Highly Selective Hierarchical ZnO/ZSM-5 Catalysts for Propane Aromatization

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ABSTRACT: Hierarchical ZnO/ZSM-5 catalysts were prepared by desilication and impregnation with 2 wt % metallic ZnO. X-ray diffraction and Fourier transform infrared (FTIR) results showed that the structures of the hierarchical zeolites were relatively preserved despite desilication but were accompanied with sequential loss in crystallinity, likewise Brønsted acidity causing decline in conversion or activity of the catalyst. However, pyridine FTIR shows enhancement of the Brønsted acidic sites. Throughout the activity test, the hierarchical ZnO/ZSM-5 catalysts showed an outstanding performance within 5 h on stream with the average aromatic (benzene, toluene, and xylenes) selectivity trend, represented by their NaOH concentrations 0.3 M > 0.4 M > 0.2 M > 0.1 M corresponding to 61.0, 53.5, 40.3, and 36.8%, respectively. Their average propane conversions within the same period followed a consecutive trend 0.1 M > 0.2 M > 0.3 M > 0.4 M conforming to 34.1, 24.8, 17.3, and 10.2%, respectively. These were compared with that of the reference (ZnO/ZSM-5), which exhibited an average aromatic selectivity of 25.2% and propane conversion of 39.7%. Furthermore, the hierarchical catalyst generally displayed a low amount of C9+ heavier aromatics with the ZnO/ZSM-5(0.3 M) catalyst having the lowest C9+ selectivity of 23.7% compared to the reference catalyst with 72.7% at the same time on stream.

1. INTRODUCTION

The conversion of light alkanes into aromatic compounds mainly benzene, toluene, and xylenes (BTX) is one of the major industrial processes that has attracted so much attention due to the BTX’s wide range of application as intermediate materials in both chemical and petrochemical industries. They are used for blending with gasoline to enhance the octane number. In addition, toluene is used in the production of adhesives and benzene is extensively used in the downstream chemical processes such as production of styrene and phenol, while xylenes are essential for production of purified terephthalic and isophthalic acids. Currently, BTX are produced from naphtha. However, recent research efforts are focused on catalyst development for BTX production from alternative feedstocks such as light alkanes. Moreover, rapid progress has been made recently in utilizing stranded natural gas reserves for converting gas to liquid using a non-oxidative methane dehydroaromatization (DHA) catalytic route whereby the conventional gas-to-liquid (GTL) technologies become economically unaffordable. The major challenges experienced so far in its implementation are the thermodynamic barrier, which limits the benzene yield to 12−13% at 700 °C, and rapid catalyst deactivation as a result of coke accumulation on the surface of the catalyst, which accounts for 10–20% methane conversion when the Mo/H-ZSM-5 catalyst is employed. A key research question in developing such a catalyst is the relative difference in diffusivity between light alkanes and aromatics and the effects of the difference on the BTX selectivity. The H-ZSM-5 may be employed as a catalyst, but it undergoes quick deactivation and also causes cracking that leads to a large selectivity for C1 and C2 products. This problem has been overcome by the addition of transition metals such a zinc, platinum, or gallium to facilitate the dehydrogenation activity and to suppress cracking. Despite this improvement, an important drawback of the H-ZSM-5-based catalysts is their small pores, which results in poor metal dispersion and inadequate diffusion leading to the formation of bulkier aromatic products.
microporous composite that combines both the pore structure advantage of the mesopore and the strong acidity of the zeolite is one of the most promising materials that enhance the diffusion rate and expose the active sites for reactions. These materials enable mass transport of larger reactants and products and thus allow acid-catalyzed reactions to proceed on the mesopore surface and pore mouth, which alternatively serve in improving existing reactions/processes currently using zeolite catalysts. The proven qualities of hierarchical zeolites have necessitated their use extensively by some researchers in the past for propane aromatization with more utilization of gallium, platinum, and zinc as dehydrogenating metals. However, prior to the adoption of hierarchical catalysts, the formation, structure, and dispersion of active gallium species were a matter of great challenge due to its bulky nature; various methods such as hydrothermal in situ synthesis and post synthesis treatments (impregnation, ion-exchange, chemical vapor deposition (CVD), and reduction–oxidation treatments) were employed for the incorporation of gallium into H-ZSM-5. Moreover, the cases of gallium leaching have also been reported. In addition, the poisonous nature and high price of gallium compared to zinc pose a limiting role. Besides, the only disadvantage of zinc so far observed was its vaporization from the catalyst bed at severe treatments (≥550 °C).

Some of the works carried out on propane aromatization include that of Akhtar et al. who showed that the creation of intracrystalline mesoporosity into H-Ga-ZSM-11 via desilication significantly improve propane aromatization. The conversion of propane over H-Ga-ZSM-11 increased from 1.3 to 10.3% after desilication, whereas the BTX yield increased from 2.72 to 34.2%, a similar trend was also observed for n-hexane aromatization. The work carried out by Al-Yassir et al. in the synthesis of stable ordered mesoporous H-galloaluminosilicate using surfactant-mediated hydrolysis approach significantly improved the dispersion of gallium species in the form of extraframework, which enhanced its aromatization activity. The optimal ordered mesoporous H-galloaluminosilicate sample exhibited superior performance and stability with a propane conversion of 56.3% as compared with 30.8% provided by the steamed conventional H-galloaluminosilicate. Also, at comparable conversion level, ordered mesoporous H-galloaluminosilicate was more selective to BTX with 58.3% as compared with 42.5% for the steamed conventional sample. The superior aromatization was attributed to hydrothermal synthesis and hierarchical pore arrangements on the dispersion of gallium species. Another recent work by Ogunronbi et al. investigates the effects of introducing different types of mesoporosities in microporous Ga-ZSM-5, with random intracrystalline and ordered intercrystalline MCM-41 mesostructures. Using this catalyst, propane conversion increased to 33.9, 47.4, and 33.4% upon alkaline treatment, CTAB-mediated hydrolysis, and coating with the MCM-41 layer, respectively, up from 30.3% for microporous Ga-ZSM-5. At conversion of 13–15%, the mesoporous samples were more selective to BTX with ~56% as compared to 48.9% for the microporous sample. Furthermore, previous works have shown that apart from the diffusion problem sustained by the microporous ZnO/ZSM-5, a low selectivity to aromatics was observed on these catalysts. Therefore, this work focuses on improving the textural properties of the catalyst by synthesizing hierarchical ZnO/ZSM-5 with high porosity for propane aromatization.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction. The X-ray diffraction (XRD) patterns of reference and hierarchical ZnO/ZSM-5 catalysts are depicted in Figure 1. It is observed that all the synthesized catalysts showed the characteristics peaks of a typical ZSM-5 zeolite at 2θ equal to 8.00°, 8.86°, 23.14°, 24.00°, and 45.51° (JCPDS 00-042-0024), with a monoclinic crystal system. The obtained results are a clear indication that despite the desilication and ZnO deposition, the parent ZSM-5 structure is maintained. However, a closer observation of the peaks at 8°–10° and 22°–25° shows a great suppression of peak intensity as the NaOH concentration increases, which indicates a fractional dissolution of the ZSM-5 framework and decrease in crystallinity. The obtained results are in agreement with that of Sadowska et al. who reported that mild desilication of ZSM-5 (0.1 M and 0.2 M NaOH) has no obvious effect on the crystallinity. However, higher concentration of NaOH causes a noticeable effect on the crystallinity. Furthermore, there was no noticeable peak(s) to show the presence of ZnO from the XRD patterns and this could be attributed to the detection limit of the XRD analyzer used as only 2 wt % ZnO was impregnated for all the catalysts. A zinc content of 0.5–2 wt % was determined by Iwamoto et al. to exhibit good and stable activity for the aromatization reaction at 350–550 °C range.

2.2. Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra of reference and hierarchical ZnO/H-ZSM-5 in the lattice vibration region (400–4000 cm⁻¹) are shown in Figure 2. The intensity of the bands at 450, 550, and 790 cm⁻¹...
represents the bending vibration of SiO\textsubscript{2} and AlO\textsubscript{2} groups in the H-ZSM-5 framework. The 450 and 550 cm\textsuperscript{-1} bands, which also represent the five-membered ring pentasil unit of the ZSM-5 structure likewise zeolite crystallinity, are clearly reduced upon desilication treatment aimed at generating mesopores. This further supports the XRD data since the reduction in the aforementioned bands corresponds to crystallinity loss as well.\textsuperscript{14} The absorption band at 1100 cm\textsuperscript{-1} with a take-up at 1225 cm\textsuperscript{-1} represents the external asymmetric stretching of the Si–O–Si bridge. The stretching vibration of the band at 1627 cm\textsuperscript{-1} implies the existence of hydroxyl groups (OH\textsuperscript{−}) of absorbed water on the surface of ZSM-5 while the band at 3445 cm\textsuperscript{-1} signifies that stretching of internal tetrahedral Si–OH–Al hydroxyl bridges attributed to Brønsted acid sites is also broadening as compared to the parent ZnO/ZSM-5; likewise, the band at 3660 cm\textsuperscript{-1} represents the terminal Al–OH groups, which is consistent with Razavian et al. findings.\textsuperscript{20}

2.3. Nitrogen Sorption. Nitrogen (N\textsubscript{2}) adsorption–desorption isotherms of both microporous (reference) and hierarchical ZnO/ZSM-5 catalysts are shown in Figure 3.

![Figure 3. Nitrogen adsorption–desorption isotherms of reference and hierarchical ZnO/ZSM-5 catalysts at 77 K.](image)

Table 1 shows the textural properties of the reference and hierarchical ZnO/ZSM-5 catalysts. Upon alkaline treatment for 2 h at 65 °C using a Si/Al ratio of 50, ZnO/ZSM-5(Si/Al = 0.4 M) showed a complete loss of microporosity (V\textsubscript{micro} = 0 cm\textsuperscript{3}/g) implying 100% retention of mesoporosity. This is in proximity to the findings made by Xiao et al.\textsuperscript{13} who demonstrated that upon alkaline treatment at 75 °C for 2 h using a Si/Al ratio of 25, (0.5 M and 0.7 M) NaOH concentrations led to severe destruction of the micropores; moreover, several portions of the framework had collapsed and big void defects with dimensions exceeding 50 nm were formed, meaning that the pore system of the zeolite was seriously destroyed. The influence of the Si/Al ratio was also studied by Na and Somorjai\textsuperscript{24} whose work demonstrated that the higher the Si/Al ratio, the more prone the catalyst to excessive Si dissolution. The pioneering work by Groen et al.\textsuperscript{25} showed that the Si/Al ratio within the range of 25–50 is the optimal for developing a uniform mesoporous structure, which is highly dependent on temperature and time. From this, it can be confirmed that alkaline treatment conditions (temperature, time, and Si/Al ratio) play a vital role in fine-tuning mesoporosity development by desilication.

Table 1 also shows that desilication caused changes in the elemental composition as compared with the reference catalyst. The SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of ZnO/ZSM-5 decreased upon treatment with NaOH, from 47 to 41, 35, 26, and 22 as expected upon treatment with NaOH solutions of 0.1, 0.2, 0.3, and 0.4 M concentrations, respectively. A similar trend was reported by Xiao et al.\textsuperscript{23} and Groen et al.\textsuperscript{25}

2.4. Pyridine FTIR. The FTIR spectra of chemisorbed pyridine for the reference and hierarchical ZnO/ZSM5 catalysts are depicted in Figure 4. Upon alkaline treatment, there was a sequential decrease in the intensity of 1450 cm\textsuperscript{-1} band (Lewis sites) coupled with an increase in the intensity of 1550 cm\textsuperscript{-1} band (Brønsted sites). The increase in framework Al was as a result of Si leaching from the framework as shown in Table 1. This further corroborates the results shown in Figure 4. Nevertheless, the increased Brønsted acidity could be

![Table 1. Textural Properties of the Reference and Hierarchical ZnO/ZSM-5 Catalysts](image)

| Catalyst sample(s) | Si/Al\textsuperscript{4} ratio | S\textsubscript{BET} | S\textsubscript{micro} | S\textsubscript{meso} | S\textsubscript{total} | V\textsubscript{micro} | V\textsubscript{meso} | V\textsubscript{total} | V\textsubscript{t} | P\textsubscript{0} | \(\%\) | P\textsubscript{0} | P\textsubscript{t} | \(\%\) |
|--------------------|-----------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| ZnO/ZSM-5         | 47                          | 386              | 222              | 164              | 42.4             | 0.18             | 0.10             | 0.08             | 44.4             | 2.25             | 46.6             | 4.59             | 55.5             | 4.91             |
| ZnO/ZSM-5(Si/Al = 0.1 M) | 41                          | 255              | 174              | 81               | 31.7             | 0.15             | 0.08             | 0.07             | 46.6             | 4.59             | 46.6             | 4.59             | 55.5             | 4.91             |
| ZnO/ZSM-5(Si/Al = 0.2 M) | 35                          | 281              | 172              | 109              | 38.7             | 0.18             | 0.08             | 0.10             | 55.5             | 4.91             | 55.5             | 4.91             | 55.5             | 4.91             |
| ZnO/ZSM-5(Si/Al = 0.3 M) | 26                          | 273              | 136              | 137              | 50.1             | 0.22             | 0.06             | 0.16             | 72.7             | 5.52             | 72.7             | 5.52             | 72.7             | 5.52             |
| ZnO/ZSM-5(Si/Al = 0.4 M) | 22                          | 107              | 107              | 100              | 50.1             | 0.15             | 0.06             | 0.15             | 100              | 6.24             | 100              | 6.24             | 100              | 6.24             |

\textsuperscript{a}XRF analysis. \textsuperscript{b}From N2 adsorption measurement (BET method). \textsuperscript{c}From N2 adsorption measurement (t-plot). \textsuperscript{d}From N2 adsorption measurement at P/P\textsubscript{0} = 0.9956. \textsuperscript{e}From N2 adsorption measurement (t-plot). \textsuperscript{f}V\textsubscript{meso} = (V\textsubscript{total} – V\textsubscript{micro}). \textsuperscript{g}BJH adsorption average pore diameter.
2.5. Propane Aromatization. Aromatization of propane over bifunctional zeolite catalysts involves a series of complex heterogeneous reactions that include dehydrogenation, oligomerization, cyclization, and aromatization with excessive cracking as the side reaction. In the propane aromatization process, the Brønsted acid sites are responsible for the oligomerization, cyclization, and cracking of olefins while the Lewis acid sites catalyze the dehydrogenation of alkanes and cycloalkene intermediates. Porosity and acidity are generally considered to be the main factors influencing product selectivity and stability.

The catalytic performances of the reference and hierarchical ZnO/ZSM-5 catalysts are shown in Figure 5A–E. Figure 5A shows the result on a catalyst that has not been subjected to NaOH treatment but was impregnated with 2 wt % zinc oxide just like other catalysts. Its performance depicts a gradual decrease in propane conversion that was observed within 5 h on stream. This began with a sharp conversion of around 47% at 1 h and then declined gradually with time to 32% at 5 h on stream.

Figure 4. Pyridine FTIR of reference and hierarchical ZnO/ZSM-5 catalyst.

Figure 5. (A–E) Time on stream experiment of propane aromatization over reference and hierarchical ZnO/ZSM-5 catalysts at 540°C. Propane: nitrogen ratio of 1:2 and WHSV of 1200 mL/g h.
stream. The high propane conversion within 2 h signifies good dehydrogenation activity of the reference ZnO/ZSM-5 influenced by the Brønsted acid sites and the active metal ZnO species. Zinc cations are unable to perform propane dehydrogenation steps without the simultaneous presence of strong Brønsted acid sites, which appear to be involved in the initial activation of C−H bonds in alkanes. The decline in conversion after 2 h may possibly be due to poor diffusion of the propane molecules to acidic sites located within the zeolite cavities as a result of smaller pore size or pore blockage. The propane conversion within 5 h on stream could be ascribed to its higher dehydrogenation activity in the reference ZnO/ZSM-5 catalyst, which could be attributed to its higher dehydrogenation activity influenced by the deposited metal species. In addition, an increased aromatic selectivity was observed from 30 to 55% within 2 to 5 h on stream. The improved selectivity could be as a result of the superior acidity and textural properties of the catalyst.

The ZnO/ZSM-5(0.3 M) catalyst (Figure 5D) shows a low conversion (23%), which consistently declined to 17% within 5 h on stream. This shows a drop-in dehydrogenation activity influenced by the acid sites responsible for cracking and the active metal phase, which facilitate the dehydrogenation process. Moreover, the increased aromatic selectivity from 43−71% within 5 h on stream could be attributed to improved acidity and porosity, which enables efficient transport of the reactant and desired product out of the intramolecular mesoporous channels of the catalyst.

2.6. Effect of NaOH Treatment on Catalyst Performance within 5 h on Stream. The effect of NaOH treatment on catalyst performance is shown in Figure 6. It can be seen that propane conversion decreases with the increase in NaOH concentration. The reference ZnO/ZSM-5 catalyst has the highest conversion of 39.7% while for the hierarchical catalysts, the conversion values were 34.1, 24.8, 17.3, and 10.2%. The reason for higher conversion for the reference ZnO/ZSM-5 catalyst could be attributed to the Brønsted acid sites responsible for cracking and the active metal phase, which enables high dehydrogenation activity of the catalyst. However, a low aromatic selectivity of 25.2% was observed for the reference ZnO/ZSM-5 catalyst, which could be attributed to its pore geometry (size and shape) exhibiting an average pore width of 2.25 nm (from Table 1). The hierarchical catalyst selectivity increases progressively with increasing NaOH concentration from 0.1 to 0.3 M (36.8 to 60.9%) but decreases the 0.4 M NaOH concentration to 53.5%. These improvements could be attributed to the enhanced acidity as evidenced by the decrease in a Si/Al ratio from 47 to 22 and porosity of these materials from 4.59 to 6.24 nm (from Table 1), which accelerates the reaction and better transport of the products out of their channels.

2.7. Product Distribution of Reference and Hierarchical ZnO/ZSM-5 Catalysts. The liquid product distribution of the reference and hierarchical ZnO/ZSM-5 catalysts is shown in Figure 7. The ZnO/ZSM-5 microporous catalyst is more selective toward C9+ and its selectivity toward aromatic products is negligible. The poor selectivity toward aromatic compounds could be attributed to the highly crystalline nature as portrayed by the XRD diffraction patterns in Figure 1 and possibly pore blockage as a result of insufficient ZnO deposition into its narrow pores of 2.25 nm with a high surface area of 386 m²/g as shown from the BET results in Table 1. The aromatic products tend to be retained in the microporous domains of the catalyst, which prolongs the preferential deactivation of strong Brønsted and Lewis acid sites, which promotes hydride abstract that could be the factor contributing to the selectivity decline with time on stream.

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\text{Conversion} = \frac{\text{Propane converted}}{\text{Initial propane concentration}} \\
\text{Aromatic selectivity} = \frac{\text{Aromatic products}}{\text{Propane converted}}
\]

Figure 6. Effect of desilication sequence on catalyst performance within 5 h on stream.
residence time, thereby resulting in the formation of gaseous products due to cracking.14,32,33

However, with respect to individual aromatic products, the best performing catalyst, ZnO/ZSM-5(0.3 M), depicts a lesser crystalline material (Figure 1), exhibiting a wider pore size of 5.52 nm and a relatively lower surface area of 273 m²/g (Table 1), which dropped by 29% as compared with the reference material, likewise had its highest selectivity toward toluene, benzene, and m-xylene products with 33.3, 13.4, and 12.8%, respectively. ZnO/ZSM-5(0.1 M) was relatively crystalline, portraying 4.59 nm pore width and an abnormal drop in total surface area by 34% (255 m²/g) as compared to the reference catalyst. This inconsistent drop in the surface area could be attributed to pore blockage as a result of realumination caused by leached alumina during desilication back into the framework. However, the catalyst favored mostly the production of ethyl benzene with 6.4% while ZnO/ZSM-5(0.2 M), a fairly crystalline material (Figure 1), depicts 4.91 nm pore width and a surface area of 281 m²/g (27% drop in surface area) compared to the reference material. This catalyst favored the o-xylene product most with 12.4%. The reference catalyst exhibits the highest negligible selectivity of 1.9% for the p-xylene isomer as compared with the hierarchical catalysts. Another critical trend to note from Figure 7 is that a further increase in amorphous nature of the material or loss in crystallinity from 0.1 to 0.4 M desilication range yields more (C1−C5) gaseous products due to excessive cracking despite wider pore width, which facilitates transport to and from the catalyst. ZnO/ZSM-5(0.4 M), a highly amorphous material (Figure 2), with a widest pore width of 6.24 nm and a surface area of 107 m²/g (72% drop in surface area) as compared with the reference catalyst produced the highest amount of (C1−

In general, benzene, m-xylene, and toluene selectivities increase gradually for the 0.1, 0.2, and 0.3 M NaOH-treated catalysts but decrease for the 0.4 M NaOH-treated catalyst. These increased trends demonstrated by benzene, toluene, and m-xylene products could be attributed to the alkylation reaction, which is an acid catalyzed reaction predominantly favored by catalysts with higher acidity. Alkylation is a subsequent step in the aromatization of propane, which is the backbone of producing various aromatics products. Alkylation is directed by electrophilic substitution in which an electrophile, usually an alkyl substituent, attacks the benzene ring leading to the formation of a resonance-stabilized carbocation known as an arenium ion.34 Furthermore, the most stable carbocation intermediate will have the lowest activation energy (Ea); likewise, the fastest rate and therefore would be the major product.35,36 As such, the reason for high toluene composition in ZnO/ZSM-5(0.3 M) could further be explained based on the stability of the toluene molecule by the presence of a methyl group on the benzene ring, that is, this activates the aromatic ring by increasing the electron density on the ring through an “inductive donating effect”, and this electron donating property allows the alkyl group to stabilize the carbocation on the benzene ring. Benzene also showed similar behavior at ZnO/ZSM-5(0.3 M) and this could be related to its high thermodynamic and chemical stability due to the presence of its delocalized π-electrons above and below the plane of the ring.34 Meanwhile, the reason for the decreased selectivities of o- and p-xylene and an increased selectivity of m-xylene within the range of 0.1−0.3 M desilicated catalysts could be explained on the basis of their thermodynamic and kinetic stabilities. The m-xylene isomer is a thermodynamically controlled product, whereas the other two isomers are kinetically controlled products, which can influence the composition of the respective products, and m-xylene is the most stable product among the xylene isomers because in ortho- and para-xylene, electron density becomes high due to resonance or mesomeric (+R) effect of the methyl (CH₃) group.34 That is, since it is an ortho−para directing group, this is not seen in the case of the meta-xylene isomer. During the isomerization reaction, rearrangement involving hydride shift

Figure 7. Liquid product distribution of the reference and hierarchical ZnO/ZSM-5 catalysts at 5 h on stream.
instead of methyl shift could also occur, with the exception of the meta-carbocation ion, its two methyl groups in one of the canonical structures are capable of partially neutralizing the positive charges on the carbon ring atoms, while in the other two isomers, only one methyl group can behave this way; thus, its meta-carbocation ion will be more stable than the other two and as such equilibrium is shifted to the formation of the m-xylene isomer.\textsuperscript{35,37} In contrast to methyl-benzene (toluene) selectivity, ethyl-benzene selectivity decreased within 0.2–0.4 M desilication series, which is least stable compared to the latter. This could be explained on the concept of hyperconjugation of the alkyl substituents.\textsuperscript{34} This is due to the fact that the hyperconjugation effect dominates over the inductive effect. The methyl group has three \( \alpha \)-hydrogen atoms, which will fill the carbonium ion deficiency and increase the electron density of the benzene ring to a greater extent, whereas the ethyl group has two \( \alpha \)-hydrogens, which is less when compared.

3. CONCLUSIONS

Hierarchical ZnO/ZSM-5 catalysts were successfully synthesized, characterized, and tested in a microfixed bed reactor at a pressure of 1 atm, temperature of 540 °C, and weight hourly space velocity (WHSV) of 1200 mL/g h. The XRD analysis showed a progressive loss of zeolite crystallinity as concentration of NaOH increases from 0.1 to 0.4 M, which was attributed to silica leaching from the framework without complete lattice destruction. ZnO/ZSM-5(0.3 M) showed the optimal performance with the highest aromatic selectivity of 61.0% at the expense of propane conversion of 17.3% within an average of 5 h on stream compared to the reference catalyst with 25.2% aromatic selectivity and a propane conversion of 39.7%. The ZnO/ZSM-5(0.3 M) hierarchical catalyst also displayed the lowest C9+ (heavier hydrocarbons) selectivity of 23.7% while for the reference, the selectivity was 72.7% at 5 h on stream. The average aromatic selectivity for the reference and hierarchical catalysts within 5 h on stream followed the trend: 0.3 M > 0.4 M > 0.2 M > 0.1 M > reference ZnO/ZSM-5 while the average propane conversion followed a consecutive trend: reference ZnO/ZSM-5 > 0.1 M > 0.2 M > 0.3 M > 0.4 M. The reference ZnO/ZSM-5 favored mostly C9+ and a negligible amount of the p-xylene isomer. The best performing catalyst, ZnO/ZSM-5(0.3 M), had its highest selectivity toward toluene, benzene, and m-xylene products, which are all influenced by increased acidity and hierarchical pore geometry. It also displayed a low amount of C9+ heavier aromatics, which are influenced by the presence of mesopores. ZnO/ZSM-5(0.1 M) displayed its optimum selectivity toward ethyl-benzene while ZnO/ZSM-5(0.2 M) favored o-xylene the most. The synthesized hierarchical catalysts exhibited very good aromatic selectivity and stability when compared with the reference microporous catalyst.

4. MATERIALS AND METHODS

4.1. Materials. The commercial ZSM-5 catalyst (Si/Al ratio of 50, Zeolyst International), sodium hydroxide (Sigma-Aldrich, reagent grade, 98% anhydrous pellets), zinc nitrate (Sigma-Aldrich, 98% purity), nitrogen gas (99.9% purity), and propane gas (99.9% purity) are the reagents used in this work, whereas equipment and analytical tools used were microfixed bed reactor (fine reactor 4100, Fine Tec), surface area and porosimetry analyzer (V-Sorb 2800P, Gold APP), hydrogen generator (QL-500, Global sources), XRD analyzer (Empyrean, Panalytical), FTIR analyzer (8400-S, Shimadzu), XRF analyzer (X-Supreme 8000, Oxford instruments), and gas chromatograph (GC) (model 910, Buck).

4.2. Alkaline Treatment of Parent ZSM-5. The parent ZSM-5 zeolite with a Si/Al ratio of 50 (Zeolyst International) obtained in the form of NH\(_4\)-ZSM-5 was calcined at 550 °C for 5 h at a heating rate of 30 °C/min to convert the NH\(_4\)-ZSM-5 to H-ZSM-5. A calculated amount of the H-ZSM-5 was dispersed in 300 mL of 0.1 M NaOH solution and heated at 65 °C for 2 h under stirring. The suspension was then cooled in an ice bath and the solid was recovered by suction filtration. The solid was subsequently washed with deionized water until a pH of 7 was obtained. This was subsequently dried at 90 °C for 1 h and then ion-exchanged with 0.5 M NH\(_4\)Cl at 70 °C for 3 h. The resultant mixture was cooled, filtrated, and washed. Drying was done at 95 °C, and then the mixture was calcined at 550 °C for 5 h to obtain protonic hierarchical H-ZSM-5. A similar procedure was repeated using 0.2, 0.3, and 0.4 M NaOH solutions.

4.3. Zinc Impregnation on the Parent and Hierarchical H-ZSM-5 Catalysts. Zn was impregnated onto the H-ZSM5 and the protonic hierarchical H-ZSM-5. For this work, a ZnO loading of 2 wt % was used for all the catalyst preparation. In a typical synthesis, Zn (NO\(_3\))\(_2\)-6H\(_2\)O (Sigma-Aldrich, 98% purity) containing 2 wt % ZnO was dissolved in 100 mL of deionized water and subsequently introduced (dropwise) into another beaker containing H-ZSM-5 or hierarchical H-ZSM-5. This was then evaporated at 70 °C under stirring until dryness and dried overnight at 95 °C. The samples were calcined at 550 °C for 5 h to obtain the ZnO/ZSM-5 catalysts. The catalyst samples were denoted as ZnO/ZSM-5 as the reference catalyst without alkaline treatment, while hierarchical ZSM-5 catalysts were denoted as ZnO/ZSM-5(0.1 M), ZnO/ZSM-5(0.2 M), ZnO/ZSM-5(0.3 M), and ZnO/ZSM-5(0.4 M) with alkaline treatment with 0.1, 0.2, 0.3, and 0.4 M NaOH concentrations, respectively.

4.4. Catalyst Characterization. X-ray diffraction (XRD) was performed to determine the structural properties of the samples and the patterns were recorded with an Empyrean diffractometer system using Cu K\(\alpha\) radiation (\(\lambda_{\alpha}=1.540598\ \text{Å}, 45\text{kV}, 40\text{mA})\). Each sample was scanned over a range of 4° to 80° (2\(\theta\)) and a step size of 0.026261°. Analysis was carried out using HighScore Plus analysis software by Panalytical while the elemental compositions of the respective catalysts were analyzed using an X-Supreme 8000 XRF analyzer by Oxford Instruments. The \(\text{N}_2\) adsorption—desorption measurements were conducted on a V-Sorb 2800P surface area and porosity analyzer (V-Sorb 2800P, Gold APP) at −196 °C. Prior to the analysis, all the samples were degassed under vacuum at 250 °C for 9 h. The Brunauer—Emmett—Teller (BET) model was used to calculate the total surface areas, which were derived within the relative pressure (\(p/p_0\)) range of 0.0731–0.2383. The micropore volume and micropore and mesopore surface areas were derived from the \(t\)-plot. The pore size distribution was calculated by the BJH method applied to the adsorption branch of the isotherm.

Transmission FTIR spectra of lattice vibration were recorded in the 400–4000 cm\(^{-1}\) range at 2 cm\(^{-1}\) resolution, averaging 10 scans, using a Shimadzu FTIR spectrometer (8400S) with IR solution software, while for the pyridine-FTIR, the samples were weighed in crucibles (about 25 mg.
and degassed in an oven at 250 °C for 2 h. After degassing, the samples were placed in a desiccator containing pyridine in a Petri dish. The desiccator was vacuumed continuously using a vacuum pump for an hour before the samples were taken for FTIR analysis. Transmission FTIR spectra of adsorbed pyridine were also recorded using a Shimadzu FTIR spectrometer (8400S) to determine the nature of acid sites (Brønsted and Lewis acid sites).

4.5. Catalyst Performance Test. Catalytic activity tests were carried out in a fixed bed stainless steel microreactor (4100, FINETEC Instruments) at 540 °C, atmospheric pressure, weight hourly space velocity (WHSV) of 1200 mL/g h, and propane-to-nitrogen ratio of 1 to 2. A total of 1 g of a catalyst, comprising of 0.5 g of zeolite and 0.5 g of powdered glass bead, was loaded into the reactor with a diameter of 9 mm and length of 64 mm. Initially, nitrogen was fed into the reactor at ambient temperature flowing at a rate of 20 mL/min and preheated gradually to a reaction temperature of 540 °C. The feed (consisting of 33 wt % propane and 67 wt % nitrogen) was passed into the catalyst bed at a flow rate of 60 mL/min after being preheated to the reaction temperature. The experimental setup is shown in Figure 8. The gaseous and liquid products were analyzed using an online gas chromatograph (model 910 by Bulk) equipped with a flame-ionized detector (FID) and a (Restek MXT-1) column. The TCD was equipped with (molecular sieve 13X and Hayesep D) columns.

The propane conversion $X_{\text{propane}}$ and product selectivity $S_i$ were calculated using eqs 1 and 2 while a schematic drawing of the reactor setup is shown in Figure 8.

\[
X_{\text{propane}} = \frac{C_{\text{propane}}(\text{in}) - C_{\text{propane}}(\text{out})}{C_{\text{propane}}(\text{in})} \times 100
\]

(1)

\[
S_i = \frac{C_i}{\sum (C_i) - C_{\text{propane}}(\text{out})} \times 100
\]

(2)

where $C_i$ and $C_{\text{propane}}$ are the concentrations for species $i$ and propane in wt %, respectively.

Figure 8. Schematic diagram flow of the reactor setup.

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**Notes**

The authors declare no competing financial interest.

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