

Research Article

Influence of Bifunctional PtZn/SiO₂ and H-ZSM-5 Catalyst on the Rates and Selectivity of Propene Aromatization

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Abstract

Previous studies on the conversion of olefins to aromatics with bifunctional Ga- or Zn-ZSM-5 catalysts have concluded that benzene, toluene, and xylenes (BTX) yields are significantly higher than for ZSM-5 alone. These results were attributed to the higher aromatic dehydrogenation rate of Ga or Zn. In this study, a highly active, bifunctional PtZn/SiO₂ (1.3 wt% Pt, 2.6 wt% Zn) with H-ZSM-5 (Si/Al = 40) catalyst is investigated for propene aromatization at 723 K and 823 K. At low to moderate propene conversions, in addition to BTX, small alkanes and olefins are produced. Many of these may also be converted to aromatics at higher propene conversion while others are not, for example, methane, ethane and propane. When compared at equivalent space velocity or propene conversion, the bifunctional catalyst has a much higher selectivity to aromatics than ZSM-5; however, when compared at equivalent conversion of all reactive intermediates, the bifunctional catalyst exhibits very similar BTX selectivity. At 723 K, for ZSM-5 the primary non-reactive by-products are propane and butane; while, for the bifunctional catalyst the major non-reactive product is propane. At 823 K, both



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ZSM-5 and the bifunctional catalyst convert propane and butane to aromatics increasing the aromatic yields, and the by-products are methane and ethane.

Keywords

Propene aromatization; platinum-zinc intermetallic alloy; bifunctional olefin reactions; H-ZSM-5

1. Introduction

Advances in mining and extraction techniques such as hydraulic fracturing and horizontal drilling have led to an abundance of light hydrocarbons from shale formations (i.e., shale gas) [1]. Shale gas consists mainly of methane, ethane, propane, and butane. These natural gas liquids can be converted to light alkenes via dehydrogenation [1-6] or cracking [6-10], which can be further converted to valuable aromatic hydrocarbons, such as benzene, toluene, xylenes (BTX), and high-octane gasoline [11-15].

Alkene aromatization reactions are generally catalyzed using ZSM-5 at higher temperatures and lower pressures [16-18]. For example, propene aromatization by H-ZSM-5 (Si/Al = 50-100) at 523 K-850 K gives low selectivity to aromatic products (~35%) and high selectivity to low value light paraffins (~60%); while with higher Si/Al ratios (from 140-500) at 573 K, trace amounts of aromatics were observed [17]. Similar aromatic yields were observed by Norval and co-workers for propene, 1-butene, and 2-methylpropene conversion over H-ZSM-5 at 663-773 K [18]. The mechanism for acid catalyzed olefin aromatization was proposed by M.L. Poutsma in 1976, suggesting that aromatic molecules are formed from olefins via successive deprotonation and hydride transfer to carbenium ions [19]. On Bronsted acid catalysts, olefins undergo many cycles of oligomerization [20-22], to make a larger olefin, and cracking [10, 23-25], to give smaller olefins of different chain lengths than initially present as a reactant. Larger hydrocarbons may also undergo cyclization, which may then be subsequently converted to aromatics via dealkylation [19, 26-28]. The formation aromatics also leads to the formation of small alkanes, typically propane, with an alkane/aromatic mole ratio = 3. Ono and co-workers confirmed the validity of this mechanism on H-ZSM-5 for butene aromatization at 773 K, reporting an alkane/aromatic molar ratio = 2.9 [29].

Using bifunctional catalysts having both Brønsted acid sites (H⁺) and a dehydrogenation function (e.g., Ga [28-31], Zn [17, 28], or Cu [32, 33]), the aromatic selectivity can be increased to about 70%. The other by-products were methane, ethane, ethene, propane, butenes, and C₅₊ olefins. For bifunctional catalysts the alkane/aromatic mole ratio decreases to less than 1, suggesting that aromatics are formed by a different mechanism, i.e., dehydrogenation of cyclo-paraffins on Zn or Ga [28-30, 34].

While metallic Pt has a much higher rate for dehydrogenation than Ga or Zn oxides, Pt is highly selective to methane by hydrogenolysis giving low aromatic yields. In addition, Pt nano-particles form coke and rapidly deactivate ZSM-5 [35]. However, intermetallic alloys of Pt, for example, Pt₁Zn₁, minimize methane and coke formation and have significantly improved deactivation stability [2, 36, 37]. In this study, bifunctional (PtZn/SiO₂ + H-ZSM-5) catalysts are compared to H-ZSM-5 for propene aromatization at 723 and 823 K. This study demonstrates that bifunctional H-ZSM-5 catalysts do

increase the aromatic selectivity when compared at constant propene conversion or reaction conditions [28-31], but do not increase the aromatic selectivity, when compared at equivalent conversion of all reactive intermediates. The unreactive alkane products, i.e., methane, ethane, propane and butane, also differ depending on the reaction temperature and catalyst.

2. Materials and Methods

Commercial ammonium ZSM-5 (NH₄-ZSM-5, Zeolyst International, CBV 8014, Si/Al = 40) was first calcined at 773 K for 3 h (5°C/min ramp rate) to convert to the acidic form of H-ZSM-5. The H-ZSM-5 was then pelletized to 35-50 mesh (similar size to the PtZn/SiO₂).

PtZn/SiO₂ was synthesized similar to previously reported methods [2, 37]. First, Zn is deposited on silica (SiO₂; Davisil Grade 646, Sigma Aldrich, 35-60 mesh) using strong electrostatic adsorption of Zn⁺² ions. To prepare 5 g PtZn/SiO₂, 0.68 g zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Sigma Aldrich) was dissolved in approximately 50 mL Millipore water. Concentrated ammonium hydroxide was then added to the solution until pH > 11. The 5 g SiO₂ was added to the Zn solution and stirred using a Teflon stir bar for 10 minutes. The suspended SiO₂ was filtered and washed with 50 mL Millipore water three times before drying overnight at 398 K in stagnant air. Subsequently, it was calcined at 573 K for 3 h (10°C/min), yielding approximately 3 wt % Zn on silica (Zn/SiO₂).

Pt was added to the Zn/SiO₂ by incipient wetness impregnation. Its pore volume was determined by adding Millipore water dropwise until visibly saturated (measured to be 1.0 mL/g SiO₂). The Pt impregnation solution was prepared by dissolving 0.2 g tetraamine platinum (II) nitrate (Pt(NH₃)₄(NO₃)₂, Sigma Aldrich) in 2 mL Millipore water. Concentrated NH₄OH was then added to the solution until pH > 11, approximately 1.5 mL. Millipore water was added to the solution to yield 5 mL total solution volume. The solution was then added dropwise to the Zn/SiO₂ while stirring until the entire solution was consumed. The Pt-impregnated Zn/SiO₂ was then dried overnight at 398 K in stagnant air and calcined at 473 K for 3 h (5°C/min ramp rate) before being reduced at 498 K under flowing 5% H₂ (balance N₂, 100 cm³/min). To confirm Pt₁Zn₁ intermetallic alloy was synthesized, the catalyst was tested for propane dehydrogenation to ensure >97% propene selectivity up to about 70% conversion at 823 K.

Elemental analysis of the PtZn/SiO₂ catalyst was determined using Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES) measurements performed on a Thermo Scientific iCAP 7000 Plus Series spectrometer. Preparation involved digestion of 0.272 g of sample with 2.07 g HF (Sigma Aldrich, 48%) for 48 h, then dilution with 49.5 g of deionized water. After digestion and dilution, a 2.14 g aliquot was removed and mixed with 0.54 g of HNO₃ (Sigma Aldrich, 70%). Calibration standards were prepared by diluting stock standard solutions of Pt, Zn, Al, and Si (Sigma Aldrich). The concentration of Pt and Zn was measured to be 1.3% and 2.6%, respectively.

The bifunctional catalyst was prepared to give a 1:1 mass ratio of PtZn/SiO₂ and H-ZSM-5. Catalyst weights from 0.005-1 g were diluted to a total sample bed mass of 1 g using SiO₂. The sample mixture was then loaded into a 10 mm I.D. quartz tube, using quartz wool to support the catalyst with an internal thermocouple monitoring the temperature of the catalyst bed. The quartz reactor was loaded into a vertically aligned clamshell furnace. The catalyst was heated to approximately 373 K while flowing 100 cm³/min N₂ and held for 15 minutes before heating to the reaction temperature (723-823 K) in flowing N₂. After reaching the reaction temperature, a flow of 100 cm³/min 5% H₂ (balance N₂, Indiana Oxygen) for 30 minutes reduced the catalyst forming the PtZn alloy. The

reaction is then initiated by flowing 100 cm³/min 3% C₃H₆ (balance N₂, Indiana Oxygen) over the catalyst bed. The rates and selectivity for cyclohexene conversion on PtZn/SiO₂ and H-ZSM-5 determined by bubbling 10-100 cm³/min N₂ through cyclohexene (Sigma Aldrich, 99%). Products were analyzed using a Hewlett Packard 7890 gas chromatograph with an Agilent HP/AL-S column and a flame ionization detector. The feed molar flowrate was determined assuming a saturated feed of cyclohexene, and the conversion of cyclohexene was determined by comparing relative peak areas of a bypass cyclohexene injection to that of the reactor effluent. Cyclohexene was highly reactive; thus, the rate was determined at high conversion. The BTX formation rate was determined by multiplying the BTX selectivity times the conversion rate. Similarly, the cracking rates were determined by multiplying the C₂₋₅ non-aromatic hydrocarbons selectivity by the cyclohexene conversion rate.

3. Results

3.1 H-ZSM-5 Catalyzed Propene Aromatization Product Distribution

As shown in Figure 1, reaction products on H-ZSM-5 include light alkanes, (methane, ethane, propane, butane), olefins (ethene, butenes, pentenes and hexenes), and aromatics (benzene, toluene, and xylenes). At 723 K, the selectivity of CH₄ and C₂H₆ increases with increasing propene conversion (Figure 1A); however, the carbon selectivity of both remains low at all conversions (<2%). The propane selectivity increases from about 5% to 22% as the propene conversion increases from 30 to 85%. The selectivity of butane also increases, from 0.5% to 17%, at propene conversions from 4% to 85%.

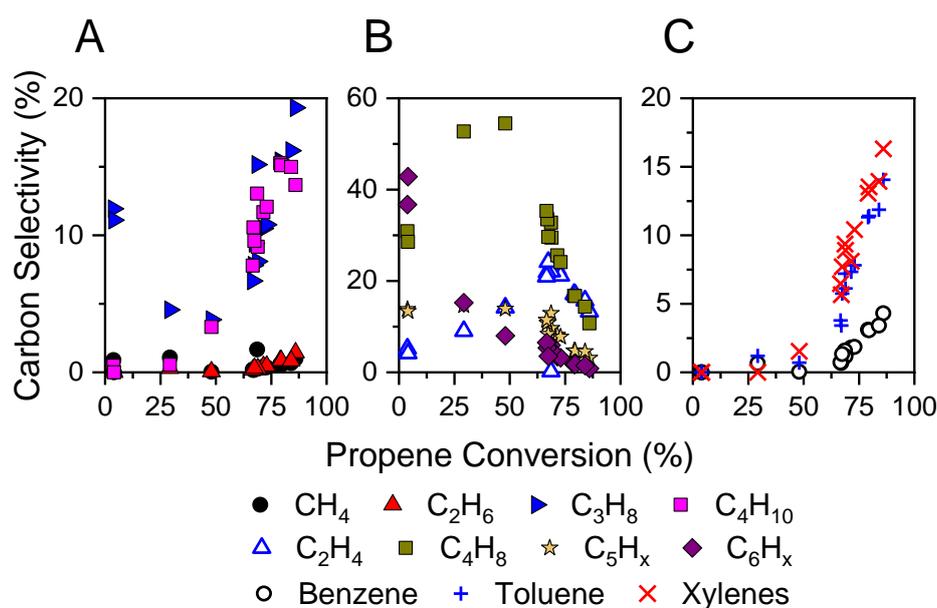


Figure 1 The carbon selectivity to A) light paraffins: CH₄, C₂H₆, C₃H₈, and C₄H₁₀; B) alkenes and heavy alkanes: C₂H₄, C₄H₈, C₅H₁₀, C₅H₁₂, C₆H₁₂, and C₆H₁₄; and C) aromatics: C₆H₆, C₇H₈, and C₈H₁₀ as a function of C₃H₆ conversion at 3 kPa C₃H₆ on H-ZSM-5 at 723 K.

The ethene selectivity initially increases from 4% to 27% between propene conversions of 4% to 75%, and then decreases to 13% at 86% conversion (Figure 1B). Similarly, initially the selectivity of butene increases from 30% to 55% at propene conversions of 4% to 48%, and then decreases to 10% at 86% propene conversion. The C₅ (C₅H₁₀, C₅H₁₂) selectivity decreases from 13% to 3% and C₆ (C₆H₁₂, C₆H₁₄) decreases from 43% to 0.8% with increasing propene conversions from 4% to 86%.

Selectivity towards aromatic products increases with propene conversion, from near 0% at 4% conversion to about 40% at 86% conversion (Figure 1C). Toluene selectivity increases from 0% to 20% and xylene selectivity increases from 0% to 16%. Benzene forms the least abundant aromatic product at 723 K; selectivity increases from 0% to 5% as propene conversion increases from 4% to 86%.

At 823 K, the methane selectivity increases from 0.2% at 1% conversion to about 10% at 97% conversion (Figure 2A), approximately three times higher than at 723 K. The ethane selectivity increases from 1% to 3% as the propene conversion increases from 1 to 97%. The propane selectivity is initially low at approximately 4% at about 20% propene conversion. With increasing conversion, the propane selectivity increases to about 8% at 75% conversion but is less than 2% as the propene conversion approaches 100%. The selectivity towards butane increases slowly from undetectable levels at 1% conversion to 4% at 70% propene conversion. At higher propene conversion, the butane selectivity decreases to <0.1% at 97% conversion. The propane and butane selectivities at high propene conversion at 823 K are much lower than those at 723 K.

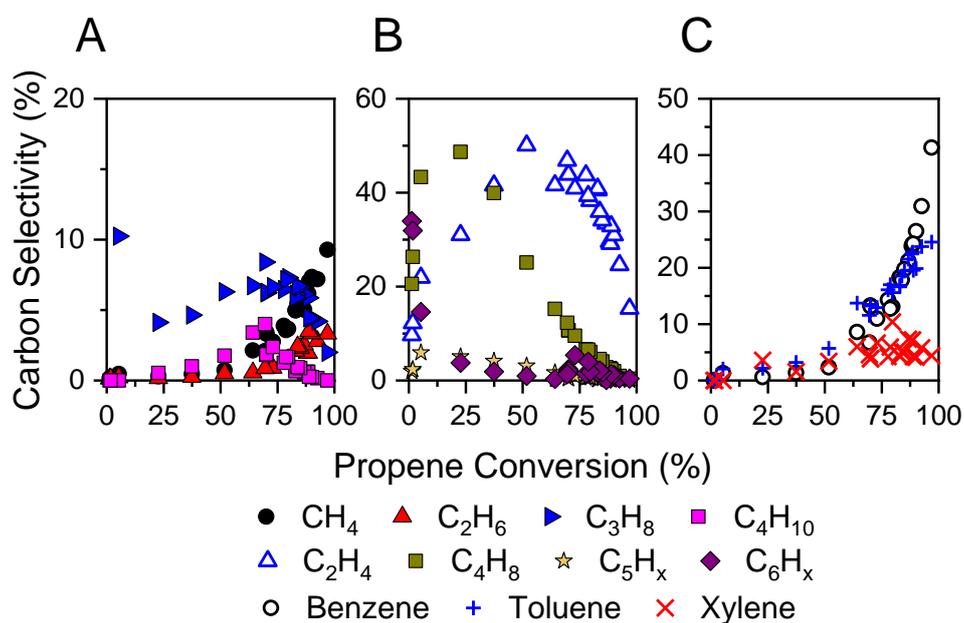


Figure 2 The carbon selectivity to A) light paraffins: CH₄, C₂H₆, C₃H₈, and C₄H₁₀; B) alkenes and heavy alkanes: C₂H₄, C₄H₈, C₅H₁₀, C₅H₁₂, C₅H₁₂, C₆H₁₂, and C₆H₁₄; and C) aromatics: C₆H₆, C₇H₈, and C₈H₁₀ as a function of C₃H₆ conversion at 3 kPa C₃H₆ on H-ZSM-5 at 823 K.

The ethene selectivity first increases from 10% at 1% conversion to a maximum of 50% at 52% conversion, and then decreases significantly to 15% as the propene conversion increases to >90% (Figure 2B). The selectivity of butene at 823 K increases rapidly from 20% to 48% at propene

conversions of 1% and 22%, respectively, followed by decreasing selectivity to 0.3% at 97% conversion (Figure 2B). The selectivity of C₅ and C₆ hydrocarbons decreases to <1% at propene conversions above about 5%.

The selectivity to BTX aromatics increases with increasing conversion, especially above about 50% propene conversion. Both experimental [28-30] and kinetic modelling studies [28] of propene oligomerization report similar results, where the aromatization selectivity increases at conversions above approximately 60%. At near complete propene conversion, the BTX selectivity is about 70% (Figure 2C). Also, at 823 K, benzene is the major aromatic product with low selectivity to xylenes; while at 723 K, the xylenes are the major aromatic product with low selectivity to benzene. The shift in product distribution to favor toluene and xylenes at lower temperatures and benzene at higher temperatures has been previously observed in literature at conditions similar to those in this study [29, 30].

Two general trends are observed among the various products formed during propene aromatization. At 723 K, for one set of products, i.e., ethene, butenes, pentanes/enes, and hexanes/enes, initially the selectivity increases with increasing conversion; while at higher conversion, these products undergo secondary reactions and the selectivity decreases to low levels as the propene conversion approaches 100%. The second set of products, i.e., methane, ethane, propane, butanes, benzene, toluene, and xylenes, increase with increasing conversion, although formation of these products generally occurs at propene conversions greater than about 50%. Methane and ethane selectivities increase with increasing conversion, although the selectivity is low. At 823 K, all products follow the same trends except for propane and butane, where the selectivity increases initially and then decreases to low levels at higher conversion. Additionally, at the higher reaction temperature, the methane selectivity significantly increases compared to that at lower temperature. At 823 K, monomolecular cracking rates become significant [37] leading to higher methane selectivity. These trends have previously been observed in several experimental studies and modelling studies of olefin aromatization [28-30, 33, 34, 38, 39].

3.2 Product Distribution on Bifunctional PtZn/SiO₂ + ZSM-5

The structure of the 2-3 nm Pt₁Zn₁ alloy nano-particles on SiO₂ has previously been determined by in situ X-ray diffraction (XRD) and X-ray absorption spectroscopies (XAS) [37]. In this body centered, Au₁Cu₁ structure type, intermetallic alloy [40], Pt has eight Zn neighbors at 2.63 Å, and Pt is present at a non-bonding distance of 2.90 Å. This structure is highly selective for ethane [2] and propane dehydrogenation [36, 37]. The catalytic performance of our catalyst was determined for propane dehydrogenation at 823 K. Similar to previous studies [37], the propene selectivity was about 97% for propane conversions from 30 to 70% consistent with the Pt₁Zn₁ intermetallic alloy. In addition, the previous studies have shown that the intermetallic alloy is more resistant to deactivation than monometallic Pt catalysts [2, 36, 37].

The same reaction products are formed for the bifunctional catalyst as ZSM-5 and include light alkanes: methane, ethane, propane and butane; olefins: ethene, butenes, pentenes, and hexenes; and aromatics: benzene, toluene, and xylenes. At 723 K, the selectivity of methane and ethane is low up to about 70% propene conversion but increases to 9% and 26%, respectively, at 96% conversion (Figure 3A). Similar to ethane, the selectivity to propane increases from 5% to 22% across

the conversion range. Unlike ethane and propane, the selectivity to butane first increases to about 7%, and then decreases to <1% at high propene conversion.

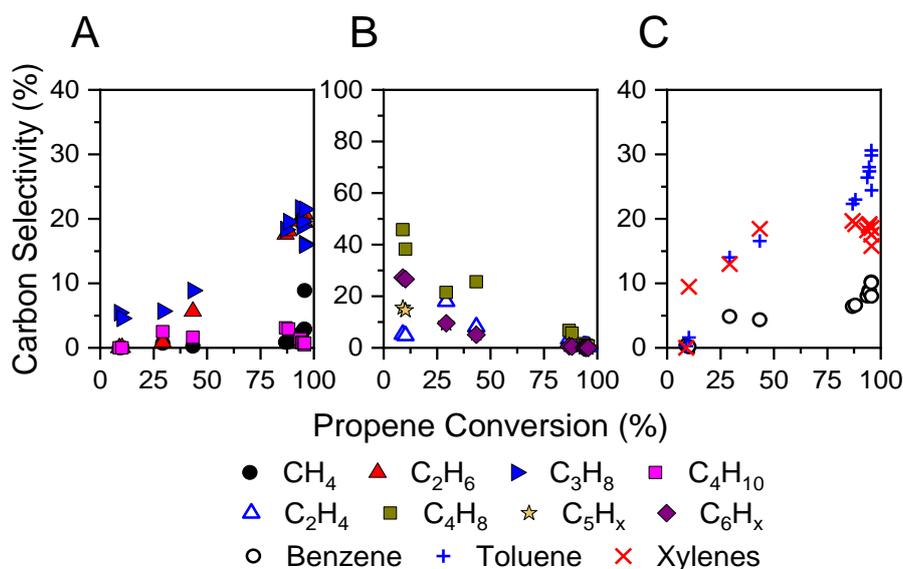


Figure 3 The selectivity of A) light paraffins: CH₄, C₂H₆, C₃H₈, and C₄H₁₀; B) alkenes heavy alkanes: C₂H₄, C₄H₈, C₅H₁₀, C₅H₁₂, C₆H₁₂, and C₆H₁₄; and C) aromatics: C₆H₆, C₇H₈, and C₈H₁₀ as a function of C₃H₆ conversion at 3 kPa C₃H₆ on bifunctional PtZn/SiO₂ + H-ZSM-5 at 723 K.

The ethene selectivity increases from 5% at 9% propene conversion to 22% at 70% conversion; while at higher conversion the selectivity decreases to <1% at 96% conversion (Figure 3B). Initially, the selectivities for C₄ olefins and C₅₊ hydrocarbons (C₄H₈, C₅H₁₀, C₅H₁₂, C₆H₁₂, C₆H₁₄) increase, go through a maximum, and then decrease at high propene conversion. The BTX aromatic selectivity increases with increasing conversion (Figure 3C). At 723 K, the selectivities of toluene and xylenes are higher than that of benzene. All three aromatics have selectivity <2% at conversions below 50%, and then the selectivity to benzene, toluene, and xylene increase to about 5%, 15%, and 15%, respectively.

At 823 K, the methane and ethane selectivities increase from <1% at low conversion to 10% and 12%, respectively at 99% propene conversion (Figure 4A). The propane selectivity, however, decreases from 16% to 1% as the conversion increases. Ethene selectivity increases rapidly to 15% at 3% propene conversion; however, it is lower, ca. 3%, at 99% propene conversion (Figure 4B). All other reactive hydrocarbons are minor products. For example, at 72% conversion, butanes and butenes comprise about 6% of products, while C₅ and C₆ hydrocarbons are less than 1%. At 823 K, the aromatics selectivity is higher than at 723 K, approximately, 80% (45% B, 30% T and 5% X) and 60% (10% B, 30% T and 20% X), respectively (Figure 4C).

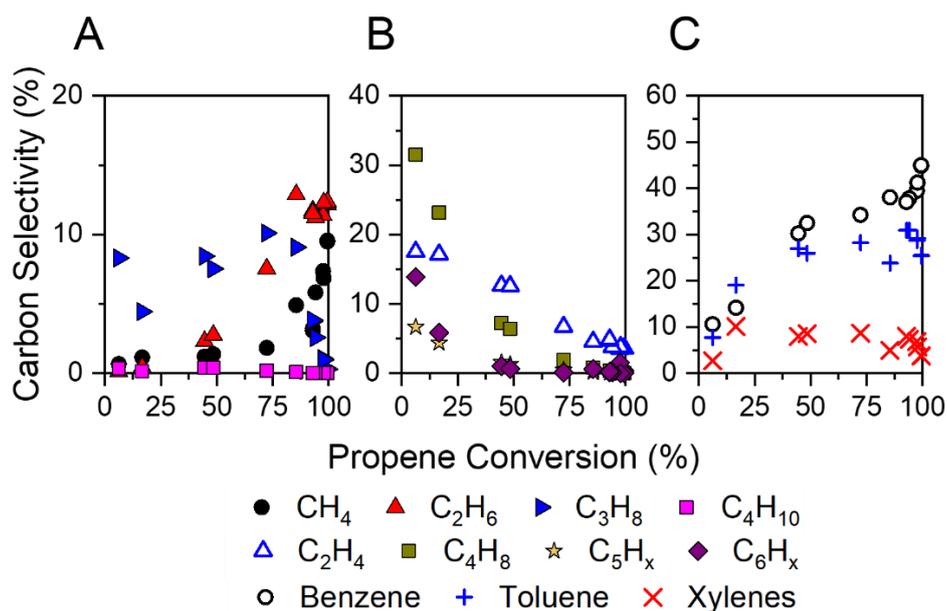


Figure 4 The selectivity of A) light paraffins: CH₄, C₂H₆, C₃H₈, and C₄H₁₀; B) alkenes heavy alkanes: C₂H₄, C₄H₈, C₅H₁₀, C₅H₁₂, C₅H₁₂, C₆H₁₂, and C₆H₁₄; and C) aromatics: C₆H₆, C₇H₈, and C₈H₁₀ as a function of C₃H₆ conversion at 3 kPa C₃H₆ on bifunctional PtZn/SiO₂ + H-ZSM-5 at 823 K.

Similar to ZSM-5, there are trends of the various products for propene aromatization with the bifunctional catalyst. At 723 K, for one set of products, i.e., ethene, butenes, butane, pentanes/enes, and hexanes/enes, the initial selectivity increases with increasing conversion; while at higher conversion, these products undergo secondary reactions and the selectivity decreases to low levels as the propene conversion approaches 100% (Figure 1B). The second set of products, i.e., methane, ethane, propane, benzene, toluene, and xylene, increase with increasing conversion, although high selectivities for these products, generally, occur at propene conversions greater than about 50% (Figure 1A and Figure 1C). While methane and ethane selectivities are low at 723 K with ZSM-5, these are significantly higher for the bifunctional catalyst. Another selectivity difference is that at 723 K for ZSM-5, the butane selectivity is high and is a final product, but is lower for the bifunctional catalyst and undergoes secondary reactions at higher propene conversion. At 823 K (Figure 2), on the bifunctional catalyst, the methane and ethane selectivities are low until about 70% conversion but increase to about 10% for each at 97% propene conversion. The lower ethane and propane selectivities lead to a higher BTX selectivity at the higher reaction temperature. While addition of PtZn to H-ZSM-5 has not been studied for propene aromatization, bifunctional catalysts with Ga and Zn-ZSM-5 have been extensively reported to lead to higher aromatic selectivities at equivalent propene conversion [12, 26, 28, 33, 34, 38, 39], similar to what was observed in this study.

3.3 Cyclohexene Conversion on PtZn + H-ZSM-5 and H-ZSM-5

To better understand how aromatics are formed on these catalysts, the rates and product selectivities of a model cyclohexene reaction to benzene and was determined on H-ZSM-5 and PtZn/SiO₂ catalysts. ZSM-5 is highly reactive to cyclohexene (Table 1); however, the reaction products are predominantly higher molecular weight oligomeric products, with lower selectivity to

C₂-C₄ cracked products (Figure 5). Even at 94% cyclohexene conversion at 723 K, ZSM-5 forms 90% oligomeric and cracked products with approximately 10% BTX aromatics. Surprisingly, the selectivity of xylene and toluene are much higher than benzene (i.e., 0.6% benzene, 3.3% toluene, and 6.2% xylene). The low benzene and high toluene and xylene selectivities for reaction of cyclohexene with ZSM-5 suggests that aromatics are formed through a complex series of cracking, oligomerization, cyclization, and dealkylation reactions giving methyl substituted aromatics [10, 20-28]. The rate of cyclohexene conversion on PtZn/SiO₂ (Table 1) is also high but forms primarily benzene by dehydrogenation with much lower amounts of oligomeric products. At 94% conversion, benzene is the only aromatic product with a selectivity of 92.3%. Multiplying the conversion rates by the selectivities gives an estimate of the rate of aromatic and cracking plus oligomerization reactions. For the PtZn intermetallic alloy, the rate of aromatic formation is ten times that of ZSM-5.

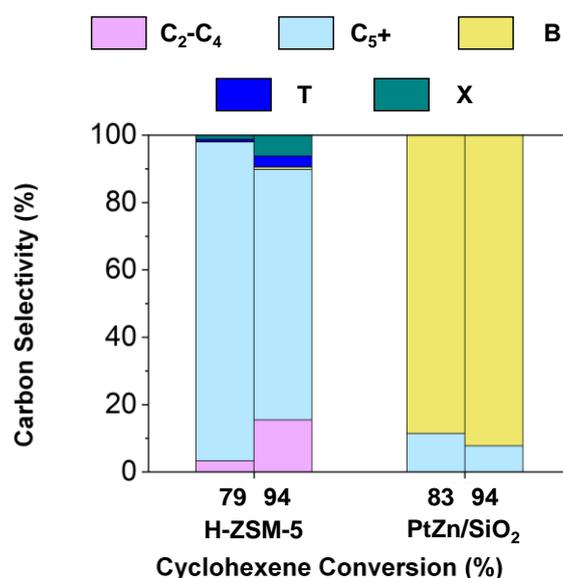


Figure 5 The product distribution of cyclohexene conversion on H-ZSM-5 and PtZn/SiO₂ at 723 K.

Table 1 Cyclohexene conversion, BTX formation, and cracking rates at 723 K.

Catalyst	Cyclohexene Conversion Rate	BTX Formation Rate	Cracking Rates
	$10^{-3} \text{ mol C}_6\text{H}_{10} (\text{g}_{\text{cat}} \text{ s})^{-1}$	$10^{-3} \text{ mol BTX} (\text{g}_{\text{cat}} \text{ s})^{-1}$	$10^{-3} \text{ mol C}_{2-5+} (\text{g}_{\text{cat}} \text{ s})^{-1}$
H-ZSM-5	4.2	0.43	3.8
PtZn/SiO ₂	4.2	3.9	0.33

4. Discussion

Previous studies on the conversion of olefins to aromatics concluded that bifunctional catalysts give higher BTX yields than H-ZSM-5 [28-31, 41]. However, these studies compared the BTX selectivity at constant reaction conditions [30]. For example, aromatic yields for propene conversion by ZSM-5 and bifunctional Ga oxide + ZSM-5 were determined at 773 K, 20 kPa propene, and W/F from 0.1-10 g h mol⁻¹. At an equivalent W/F of 10 g h mol⁻¹, the aromatic selectivity on ZSM-5 and

Ga-ZSM-5 were 31% and 80%, respectively. Similar large differences in aromatic yields were observed at other reaction conditions; for example, at 0.1 g h mol^{-1} , the BTX selectivity on the bifunctional catalyst is 12%; while under the same conditions ZSM-5 did not produce any aromatic products. In a similar study of propene aromatization comparing ZSM-5 and bifunctional Zn-ZSM-5, the BTX selectivity at 773 K and 5.3 g mol h^{-1} was 42% for the former but 68% for the latter [29]. Similar increased aromatic yields were obtained for 1-butene conversion at 773 K and 5.3 g h mol^{-1} . The BTX selectivity was 36% on ZSM-5 and increased to 71% on Zn-ZSM-5. Each of these studies concludes that addition of a dehydrogenation catalyst to ZSM-5 increases the yields of BTX aromatics.

In each of the previous studies the aromatics selectivity is compared at constant reaction conditions, for example, equivalent space velocity. Thus, in Figure 6 the data for the bifunctional PtZn + ZSM-5 catalyst was compared at equivalent space velocity. At both temperatures, the BTX selectivity is higher for the bifunctional catalyst at every space velocity consistent with previous studies on bifunctional Ga- and Zn-ZSM-5 catalysts. The BTX selectivity, however, is dependent on and decreases at higher space velocity. At higher space velocity the conversion is lower giving lower selectivity to aromatics. In addition, the BTX selectivity is higher at higher reaction temperature. At 723 K, the maximum BTX selectivity is about 60%; while at 823 K the BTX selectivity increases to about 80%.

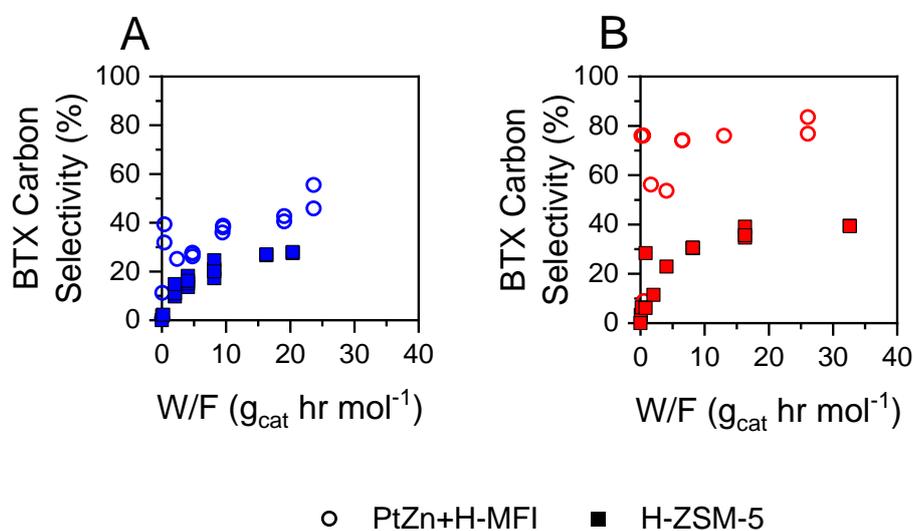


Figure 6 The carbon selectivity of benzene, toluene, and xylene (BTX) as a function of W/F on H-ZSM-5 and PtZn + H-ZSM-5 at 3 kPa C_3H_6 , A) 723 K (blue) and B) 823 K (red).

Since secondary reactions alter the selectivity as the conversion increases and aromatics are formed through a complex series of multiple reaction steps, to determine differences in selectivity between catalysts, one should compare at constant conversion. Figure 7 shows the BTX selectivities for propene conversion with ZSM-5 and bifunctional PtZn + ZSM-5 at 723 and 823 K. At both reaction temperatures, for ZSM-5 little BTX is formed until the propene conversion is greater than about 50%; while for the bifunctional catalyst, aromatics form at propene conversions of less than 10%. At propene conversion below about 90%, the BTX selectivity is always higher for the bifunctional catalyst. However, as the propene conversion approaches 100%, the BTX selectivities are very similar. Comparison of the aromatic selectivity at incomplete propene conversion would lead to the

conclusion that bifunctional catalysts produce more aromatic products; while at high propene conversion, one would conclude that both catalysts give similar selectivity. Thus, the conclusion about the improved aromatics yield of bifunctional catalysts is conversion dependent.

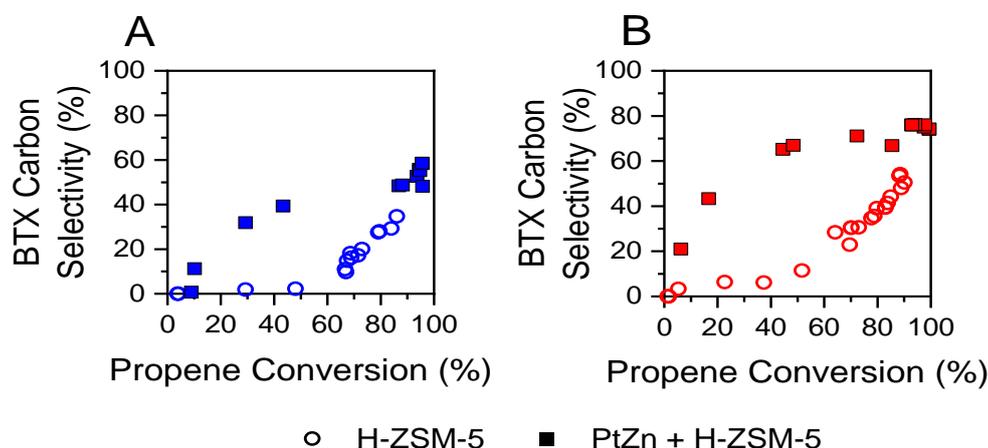


Figure 7 The carbon selectivity of benzene, toluene, and xylene (BTX) as a function of propene conversion on H-ZSM-5 and PtZn + H-ZSM-5 at 3 kPa C_3H_6 , A) 723 K (blue) and B) 823 K (red).

Results in Figure 1 and Figure 2 indicate that there are two types of products for propene conversion, those that continually increase with increasing conversion and those where the selectivity initially increases, but at higher conversion decreases. The latter are olefins and reactive alkanes that undergo secondary reactions. For example, in Figure 1C, for ZSM-5 at 723 K, the butene selectivity increases to a maximum (approximately 50%) at near 50% propene conversion and then decreases to near 0% selectivity at 100% propene conversion. With the extensive oligomerization and cracking that occurs on ZSM-5, all olefins give similar aromatic products [10, 17-28]. As a result, if one considers all intermediates that undergo secondary reactions to be reactants along with propene, a new conversion scale is defined.

The conversion is determined from the sum of all reactive species. As observed in Figure 1 and Figure 2, the reactive species at 723 K are ethene, butenes, C_5 , and C_6 hydrocarbons (Figure 1B). At 823 K, in addition to ethene, butenes, C_5 , and C_6 reactive intermediates, propane and butane are now reactive intermediates (see Figure 2B at high conversion). At the higher reaction temperature, the rate of monomolecular cracking of propane and butane increases giving methane, ethene and propene. This leads to higher aromatic yields, but also increases the selectivity to methane, see Figure 4A.

For bifunctional PtZn + ZSM-5, at 723 K, the reactive species are ethene, butenes, C_5 , and C_6 hydrocarbons, equivalent to H-ZSM-5 (Figure 3B). However, unlike ZSM-5 at this temperature for the bifunctional catalyst, butane is also a reactive intermediate due to alkane dehydrogenation, i.e., giving butene + H_2 (Figure 3A) [36, 37, 42]. At 823 K, the reactive species for PtZn + ZSM-5 are the same as those for H-ZSM-5: ethene, propane, butane, butenes, C_5 , and C_6 hydrocarbons (Figure 4A and Figure 4B), although the reaction of propane occurs by dehydrogenation on the PtZn alloy, giving propene + H_2 , rather than by monomolecular cracking, giving methane + ethene, for ZSM-5.

Replotting the BTX selectivity as a function of conversion of reactive intermediates is shown in Figure 8. While there is some scatter at high and low conversion, using this definition produces a plot where the aromatic selectivity is nearly constant over a wide conversion range. Furthermore, the selectivity of ZSM-5 and the bifunctional catalyst are very similar. For both catalysts, at 823 K, the aromatic selectivity is significantly higher than that at 723 K.

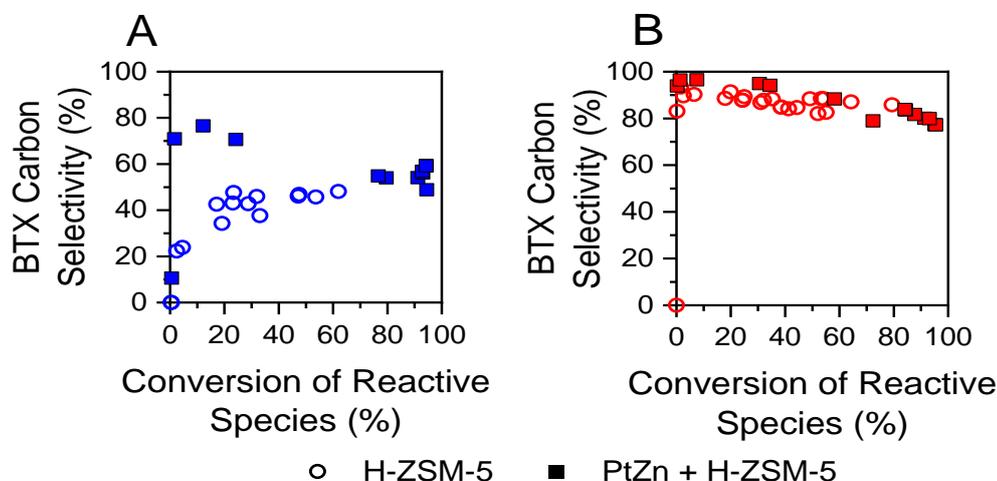


Figure 8 The carbon selectivity of benzene, toluene, and xylene (BTX) as a function of conversion of reactive intermediates on H-ZSM-5 and PtZn + H-ZSM-5 at 3 kPa C_3H_6 , A) 723 K (blue) and B) 823 K (red).

In addition to the similar total aromatic selectivity for both catalysts (Figure 8), the selectivities of the individual aromatics are also very similar (Figure 9). This analysis shows that at 723 K, the benzene and toluene selectivities are near zero at low conversion; however, the selectivity of both increase as the conversion increases. By contrast, the xylenes selectivity is high at low conversion, but decreases with increasing conversion. The results suggest that on ZSM-5 xylene is the primary aromatic that is formed, consistent with Figure 5 where xylenes are the dominant aromatics formed even when feeding cyclohexene as a reactant. Benzene and toluene appear to be formed by secondary reactions at higher conversion, resulting in their lower selectivity at lower conversion. Similarly, at 823 K, both toluene and xylene are formed at low conversion; while benzene appears to form at higher conversion.

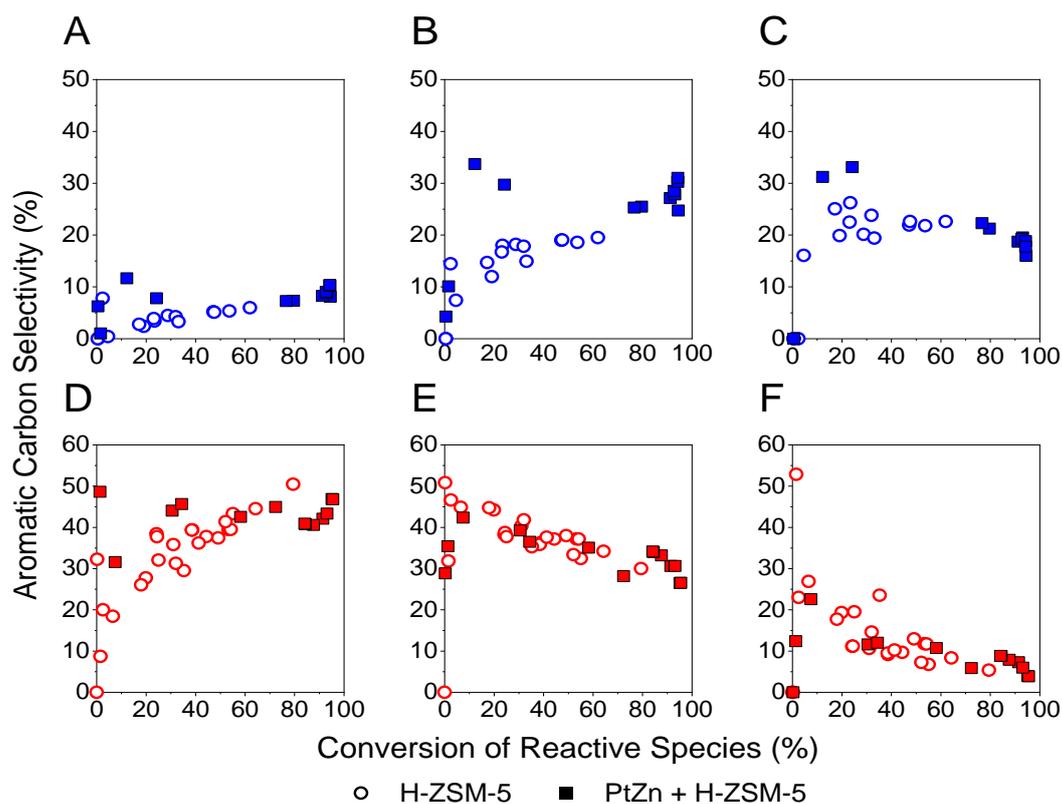


Figure 9 The carbon selectivity of benzene (A, D), toluene (B, E), and xylenes (C, F) at 723 K (blue: A, B, C) and 823 K (red: D, E, F) as a function of conversion of reactive intermediates.

In addition to BTX, the other final products consist of methane, ethane, propane (and butane for ZSM-5) at 723 K and methane and ethane at 823 K. At 723 K, the methane selectivities are low and similar for both ZSM-5 and the bifunctional catalyst (Figure 10A). At 823 K, however, there are differences depending on the catalyst (Figure 10B). For example, the methane selectivity at 823 K is higher on ZSM-5 likely due to monomolecular cracking of propane and butane [37]. Monomolecular cracking of both propane and butane produces methane and ethene (from propane) and propene (from butane). Conversion of these olefins also gives higher aromatic yields. For ZSM-5, the higher aromatic yields are accompanied by higher methane yields. For the bifunctional catalyst, at 823 K, propane and butane can form olefins (and hydrogen) by dehydrogenation. Because of the high alkane dehydrogenation rates and selectivity, little methane is formed. These olefins also give higher aromatic yields; however, the co-produced H_2 leads to ethene hydrogenation, i.e., higher ethane selectivity, Figure 11.

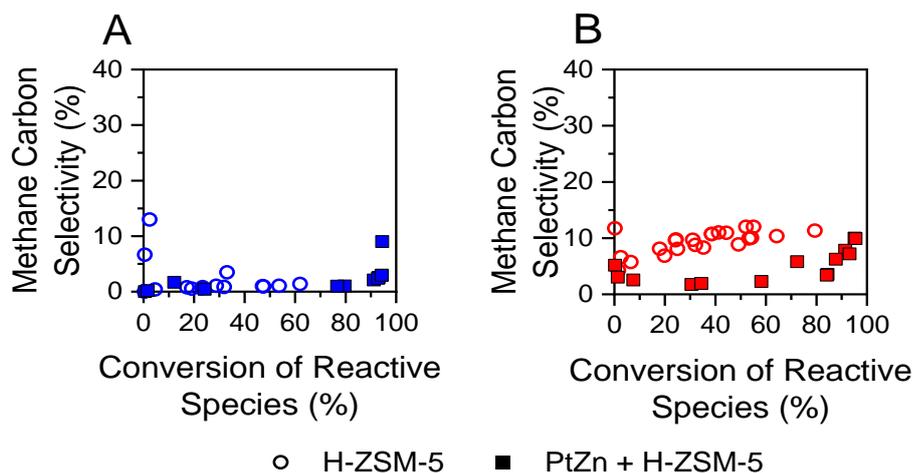


Figure 10 Methane carbon selectivity on H-ZSM-5 and PtZn + H-ZSM-5 as a function of conversion of reactive intermediates at A) 723 K (blue) and B) 823 K (red).

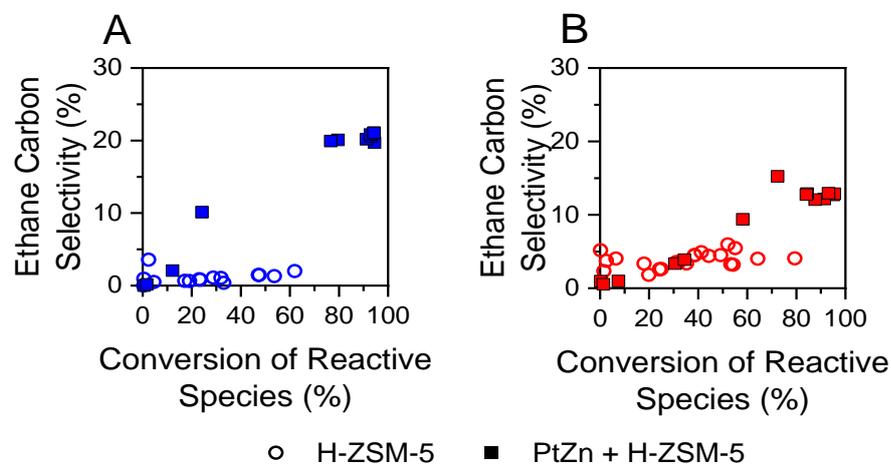


Figure 11 Ethane carbon selectivity on H-ZSM-5 and PtZn + H-ZSM-5 as a function of conversion of reactive intermediates at A) 723 K (blue) and B) 823 K (red).

At 723 K, propane is a non-reactive product on both ZSM-5 and PtZn + ZSM-5. For ZSM-5, the propane selectivity is higher than that of the bifunctional catalyst (Figure 12) since it is a co-product of aromatic formation [29] and the reaction temperature is too low to convert propane to ethene and methane by monomolecular cracking. For the PtZn catalyst, the dehydrogenation rate is also too low resulting in little conversion of propane to propene again leading to propane as a final product.

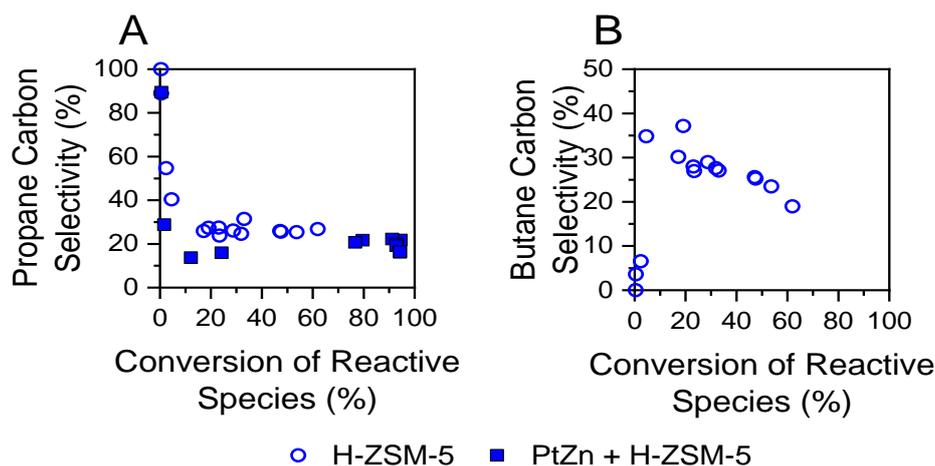


Figure 12 Carbon selectivity of A) propane and B) butane at 723 K on H-ZSM-5 and PtZn/H-ZSM-5 as a function of conversion of reactive intermediates.

These analyses indicate that for ZSM-5 there is a lower selectivity to ethane (Figure 11), especially at 723 K, but a higher selectivity to propane (Figure 12); while for the bifunctional catalyst there is a higher selectivity to ethane (Figure 11), but lower selectivity to propane. Additionally, butane is reactive on the bifunctional catalyst at 723 K, whereas it is unreactive on H-ZSM-5. Although the two catalysts differ in how the pathways form aromatic and non-reactive alkanes, the selectivity to total aromatic products are very similar at each reaction temperature (Figure 8 and Figure 9). When compared at constant conversion of all reactive intermediates, bifunctional catalysts do not give much higher yields of aromatics than ZSM-5 alone, although there are some differences in selectivity of the non-aromatic by-products, especially, methane and ethane, Figure 10 and Figure 11.

5. Conclusion

This study highlights the differences between olefin conversion to BTX by ZSM-5 and bifunctional PtZn + ZSM-5 catalysts. As the reaction proceeds, there are two types of products for propene conversion, i.e., those that continually increase with increasing conversion and those where the selectivity initially increases, but decreases at higher conversion. The former are BTX and non-reactive alkanes; while the latter are olefins and reactive alkanes that undergo secondary reactions. Furthermore, the specific non-reactive alkanes differ depending on the reaction temperature. For example, propane is non-reactive at 723 K for both ZSM-5 and the bifunctional catalyst, but at 823 K is reactive on both catalysts leading to significantly higher aromatic yields at higher temperature. Conversion of all reactive intermediates at both 723 and 823 K gives very similar BTX yields for both catalysts; although because of the difference in reaction pathways for activating propane and butane, the yield of non-reactive alkanes is slightly different. On ZSM-5 propane and butane form reactive intermediates by monomolecular cracking, which also produces methane; while for the bifunctional PtZn + ZSM-5 catalyst, propane and butane dehydrogenation lead to reactive olefins along with H₂. For the latter, the higher hydrogenation rates of the PtZn alloy also results in higher yields of ethane, which is unreactive at these temperatures.

Author Contributions

C. K. R.: conceptualization, methodology, investigation, writing – original draft, writing – review & editing, visualization. A. S.: methodology, investigation, writing – original draft, writing – review & editing, visualization. J. T. M.: conceptualization, methodology, writing – review & editing, visualization, project administration, funding acquisition.

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Competing Interests

The authors have no competing interests.

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