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In-situ preparation of functionalized molecular sieve material and a methodology to remove template

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Rekha Yadav, Maqsood Ahmed, Arvind Kumar Singh & Ayyamperumal Sakthivel†

A series of diaminosilane-functionalized silicoaluminophosphate molecular sieve (SAPO-37) was prepared by *in-situ* synthesis, and a novel method was developed for the selective removal of structure directing agent (SDA)/template from the functionalized SAPO-37.The complete removal of the SDA was evident according to FT-IR, TGA, ^{13}C MAS-NMR and elemental analysis. The developed method was found to be efficient for removal of template from microporous molecular sieve viz., SAPO-37 and can be applied for other microporous molecular sieves such as SAPO-5, SAPO-40, etc. The powder XRD pattern of the template-removed samples showed a highly crystalline SAPO-37 phase. Argentometric titration revealed that more than 90% of diamine functionality exposed on the surface was accessible for catalytic applications. The resultant materials showed promising activity for ring opening of epoxide with aniline to yield β-amino-alcohol.

The synthesis of zeolite and zeolite like microporous molecular sieves with organic functional groups within the channels and framework can tailor their textural as well as catalytic properties depending on the nature of the functional groups incorporated[1–11]. In general, organic functional groups have been introduced on the surface of molecular sieve materials either through *in-situ* co-condensation using organosilane precursors or by post-synthetic functionalization. The *in-situ* introduction of organic functional group in inorganic framework, results in organic-inorganic hybrid materials possessing unique properties such as hydrophobic environment, adsorption capacity etc. The hybrid materials are synthesized in hydrothermal conditions and have organic group either as pendent hung within pore or partially substituted either inside the framework or on external surface[12–15]. The post-synthetic grafting method has been studied extensively for mesoporous materials which are applied in various applications, such as CO_2 capture[16–18] and base-catalyzed reactions[19–24]. Though mesoporous molecular sieves based materials shown promising applications, their commercial applications are limited owing to poor stability and amorphous wall properties[25]. Although, post-synthetic method covalently anchors functional groups on the surface of molecular sieve materials increasing in surface functionality, it is difficult to control the distribution of functional groups which results in non-homogeneous allocation of functional groups on surface and within the channels[26].

Faujasite (FAU) type microporous molecular sieve possessing 3-D pore structure with pore opening of 12-membered ring and large sodalite cages are commercially important in crude oil industries (about 40% conversions)[27]. Further introduction of organic functionality in microporous molecular sieves will result in new class of shape selective catalysts with organic active group. Three-dimensional framework materials with organic groups were first reported by Maeda *et al.*[1] by *in-situ* hydrothermal synthesis of an aluminophosphate molecular sieve with methyl functionality. Aluminophosphate materials are important owing to the flexible framework where different metal ions can be incorporated to tune the acidity[28,29]. Subsequently, a series of molecular sieves containing different functional groups have been synthesized, and they have been proven important for hydrocarbon sorption and several other applications[1–11,19–23]. For microporous molecular sieve materials, the co-condensation method can facilitates high-loading of functional groups by accommodating the organosilane into the framework[24] or complete distorted products due to disturbance in the crystal growth. In particular, for silico-aluminophosphate (SAPO) based materials, there are only limited reports on functionalization[7,15–18]. In this regard, it is emphasized that faujasite type zeolites showed immense potential for petrochemical processes.

Inorganic Materials & Catalysis Laboratory, Department of Chemistry, University of Delhi, Delhi 110 007, India. †Present address: Department of Chemistry, Central University of Kerala, Reverside Transit Campus Padnekkad, Nileshwar Kasaragod District - 671 314 Kerala. Correspondence and requests for materials should be addressed to A.S. (email: sakthiveldu@gmail.com or asakthivel@chemistry.du.ac.in)