# ABSTRACT

Catalytic Conversion of Ethanol to Gasoline Range Hydrocarbons using Zeolites

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In the search for renewable energy sources, the production of gasoline range hydrocarbons was examined using ethanol as feedstock. A continuous flow microreactor was used and studies on the conversion of ethanol were carried out for a number of different zeolites and operating conditions.

It was found that although H-ZSM-5 zeolite can be prepared from readily available and cheap reagents, its potential as a catalyst for the conversion of ethanol is dependent on the conditions used for its preparation. Though a gasoline product comparable to its commercial counterpart was obtained, the operating conditions of the catalytic reactor played a significant role in determining the nature and concentration of the hydrocarbons obtained.

A high percentage conversion (>98 %) was achieved at temperatures greater than 300°C and gave approximately 60 % of hydrocarbons. The nature of the products changed from predominantly gaseous hydrocarbons at lower temperatures to aromatics at higher temperatures as a result of increased polymerization and aromatization processes. Significant cracking activity accompanied these processes resulting in the formation of light olefins and paraffins, mainly C3s. The shape selective nature of the catalyst resulted in the predominance of hydrocarbons less than C9 and of these benzene, toluene and xylenes were the main aromatic species.

The highly active nature of the catalyst resulted in its tendency to generate "coke precursors" (alkylated fused aromatic rings) which resulted in it eventually

becoming deactivated. The production of liquid hydrocarbons ($C5^+$) therefore ceased after approximately 17 hr on stream. High catalytic activity was restored following the removal of most of the coke deposits by calcination of the catalyst in air at 550°C for 24 hr.

The activity was quite responsive to the Al content of the catalyst which defines the amount of available acid sites. A linear increase in activity was observed with catalyst samples having a Si/Al ratio as low as 22. Higher concentration of Al in the catalyst resulted in its deposition in the channels of the zeolites, obstructing the mobility of reactants, hence causing a significant reduction in catalytic performance.

Our research has shown that the particle size of the catalyst could be modified with the novel use of Jeffamine EDR148, (3,6-dioxa-1,8-octanediamine) as organic template. It was observed that catalytic conversion conducted using samples of different particle sizes showed that larger particles gave higher para-selectivity in reaction products, but resulted in a faster rate of deactivation. Para-selectivity in zeolite catalysis is extremely important: (1) it represents a means of monitoring the shape selective nature of the catalyst and (2) p- isomers are of great commercial importance.

The distribution of the products was found to be insensitive to water content of up to 60 % in the ethanol feed. This could be of tremendous economic benefit since more readily available aqueous ethanol feedstocks could be used.

In addition to the ZSM-5 studies, a range of metal substituted aluminophosphates "zeolites" were prepared and extensively characterized. In their use for the catalytic conversion of ethanol, they were found to be highly selective for the production of ethylene, even at high temperatures.