

Reaction of Alcohols over H⁺/ZSM-5

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Introduction

The conversion of methanol to gasoline-range compounds over ZSM-5 are a widely studied class of reactions.¹⁻³ The conversion of higher alcohols over ZSM-5 to produce hydrocarbons has not been studied as extensively.⁴

Reactions of various alcohols like methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol over H⁺/ZSM-5 were carried out in a batch reactor. The effects of pressure, temperature and reaction time on the methanol to gasoline reaction were studied. Other alcohols were also examined to evaluate their product distributions under similar operating conditions.

Materials and Methods

The reactions were carried out in a 450cc batch reactor (Parr Instrument Co.) equipped with a fixed catalyst basket. The reagents used were at least 99% pure. The catalyst used was H⁺/ZSM-5 prepared by calcining the NH₄/ZSM-5 (CBV-2314 from Zeolyst International) at 550°C. Twenty (20) grams of the reactant alcohol were placed in the reactor and heated under autogenous pressure to 300°C and maintained under these conditions for 4 hours. After the reactor was cooled to room temperature, gas and liquid samples were collected. Each liquid sample was mixed with 10cc of dichloromethane to induce phase separation, the aqueous and dichloromethane phases were collected and then each analyzed using the GC-MS.

Results and Discussion

The effect of initial He pressure on the yields of xylene and tetramethylbenzene for the methanol reaction is shown in Figure 1. From these results it can be concluded that pressure does not have a significant effect in modifying the yield of aromatics in the methanol to gasoline reaction. However, the yield of aromatics increased with increased reaction time.

The methanol reaction over H⁺/ZSM-5 gave aromatics including *p*-xylene, 1,2,3-trimethylbenzene and 1,2,4,5-tetramethylbenzene and oxygenates including dimethyl ether, 3-methyl-2-butanone and acetone among others. The reaction of ethanol under similar conditions gave ethyl-substituted aromatic compounds including 1,3-diethyl benzene and 1,2-diethyl benzene, and alkanes like 3-methyl heptane, 4-methyl octane among others. When ethanol was used, the production of oxygenates was less than that obtained for methanol.

Propanols when reacted over H⁺/ZSM-5 resulted in different product distributions for 1-propanol and 2-propanol. Employing 1-propanol as the reactant resulted in product distribution almost exclusively composed of alkenes and branched alkanes like 2-methyl-1-propene, 4-methyl hexane, 4-methyl heptene among others. No traces of aromatic compounds were observed. In contrast, employing 2-propanol as a reactant resulted in product distribution containing both aromatics including *p*-xylene and 1-ethyl-2-methyl benzene and olefins including 3-methyl-2-hexene and 3-methyl-2-pentene, etc. Another interesting observation was the presence of 2-propanol in the product when 1-propanol was used as a feed.

Of all the butanols reacted over H⁺/ZSM-5, only 2-methyl-2-propanol (*tert*-butanol) gave significant aromatic yield. The remaining butanol isomers mainly gave branched alkanes and alkenes.

Thus, it can be concluded that the tendency for aromatics formation increases as follows:
tertiary alcohol > secondary alcohol > primary alcohol

It appears that the stability of carbocations plays an important role in formation of aromatics.

Significance

The discovery of the above phenomenon could be used to selectively make different compounds (olefins or aromatics) over the same catalyst simply by changing the alcohol feedstock.

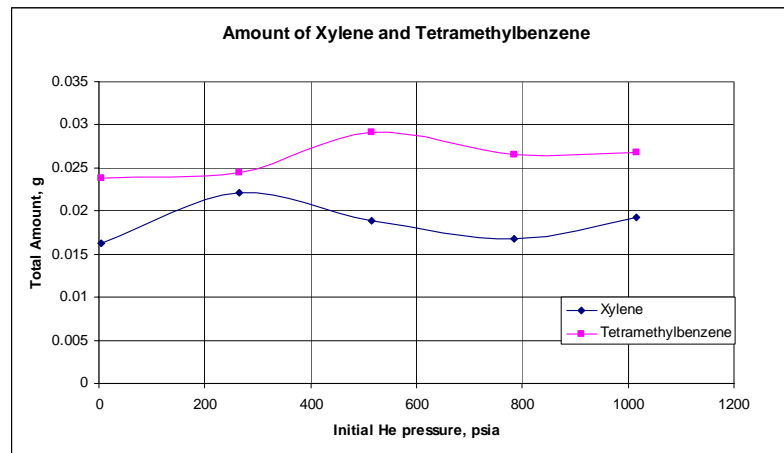


Figure 1. Yield of aromatics with change in total initial He pressure of the batch reactor.

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