

**I. DEVELOPMENT OF FACILE ROUTE TO FLUORIDE-MEDIATED,  
PURE-SILICA ZEOLITE THIN FILMS**

**II. REMOVAL OF STRUCTURE-DIRECTING AGENTS FROM  
MOLECULAR SIEVES VIA THE USE OF PHOTOLABILE STRUCTURE-  
DIRECTING AGENTS**

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## Abstract

This thesis consists of two projects related to the development of new routes to zeolite films. In an effort to expand the known library of pure-silica zeolites accessible in planar conformation, Part I details the development of a new synthetic technique, the vapor phase transport of fluoride, to produce pure-silica zeolite films with the LTA, CHA, STT, ITW and –SVR topologies. The films are characterized by X-ray diffraction, field emission scanning electron microscopy, X-ray energy dispersive analyses, and mechanical testing. Such pure-silica zeolite films could be useful in a variety of applications, due to their porosity, crystallinity, and general stability. For example, these materials could be employed as low dielectric constant materials, which are needed for microprocessors as the feature size is continually reduced. Upon investigation of the aforementioned zeolite powders and films, we find that the materials with the LTA topology have the lowest dielectric constant of all the pure-silica zeolites. Additionally, all the zeolites investigated, except STT, give  $k$ -values lower than predicted from their structures using the Bruggeman effective medium model, which has been commonly employed and found able to predict dielectric constants of amorphous silicas.

The second part of this thesis presents the development of an alternative method to thermal combustion to remove organics from zeolite pores, which can degrade zeolite films, using a photolabile structure-directing agent that can be removed from the zeolite pore space using UV photolysis. Here, the synthesis, photocleavage, and structure-directing ability of two different photolabile molecules (8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxo-8-azoniaspiro[4.5]decane hydroxide (P-SDA 1) and 1-(2-nitrobenzyl)-1H-

imidazole (P-SDA 2)), are presented and discussed. Cleavage of the photolytic P-SDA 1 is demonstrated in a homogeneous solution, and intercalated into a dealuminated zeolite FAU. The structure-directing ability of P-SDA 1 is evaluated via attempts to synthesize silicate and aluminosilicate zeolites, resulting in the formation of amorphous and layered materials. The structure-directing ability of P-SDA 2 is evaluated via attempts to produce aluminophosphate zeolites, resulting in several unknown crystalline phases, in addition to dense and hydrated phases. Lastly, complete photocleavage of P-SDA 2 within the crystalline, aluminophosphate materials is also demonstrated.



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