

## **Studies on Preparation of Zeolite Films on Ceramic Honeycomb Substrates by Novel In-Situ Crystallization Methods and Fabrication of Zeolite Honeycomb Monoliths**

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Zeolite type porous materials used for environmental applications such as hydrocarbon (HC) adsorption, DeNO<sub>x</sub> catalysis, gas separation, etc are required to be prepared in the form of multi-channeled honeycomb to render a low back pressure and high surface area in the practical applications. These are achieved either by forming zeolite films on honeycomb substrates or extruding zeolites in the form of honeycomb monoliths. The raw materials, Si/Al ratios and preparation procedures greatly influence properties of the final product such as crystal morphology, adhesion to support, porous properties, solid acidity, adsorption behavior, etc. This thesis addresses some of these issues by introducing new concepts of zeolite film preparation using solid state in-situ crystallization (SSIC) and microwave assisted in-situ crystallization (MAIC) methods, and utilization of inexpensive clay as a raw material for the preparation of mesoporous and microporous materials, films and monoliths. The materials/products developed were characterized using XRD, FTIR, XRF, NMR, SEM, TEM, NH<sub>3</sub>-TPD, N<sub>2</sub>/Ar adsorption, HC adsorption, gas permeability and mechanical testing.

In SSIC method, the ZSM-5 zeolite films were formed on cordierite honeycombs by a vapour transport mechanism initiated by the water included in the gel. The silica rich interfacial layer between the substrate and zeolite film increased the amount of ZSM-5 film and physical adsorption but reduced the solid acidity and chemisorption. ZSM-5 films on ceramic supports were also formed by MAIC method, a novel two-stage synthesis technique. Thermal and microwave effects during microwave heating produced nano-sized seeds on the surface of substrate, which provided the nucleation sites over which a uniform and well-crystallized zeolite film formed during subsequent hydrothermal treatment. The dipping time, microwave-heating time, power and hydrothermal heating time influenced the amount of zeolite formation, surface area and preferred orientation of the film. The membranes formed by this method showed good permeability of H<sub>2</sub> and CO<sub>2</sub> gases.

Fast formation (in 3h) of ZSM-5 zeolite was observed when microporous silica derived from metakaolinite was used as silica source. The growth rate and morphology of the crystals were found to depend on the Si/Al ratio; higher Si/Al



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ratio resulted in more uniform and well-crystallized zeolites with preferential growth of B plane. The zeolite films prepared from metakaolinite precursor on cordierite honeycombs also showed that high Si/Al ratio of the precursor and the presence of a silica-rich interface on the substrates result in well-crystallized zeolites with dense coatings and higher micropore

surface areas. Metakaolinite was also used as a cost-effective raw material for preparing ZSM-5 honeycomb monoliths with controlled morphology and tunable Si/Al ratios. These products showed higher zeolite crystal orientation owing to platy ZSM-5 crystals and higher thermal stability compared to that prepared from alkoxide.

Al-containing mesoporous silica (pore size 2.6-2.8 nm) with very high BET surface area ( $\sim 1400\text{m}^2/\text{g}$ ) was synthesized by surfactant-templating method using leached metakaolinite as silica source. Hexagonal mesoporous structure was observed by high resolution TEM. Low density of silica wall matrix that forms the mesoporous structure is considered to be a reason for such a high specific surface area of the product.