



Ethanol conversion to hydrocarbons on HZSM-5: Effect of reaction conditions and Si/Al ratio on the product distributions



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ABSTRACT

The Conversion of ethanol to hydrocarbon over HZSM-5 zeolite with different Si/Al ratios was investigated under various reaction conditions. The catalyst with a higher Si/Al ratio (low acid density) deactivated faster and generated more unsaturated compounds at a similar time-on-stream. Temperature affects the catalytic activity with respect to liquid hydrocarbon generation and the hydrocarbon product composition. At lower temperatures ($\sim 300^\circ\text{C}$), the catalyst deactivated faster with respect to the liquid hydrocarbon formation. Higher temperatures ($\sim 400^\circ\text{C}$) reduced the formation of liquid range hydrocarbons and formed more gaseous fractions. Weight hourly space velocity was also found to affect product selectivity with higher weight hourly space velocity leading to a higher extent of ethylene formation. The experimental results were analyzed in terms of the product composition and the coke content with respect to catalyst time-on-stream and compared with the catalyst lifetime with respect to the variables tested on the conversion of ethanol to hydrocarbon.

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1. Introduction

The projected depletion of crude oil resources and the potential contribution of fossil energy resources to greenhouse gas emissions drew attention to developing technologies to produce renewable energy from biomass-derived resources. Though ethanol generated from renewable resources through fermentation is currently the dominant biofuel as a blend component for gasoline, several properties (e.g., low energy density and high water solubility) make ethanol undesirable as stand-alone transportation fuel and keep its composition in gasoline below 15 percent. In the near future, the production capacities of biomass-derived ethanol and other small oxygenates in United States of America are projected to rise beyond the blending needs due to the requirement to satisfy renewable fuel standards by producing 36 billion gallons/year of renewable fuel by the year 2022 [1]. For the successful implementation of biomass conversion processes in the transportation fuel market, it is imperative to produce biofuel products that closely resemble the properties of fuels derived from crude oil. One of the viable solutions for next-generation biofuels is conversion of biomass-derived

ethanol and other oxygenates to hydrocarbon compounds similar to those in gasoline, diesel, and jet fuel [2] using a process similar to methanol-to-gasoline (MTG) on ZSM-5 zeolites [3].

The synthesis procedure of ZSM-5 (Zeolite Socony Mobil-5) was developed in the early 1970s. ZSM-5, (structure type: mordenite framework inverted, MFI) is an aluminosilicate zeolite mineral belonging to the pentasil family of zeolites. It has a three-dimensional pore structure with intersecting systems of 10-membered ring pores. The dimensions of the HZSM-5 pores are $5.1 \times 5.5 \text{ \AA}$ (sinusoidal pore), $5.3 \times 5.6 \text{ \AA}$ (straight pore) with an internal pore space of 6.36 \AA [4]. Along with the development of ZSM-5 synthesis, ExxonMobil's discovery of the methanol-to-gasoline (MTG) process in the 1970s triggered great interest in research and development to understand the reaction mechanisms of alcohols over zeolites, especially ZSM-5 [3]. In 1985, the MTG process was commercialized in New Zealand by Mobil in a partnership with the New Zealand government. Shortly after the MTG plant in New Zealand was put into operation, crude oil prices dropped and remained low for more than a decade. Eventually, in the mid-nineties, the MTG part was shut down and the plant switched to methanol production [5]. In addition to the MTG technology, several methanol-to-hydrocarbon (MTH) processes are currently being developed, including Lurgi's methanol-to-propylene (MTP) process [6], the Topsøe integrated gasoline synthesis (TIGAS) process [7], and Honeywell's UOP/hydro methanol-to-olefins (MTO) process [8]. Since the invention of

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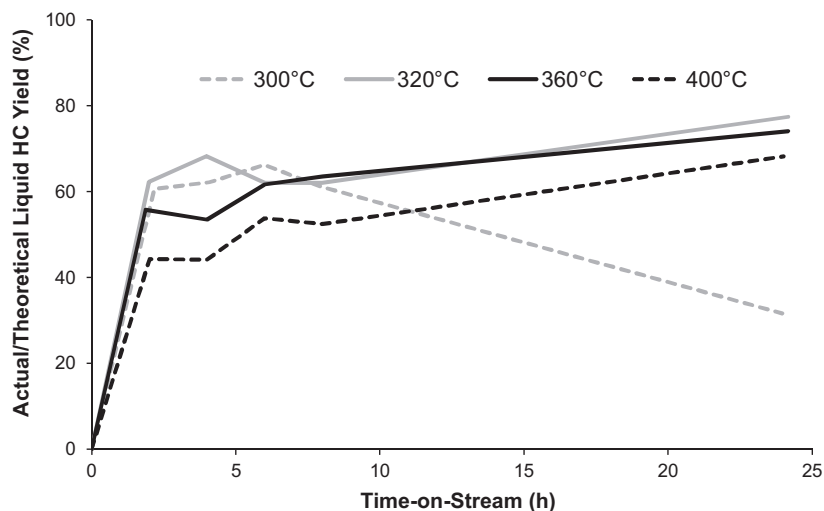


Fig. 1. Liquid hydrocarbon yield generated versus TOS for ethanol conversion over HZSM-5 catalyst with Si/Al ratio of 15 at 300 psig and $\sim 4.73 \text{ h}^{-1}$ WHSV for four temperatures (300 °C, 320 °C, 360 °C, and 400 °C).

Mobil's MTG process [4], considerable research has been done on the catalytic transformation of alcohols, with respect to the reaction mechanism and the catalyst deactivation mechanism, to obtain liquid hydrocarbon fuels and light olefins from the HZSM-5 zeolite [5,9]. The HZSM-5 zeolite-catalyzed deoxygenation of methanol accompanied by chain growth is well understood under moderate reaction conditions [10,11].

In addition to studying methanol, research has been conducted, to a limited extent, on the conversion of higher alcohols, $\geq \text{C}_2$, (e.g., ethanol, propanol, and butanol) to hydrocarbons over HZSM-5 [9,12–14]. Johansson et al. [15] compared the product compositions and the retained material on spent zeolite catalyst between methanol and ethanol conversions over HZSM-5 and concluded that methanol and ethanol go through a similar reaction mechanism to form hydrocarbons in gasoline range. We have also previously reported that over a fully active catalyst, alcohols (C_1 – C_4) generate products with similar composition while the product distribution tends to differ based on the alcohol carbon number at a longer time-on-stream (TOS) [9].

Numerous open literature information is available on the conversion of ethanol to hydrocarbon over HZSM-5 zeolite and catalyst deactivation as affected by the temperature, pressure, water content in the feed, coking mechanism, weight hourly space velocity (WHSV) and HZSM-5 Si/Al ratio. For example Costa et al. studied the effects of zeolite Si/Al ratio, ethanol dilution, and process variables such as temperature, space velocity and pressure to develop the kinetics and mechanisms for the ethanol conversion over HZSM-5 [16] and reported that the optimum yield of liquid hydrocarbon products was attained at temperature between 350 °C and 400 °C for the catalyst with Si to Al ratio between 30 and 50. Inaba et al. studied the effect of different metal loadings on the HZSM-5 catalyst toward aromatic hydrocarbons [17] and among the metals tested gallium showed the highest aromatic yield. Ingram et al. studied the formation of propylene during the conversion of ethanol using H-ZSM-5 catalyst [18] and concluded that propylene is formed primarily due to the cracking of higher hydrocarbon and the selectivity of propylene was higher for temperature greater than 375 °C. Aguayo et al. studied the HZSM-5 catalyst deactivation by coke in the transformation of aqueous ethanol into hydrocarbons [19] and reported that the presence of the water in the reaction medium has an important role in the attenuation of coke deposition. Ethanol conversion to hydrocarbon work also conducted over hierarchical (secondary mesoporosity along with the crystalline

microporosity) HZSM-5 [20] and nano crystalline HZSM-5 [21] and showed the improved catalytic activity with respect to the catalyst life time.

In this study, we specifically investigate the effect of reaction conditions (temperature and WHSV) and Si/Al ratio of the catalyst on ethanol conversion over HZSM-5 zeolite with respect to the product class distribution along the TOS of the catalyst.

2. Experimental

The zeolite catalyst materials used in this research were acquired from Zeolyst International, Inc., in ammonium form ($\text{NH}_4\text{ZSM-5}$). The properties of the catalyst tested are listed in Table 1. The powdered catalysts were pelletized and sieved to 60–100 mesh to attain uniform catalyst packing in the reactor. After sizing, the catalyst was calcined in a static air atmosphere at 500 °C for 4 h to convert it into the proton form (HZSM-5). Ethanol (200 proof) was purchased from Decon Labs, Inc., and was used in the same state as it was purchased.

Catalyst testing experiments on the ethanol conversion to liquid hydrocarbons over conventional HZSM-5 catalysts with various Si/Al ratios were carried out in a continuous fixed-bed, down-flow 3/8 inch. stainless steel tube reactor (7.75 mm internal diameter). The experiments were conducted at a range of temperatures between 300 °C and 400 °C. The reactor setup was equipped to collect condensed liquid samples under pressurized conditions without disturbing the reaction conditions. The nitrogen (N_2), used as a carrier gas for the feed ethanol and as an internal standard in the product gas analysis, flow rate was kept constant at $\sim 12.5 \text{ mL/min}$ throughout the experiment. The 60–100 mesh catalyst was packed midway along the reactor tube between thin layers of glass wool. Once reaction conditions (temperature and pressure) were established, the ethanol feed started at a flow rate of

Table 1
Properties of the catalysts tested.

| Vendor notation | Si/Al ratio ^a | Surface area ^a (m ² /g) |
|-----------------|--------------------------|---|
| CBV 3024E | 15 | 400 |
| CBV 8014 | 40 | 425 |
| CBV 28014 | 140 | 400 |

^a Vendor information.

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