensation.

1. INTRODUCTION

There has been an enormous interest in the preparation of surface modified molecular sieve materials with organic functional groups such as amine, sulfonic acid, mercapto-, amide, halogen, vinyl- etc., because of their important applications as catalysts and adsorbents.^{1–4} These materials possess reactive organic functional groups anchored on an inorganic surface (zeolites, carbon, oxides and silica) backbone and facilitating the exposure of the active sites.^{5–10} The functionalization with organic moieties allows the design of innovative catalysts for specific acid-base reactions and other environmental applications. Among the various inorganic support materials, zeolites and silica based molecular sieve materials are extensively used due to their high surface area, pore volume and thermal stability.^{11–14} Among the various organic groups (amine, aminosilane, sulfonic acid, thiol) used in these functionalized materials, amines have received a great deal of attention, especially as base catalysts for various organic transformations such as in aldol, nitroaldol, Claisen-Schmidt, and Knoevenagel reactions, which have also shown immense potential for the utilization of CO₂ as well as in the removal of toxic metal ions.^{15–25}

Although numerous reports are available on *in-situ* and post-synthesis organo-functionalization of mesoporous molecular sieves, only a limited number of studies on the introduction of functional groups into microporous zeolite

molecular sieves have been performed.^{23–25} In particular, *in-situ* preparation of functionalized microporous molecular sieve materials presents serious challenges in the selective removal of the template without altering the functional groups. On the other hand, unlike mesoporous MCM-41 or the SBA-15 molecular sieve, microporous materials do not possess sufficient silanol groups for the post-synthesis grafting of organo-functionality. In this regard, it is worth mentioning here that MCM-22(P) is a layered anionic framework structure possessing 10 MR channels which converted to three dimensional MCM-22 upon calcination, which has medium pore opening and two non-intersecting pore systems with a large amount of super-cages in the external pockets.^{26–33} The large external surface area and exposed external pockets have been post-synthetically modified by amine functionality and their importance for CO₂ capture and the trapping of nitrosamines in solutions, etc. has been demonstrated.^{34–36} It would be interesting to utilize amine functionalized MCM-22 for aldol condensation to explore the presence of external pockets on MCM-22 framework. Nitroaldol condensation is an important organic transformation, and the resultant products are bi-functional compounds. These organic bi-functional compounds act as intermediates in organic synthesis in chemical industries.^{37–39} Thus the present study is focused on the introduction of aminosilane groups to MCM-22 by a post-synthetic route and utilization of its basicity for base catalyzed nitroaldol condensation reactions.

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