

# Zeolite Membrane Microreactors for Fine Chemical Synthesis

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## ABSTRACT

Fine chemicals and pharmaceuticals are high value added products that are produced in modest quantities. They are usually seasonal products that are customer specific and have a short shelf life. These characteristics usually placed a significant constraint in their production, such that it is not uncommon to see labour intensive batch processes being used instead of the more efficient continuous process. This usually led to a significant waste generation during the scale-up from the laboratory to production scale. In addition, the use of hazardous and often toxic homogeneous catalysts makes the product purification and waste disposal an important issue in today's stringent environmental regulations. Microchemical systems offer a new paradigm for meeting these challenges. Recent advances in the design and fabrication of micromixers, microseparators and microreactors bring closer the realization of desktop miniature factories and micro-pharmacies. They represent a cheap alternative way for the production of specialty chemicals and pharmaceuticals by a *continuous* process, allowing simpler process optimization, rapid design implementation, better safety and easier scale-up through replication. This enables rapid product deployment to the marketplace and thus ensuring a significant competitive edge.

New basic zeolite catalysts obtained by grafting amino groups onto NaX and CsNaX zeolites exhibit excellent catalytic activities for Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate (ECA), ethyl acetoacetate (EAA) and diethyl malonate (DEM). The CsNaX-NH<sub>2</sub> catalyst displays higher conversion compared to aminopropylated MCM-41 for benzaldehyde reaction with ECA and DEM (Figure. 1).

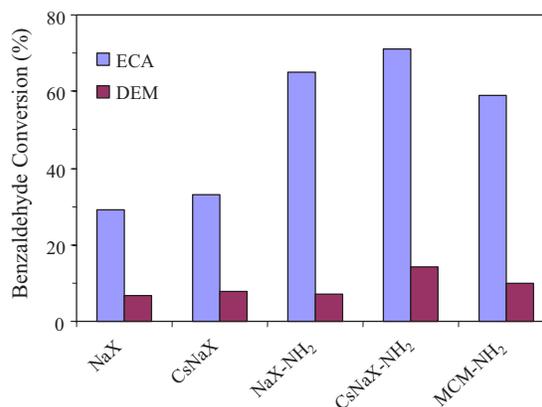


Figure 1. Benzaldehyde conversion ( $t = 60$  min) for Knoevenagel condensation reaction between benzaldehyde and (1) ethyl cyanoacetate and (2) diethyl malonate.

The performance of a membrane microreactor was tested and compared with that of microreactor, packed bed reactor (PBR) and packed bed membrane reactor (PBMR) for the Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate to produce ethyl-2-cyano-3-phenylacrylate. Cs-exchanged NaX faujasite zeolite was used as the base catalyst for this equilibrium-limited reaction. Hydrophilic zeolite membranes were employed in both membrane microreactor and PBMR for the selective removal of water byproduct from the reaction. The product yield per pass was low for the packed bed reactor. Higher yields were observed for the microreactor and PBMR, but the best performance belongs to the membrane microreactor, which displayed both supra-equilibrium conversion and better product purity (Figure 2).

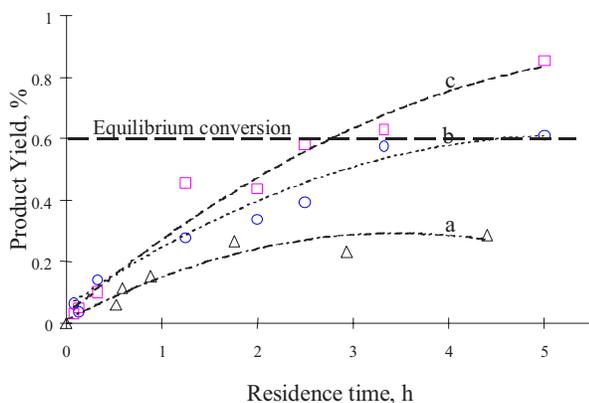


Figure 2. Ethyl-2-cyano-3-phenylacrylate product yield as a function of residence time for (a) fixed bed reactor, (b) multi-channel microreactor and (c) multi-channel membrane microreactor using CsNaX catalyst and ZSM-5 zeolite membrane.

Analysis indicated that all water produced by the condensation reaction was completely removed and the membrane was operating below its capacity. This means that the performance of the membrane microreactor is limited mainly by the kinetics, now that both thermodynamic and mass transfer constraints were removed. A nearly fourfold increase in reaction conversion was obtained for the microreactor when CsNaX-NH<sub>2</sub> catalyst was used instead of CsNaX.

**Keywords:** CsNaX zeolites, microreactor, base catalysis, Knoevenagel condensation reaction.