Ethanol-to-Hydrocarbons reaction catalysed by ion-exchanged ZSM-5 zeolites

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1. Introduction
Propene is after ethene the second most important organic chemical. Since it is currently exclusively obtained from fossil resources, a more sustainable route for its synthesis is desirable, notably using renewables such as ethanol as a feedstock [1]. Microporous HZSM-5 are known to convert ethanol to hydrocarbons up to ~C10 [2]. In order to selectively focus on propylene, ZSM-5 based catalysts were prepared, characterized and tested using a high throughput approach. The aim of this work was to analyze the main parameters influencing the reaction, notably acidity strength, number of acid sites and textural properties. Furthermore, the understanding of the deactivation mechanism involving trapped hydrocarbons was studied. The corresponding properties were determined by in situ FT-IR, UV/Vis spectroscopy, XRD, TEM, TPR-MS and have been correlated to the catalytic performances.

2. Experimental
ZSM-5 was obtained from Zeolyst International under the label CBV3024E, with an Si/Al ratio of 30 and NH4+ as counter-ion. In this work, H-ZSM5 refers to the protonated form of this material. To vary the amount of acid sites, NH4 was exchanged for sodium following an ion-exchange procedure that involved mixing the zeolite with different amounts of NaCl in deionized water, followed by three days of continuous stirring. The resulting mixture was centrifuged for 10 minutes at 4000 RPM and washed with more deionized water for a total amount of 5 times. The Na/Al ratio was varied from 0, 0.11, 0.17, 0.32 to 0.87. The catalytic performance was determined using a FLOWRENCE® unit with 16 parallel fixed bed down flow reactors. The feed composition was 336 mL/min of inert gases and 200 μL/min of liquid ethanol diluted in 120 ml/min of N2 flow, split equally on the 16 parallel reactors. The temperature and the amount of catalyst were 300°C and 50mg, respectively.

3. Results and discussion
All ZSM-5 catalysts showed full and stable ethanol conversion under reaction conditions. The higher the Na/Al ratio, the higher and more stable was the ethylene selectivity with time-on-stream (Fig. 1). However, the inverse was observed for the propylene selectivity (Fig. 2). This inverse relation between the formation of these two products suggests the role of ethylene as an intermediate for propylene via oligomerization.

Figure 1. Selectivity to ethylene over various Na-exchanged H-ZSM5 catalysts

Figure 2. Selectivity to propylene over various Na-exchanged H-ZSM5 catalysts
In the following, the catalysts were characterized in detail to study the role of ethylene as an intermediate and correlating the acidity with the performance. First, TPR-MS was performed for a spent catalyst (Fig. 3, left) showing several species: the water signal was attributed to the water molecules formed during the dehydration step of ethanol. The presence of ethylene at low temperature can be explained by olefin desorption. Near 250 °C, olefins and paraffins begin to appear, culminating near 300 °C and continued up to 400 °C. No ethanol or ether species were observed, underlining the role of ethylene as an intermediate for oligomers via a hydrocarbon pool mechanism involving ionic polyalkylbenzene (PAB) species would undergo a reaction of dealkylation potentially through a pairing route to generate the olefin. Previously, strong Brønsted acid sites of H-ZSM-5 were proposed to account for the formation of ethene [3]. This effect was evaluated based on the adsorption of pyridine measured by FT-IR spectroscopy. In figure 3, center, the amount of pyridinium-represented by the signal at 1540 cm\(^{-1}\) reveals a decrease in Brønsted acid sites with the increase of the sodium amount. On the other hand, the signal at 1440 cm\(^{-1}\) increases due to the vibration of pyridine adsorbed on sodium, which may act as weak Lewis acid sites. The level of sodium exchange and the amount of acid sites correlate almost linearly as shown in figure 3, right. The correlation of these results with the selectivity to propylene (Fig. 2) proves that the propylene formation requires Brønsted acidity, whereas the formation of ethylene also takes place for low amount of Brønsted acid sites. Taking into account the reaction mechanism involving the oligomerization of ethylene in a hydrocarbon pool mechanism, these results suggest that the Brønsted acidity is the key parameter in the oligomerization reaction.

4. Conclusions

The ethanol to propylene reaction was performed over Na exchanged H-ZSM5 as a catalyst. The acidity was successfully mediated by the NH\(_4^+\) ion-exchange, showing decreasing trend of Brønsted acid sites with increasing Na/Al ratio. The decreased Brønsted acidity was detrimental to the selectivity to propylene, which was found to be formed via a hydrocarbon pool mechanism involving ethylene as an intermediate, suggesting that the Brønsted acid sites play not only a role in the dehydration of ethanol but also in the oligomerization of ethylene.

References


Figure 3. left: MS signal of the retained hydrocarbon species during the TPR experiment conducted from a H-ZSM-5 sample quenched after 10 minutes of ETH reaction; center: spectrum of pyridine adsorbed at 200 °C on Na-ZSM-5 samples (A: Na0-ZSM-5; B: Na11-ZSM-5; C: Na17-ZSM-5; D: Na32-ZSM-5; E: Na87-ZSM-5); right: Amount of Lewis and Brønsted acid sites as function of the Na/Al ratio