Effects of HZSM-5 crystallite size on stability and alkyl-aromatics product distribution from conversion of propanal

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1. Introduction

Bio-oil contains a large fraction of small (less than C₆) oxygenated compounds that are thermally and chemically unstable and need to be deoxygenated to form fuel-compatible molecules [1,2]. Conversion of methanol to hydrocarbons has been extensively studied on HZSM-5 [3,4]. There have also been many studies of the conversion of small oxygenates such as molecules with aldehyde, ketone, alcohol, and acid functionalities [5-7] as well as large oxygenates such as methyl-esters [8,9] on HZSM-5.

The effect of crystallite size has been recognized as an important factor in methanol to gasoline (MTG), methanol to olefins (MTO), and alkylation of aromatics. These reactions have been examined with HZSM-5[10] and SAPO-34[11,12] zeolite catalysts among others. The results from those studies show that light olefins are selectively produced on crystallite sizes smaller than 2 µm. Those studies also reported that in larger crystallites, intermediates can be readily converted in consecutive steps before they desorb from the crystallite. Thus, more secondary products and faster deactivation were observed due to longer intra-crystalline diffusion path lengths. In smaller crystallites, faster equilibration of methanol and DME at low conversions, as well as excellent catalyst stability have been reported. However, it was also found that the contribution of active sites on the external surface, responsible for non-shape-selective products, is more significant on small crystallite size zeolites[13].

We have recently reported that significant yields of alkyl aromatic products are obtained from conversion of propanal at mild conditions on HZSM-5 [14]. Those results showed that the initial aromatics were significantly alkylated and were predominantly produced via an aldol condensation pathway instead of a hydrocarbon pool pathway usually associated with hydrocarbon oligomerization/aromatization [2,6,7,15-20].

Although the effects of zeolite crystallite size have been studied for some applications, there has been little research done with bio-oil derived oxygenate compounds. In this contribution, a comparative study of catalyst activity and product distribution from propanal conversion are examined on small and large crystallite HZSM-5.

2. Experimental

2.1. Catalyst preparation

Small crystallite HZSM-5 zeolite with a Si/Al ratio of 45 was obtained from Süd-Chemie, Inc. A large crystallite HZSM-5 zeolite with identical Si/Al ratio was synthesized following the procedure described elsewhere [21]. The amount of Al in the original recipe was modified to obtain the desired Si/Al ratio of 45. The proton form of this zeolite was obtained by ion-exchange with NH₄NO₃ and calcination [21].
2.2. Catalytic activity measurements

A 4 mm ID quartz tube was used as a fixed bed continuous flow reactor. The reactor was heated by a split-tube furnace (Thermal Craft) with a digital feedback temperature controller (Omega). The catalyst was treated in situ with H₂ for 1 h at 400 °C before each run. The same hydrogen flow rate was kept during the reaction experiments. Propanal, obtained from Sigma-Aldrich, was fed into the reactor by a syringe pump (kd Scientific). The reaction was carried out at atmospheric pressure at different space times, W/F, defined as the ratio of catalyst mass to organic mass feed rate, ranged from 0.1 to 1 h, with a H₂ carrier gas flow rate of 35 cm³/min.

2.3. Product analysis

For each half hour time-on-stream (TOS), products were analyzed online by GC/FID (HP6890). The products were sampled using a 6-port valve with a 250 µl sample loop heated at 290 °C. After passing through the valve, the stream passed through a condenser. After each run, the reactor was purged with dry carrier gas for 15 min to collect the residual products from the reactor, in the condenser. The condensable liquid products were collected in methanol and were then identified by GC/MS (Shimadzu Q-2010). Both GCs were equipped with HP-INNOWax columns.

2.4. Catalyst characterization

The structure and morphology of the HZSM-5 zeolites were characterized by X-ray powder diffraction (XRD) on a Bruker D8 Discover diffractometer, by scanning electron microscopy (SEM) on a Jeol JSM-880 electron microscope with an EDX elemental analyzer, and by transmission electron microscopy (TEM) on a Philips JEOL 2000-FX system. The Brønsted acidity of the catalysts was determined by a temperature programmed desorption (TPD) of iso-propyl amine (IPA) method [22] with an online mass spectrometer (MS) detector (MKS Cirrus.), as has been detailed described elsewhere [14,21].

3. Results

3.1. Catalyst characterization

The XRD patterns confirmed the MFI structure of ZSM-5 for both samples (not shown). The SEM images (Fig. 1) show that the large crystallite HZSM-5 has an average particle size around 2–5 µm, while the small crystallite HZSM-5 has a much smaller particle size, averaging around 0.2–0.5 µm. The EDX elemental analysis confirmed the Si/Al ratio of 45 for both samples (not shown). The TEM observations (Fig. 1) revealed the primary crystallite size to be less than 100 nm for the small crystallite HZSM-5, while it is larger than 1.5 µm for the large crystallite sample.

Fig. 2 shows the IPA-TPD profiles for the large and small crystallite HZSM-5. The profile of propylene shows a maximum at around 350 °C and can be quantitatively ascribed to Brønsted acid sites (related to the framework Al content) catalyzing IPA decomposition [22]. The estimated Brønsted acid density for both samples was similar, 321 and 337 µmol/g for the large and small crystallite, respectively, close to the theoretical acid density of 370 µmol/g for a Si/Al ratio of 45. These results confirm the incorporation of Al into the framework of zeolite at the expected level.

3.2. Catalyst activity

Propanal conversion was investigated over the small- and large crystallite HZSM-5 at 400 °C and atmospheric pressure. To facilitate the
comparison, the products are divided into three groups: gas (C₁–C₃, mostly propylene), isoalkenes (C₄–C₉, mostly 2-pentene and isopentene), and aromatics (C₇, C₈, mostly xylenes, and C₉, trimethylbenzene and ethylmethylbenzene).

Fig. 3 shows the evolution of propanal conversion as a function of W/F at different times-on-stream (TOS) for both crystallite sizes. The results for the small crystallite zeolite are represented by solid lines and the large crystallites by dashed lines. It is observed that for the small crystallite zeolite, the curves for different TOS are very close together, indicating a low extent of deactivation during the TOS investigated. In contrast, the results for the large crystallite zeolite show significant changes between the different TOS curves. That is, for a given W/F, the conversion decreased significantly with increasing TOS, demonstrating a greater extent of deactivation than in the first case.

Conversion and product yields obtained at 400 °C and W/F=0.2 h are shown in Fig. 4 as a function of TOS. The left figure shows the results from the small crystallite zeolite and the right figure shows the results for the large crystallite zeolite. In agreement with the results shown in Fig. 3, only a slight deactivation was observed with small crystallites under these conditions. By contrast, the large crystallites showed large decreases in conversion as well as in yields of aromatics and gas with increasing TOS. The isoalkenes yield declined more slowly, indicating an increasing selectivity as deactivation proceeded while aromatization and cracking decreased.

Fig. 5 combines the results for both W/F and TOS and shows that very similar trends were observed for product yields as a function of conversion for both sized crystallites. This remarkable similarity indicates that the intrinsic catalytic function is not significantly changed with the crystallite size, but the effect is mostly on the extent of deactivation. It should be noted that the data from both W/F and TOS fall on the same line. These results imply that the deactivation with prolonged TOS only results in a reduction in number of active sites (i.e., pore blocking) without changing the chemistry of the product distributions (i.e., intra crystalline pore narrowing is not apparent).

While some differences can be seen in the yield of isoalkenes for the large crystallites compared to the small crystallites, the greatest effects of crystallite size are observed in the distribution of alkyl aromatics. First, the most significant differences are observed in the ratio of para-xylene to the sum of the ortho- and meta-xylenes \( p/(o+m) \) as depicted in Fig. 6. At all conversion levels, the \( p/(o+m) \) ratio of the larger crystallites is much higher than that of the small crystallites. This behavior has also been observed in the literature for the conversion of hydrocarbons or methanol to aromatics on HZSM-5 and described in terms of product-shape selectivity [10]. Similarly, when comparing the ratio of \( C_9/(C_8+C_7) \) aromatics (see Fig. 7), a much higher ratio is observed for the small crystallites than for the large ones. This ratio decreases at higher W/F, where conversion approaches 100 %. That is, with increasing amounts of excess catalyst the ratio obtained for the small crystallites becomes similar to that of the large crystallites.

4. Discussion

It is widely known [11,23] that the different internal diffusivities of molecules with different sizes and shapes are the predominant factor affecting shape selectivity in the intracrystalline channels of small-
pore zeolites. The HZSM-5 pore structure is a 10-member ring with a 3-dimensional channel system with two types of intersections with window openings of 0.54×0.56 nm and 0.51×0.55 nm and a maximum diameter of the intersections of about 0.9 nm. For this reason, aromatic molecules such as benzene, having a critical diameter of 0.68 nm, and larger alkyl aromatics can easily form within the intersections of the HZSM-5 channels [24] and diffuse out. However, in a large crystallite, the diffusion path length is longer, and differences in diffusion rates can modify the selectivity.

For a given W/F, even at the shortest TOS, the large crystallites showed significantly more deactivation than the small crystallites. With the longer diffusion path length of the larger crystallites, products take longer to diffuse out and have more time to form coke precursors and coke. However, as shown in Fig. 3, the data for the large crystallite zeolite approaches that of the small crystallite as the TOS decreases, i.e. from right to left. In the limit of zero TOS, with no-deactivation present, the curves coincide.

The effect of diffusion is also apparent in the evolution of the p/(m+o) ratio, shown in Fig. 6. A much higher p/(m+o) ratio was obtained with the large crystallite HZSM-5 since the higher diffusion coefficient of para-xylene helps this molecule diffuse out of the large crystallites more rapidly than the ortho and meta isomers, which are retained longer, with a greater probability of isomerizing to the para, the preferred shape-selective product [25]. In contrast, on small crystallites, with a shorter diffusion path length, all of the products are able to exit rapidly and the p/(m+o) ratio is much lower, meta-xylene being the favored product [25].

It is generally accepted that aromatization of hydrocarbons and alcohols over HZSM-5 occurs via oligomerization of intermediate olefins forming a hydrocarbon pool, which generates aromatics and isoaikanes [15]. According to this consecutive oligomerization pathway, one would expect more isoaikanes and less aromatics from the small crystallite zeolite because they would have a smaller chance (i.e., shorter time in the channels) to complete the formation of aromatics. However, the data presented here show that aromatics are always present, even at the lowest conversion, on the small crystallite zeolites. These results suggest that aromatics are produced from a pathway other than the hydrocarbon pool mechanism. In fact, it has been recently proposed [14] that the predominant pathway for aromatics formation from propanal, under the mild conditions of this study, includes aldol condensation with cyclization and dehydration of the aldol trimer to give C9 aromatics. Indeed, it is seen here that, due
to the short diffusion path length of the small crystallites, the C9 aromatics leave the channels of a small crystallite with less chance of cracking to smaller secondary aromatic products, or coke. The effect is less pronounced, or not observed, at high conversions under conditions with excess catalyst present, increasing the cracking of larger products. As a result, lighter aromatics, and a decrease in the C9/(C8+C7) ratio shown in Fig. 7 were observed at high conversions on the small crystallite zeolite.

5. Conclusions

The effects of crystallite size of HZSM-5 have been investigated for conversion of propanal to aromatics at rather mild conditions, 400 °C and atmospheric pressure. Much slower deactivation was observed on the small crystallites than on the large crystallites, due to faster removal of products from the zeolite channels, which reduces production of coke precursors and coke. At the same time, the small crystallites, with a shorter diffusion path length, showed significantly less isomerization of xylene products to the shape-selective preferred para-xylene than the large crystallites, where para-xylene’s greater diffusion coefficient enhances its selectivity. A higher fraction of C9 aromatics, the initial aromatic products from the predominant aldol pathway, was observed on small crystallites due to a shorter time for cracking before it diffuses out of the zeolite. These results suggest that the use of smaller crystallite HZSM-5 will improve production of alkyl aromatics from light oxygenates at mild conditions that may prove useful for bio-oil upgrading.

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