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Highly selective aromatization and isomerization of *n*-alkanes from bimetallic Pt–Zn nanoparticles supported on a uniform aluminosilicate[†]

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A bimetallic-support interaction through Pt-Zn nanoparticles and uniform compact cylindrical ZSM-5 particles shows selectivity over 90% towards BTX and i-octane at controlled 60% conversion with negligible coke formation when reforming *n*-octane. This is a significant improvement compared to alternative Pt-Zn on conventional ZSM-5, with a selectivity of less than 40%.

Petroleum refinery naphtha obtained from distilled crude oil, coal liquefaction, and the Fischer-Tropsch process is catalytically reformed to improve the anti-knocking index of fuel reformates by increasing the content of BTX and i-alkanes. BTX are also highly valued by the chemical production industry because of their role in the large-scale synthesis of polymers, with xylene isomers being significant.¹ ZSM-5 has found widespread involvement as a fluid catalytic cracking additive for the octane number improvement of high n-alkane content feeds.^{2,3} An array of synthesis techniques for this support have been investigated to selectively load with various metals,⁴ construct hierarchical porous systems,⁵ and introduce structure variants.⁶ Hydrothermally synthesized ZSM-5 using organic templates has shown success in controlling the size of crystals and altering morphologies.⁷ Modern day catalysis aims for a selectivity of 100% so economic and environmental targets are realized by reduction of undesirable side reactions,⁸ a common issue with conventional ZSM-5.9 Until now, the use of ZSM-5 and other catalyst supports with/without metal loading has shown a selectivity well below 100% towards i-alkanes and aromatics from n-alkane conversion. For example, Zhao et al. reported a performance of 54.5% selectivity towards BTX, 43% selectivity towards

cracked products (<C₈), and 1.4% carbon deposition on a Pt/BaKL catalyst.¹⁰ Performances like this have been attributed to cracking over acid sites, enhanced dehydrogenation over metal sites, and continuous oligomerization of subsequent alkene intermediates, followed by cyclization and hydrogen transfer over acidic sites on the support to form higher aromatics (>C₈) and polycyclic aromatic hydrocarbons which are the major contributors to carbon deposition.¹¹

Metal addition, nominally through Zn addition, increases selectivity towards aromatics because of the increased formation of alkene intermediates, a result of their dehydrogenation capabilities.^{12,13} Although direct aromatization of alkene intermediates is promoted by Zn, alkane conversions to their isomers and aromatics are still low.¹⁴

Bimetallic interactions have enhanced the performance of catalytic systems in recent years, a result of electronic and chemical property changes that are distinctly different from those of their single parent metals.^{15,16} Ligand and strain effects have shown contributions to these changes by the formation of heteroatom bonds and metal-metal bond length variations, respectively.¹⁷ These reactive metal support interactions prove to be invaluable for enhancing the performance of catalysts used in the petrochemical industry.¹⁸ Examples of successful bimetallic systems for alkane aromatization are Pt–Zn for naphtha¹⁹ and light straight run naphtha feeds,²⁰ and Ga–Zn for hexane and heptane aromatization.²¹

Herein we have reported intermetallic nanoparticles of Pt–Zn supported on a uniform aluminosilicate catalyst (U-ZSM-5) synthesized in the absence of a reducing atmosphere. Reactions were then conducted under methane in a closed batch system. This unique material exhibits unrivalled direct aromatization and isomerization of n-alkanes that, to our knowledge, has not been seen before.

Without metal loading, U-ZSM-5 is relatively inactive for the conversion of *n*-octane (12.9%). Conversely, C-ZSM-5 easily achieves a desired conversion (65%) but accompanied by low selectivity towards BTX and i-octane (22.3%). Pt–Zn/C-ZSM-5 shows slight improvement in selectivity towards BTX and

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Fig. 1 Effect of support and Pt–Zn loading on the aromatization and isomerization performance of *n*-octane conversion. Conversions of ~60% were achieved by altering the catalyst:*n*-octane ratios. UZMS-5 was too inactive to achieve 60% conversion. Reactions were conducted at 400 °C, 3 MPa CH₄, and 1 atm N₂ for 1 h.

i-octane (30.6% and 37.8%, respectively), a result of Zn and Pt promoting dehydrogenation reactions. Most interestingly, however, is the performance of U-ZSM-5 upon loading Pt-Zn (Fig. 1). Desired conversion is achievable (62%) and the selectivity towards BTX and i-octane increases from 16.4% to 91.1%. The product distribution of this catalyst (ESI,† Table S1) suggests that very little cracking occurs, with direct aromatization (77.2% xylene selectivity) and isomerization (4.7% i-octane selectivity) of *n*-octane occurring almost inclusively. Pt-Zn/C-ZSM-5, on the other hand, shows a much broader product distribution with major product components of benzene, toluene, xylenes, higher-end aromatics, and more than 50% selectivity towards gas species. It is not uncommon for over-aromatization to occur with C-ZSM-5 because of cracking, followed by subsequent oligomerization and aromatization to form aromatics with higher carbon numbers (undesirable products in the petrochemical industry).^{22,23}

Interestingly, alkenes are not observed when Pt and Pt–Zn are loaded on U-ZSM-5 compared with significant ethylene production observed over C-ZSM-5 (ESI,† Fig. S1). Indeed, light alkene production may indicate that cracking occurs readily over C-ZSM-5, hindering total selectivity towards BTX and i-octane. For Pt–Zn/UZSM-5, the absence of alkenes in the observed gas products suggests that the catalyst is extremely efficient for oligomerization or that very little cracking occurs. However, the presence of benzene and toluene in the liquid product supports both hypotheses. The high selectivity exhibited by Pt–Zn/U-ZSM-5 towards gaseous hydrogen complements the exceptional xylene selectivity observed in the liquid products.

To further investigate the observed synergy between Pt–Zn and U-ZSM-5 support, reactions were conducted on U-ZSM-5 with metal loadings of Zn, Pt, Pt-Sn,²⁴ and Ga–Zn²⁵ (Fig. 2) to show the unique Pt–Zn synergy observed compared to others that have shown synergy with Pt and Zn in the past. The performance of



Fig. 2 Effect of metal loading on U-ZSM-5 for the aromatization and isomerization of n-octane at 60% conversion.

Pt/U-ZSM-5 is initially compelling with improved activity over the UZSM-5 support. However, this is met with similar attributes to C-ZSM-5 where BTX and i-octane selectivity is comparatively low (42.1% and 1.4% respectively), indicating formation of undesirable products.

Because of the poor performance of Pt and Zn/U-ZSM-5 as well as Zn-Ga and Pt-Sn/U-ZSM-5, we therefore conclude that a synergistic effect between Zn and Pt occurs when supported upon U-ZSM-5 as evidenced from our experimental data. The performance of Pt-Zn/U-ZSM-5 was tested at lower temperatures and at 60% conversion to analyze the catalyst's activity as a function of temperature. Whilst total selectivity remains similar, product distribution is varied with a trend towards the preferred i-octane formation at lower temperatures (ESI,† Fig. S2). These data demonstrate that the catalyst selectivity remains the same regardless of temperature, an indication of catalytic performance over thermal effects. The relatively insignificant change in total selectivity suggests that the only inhibiting factor here was the temperature requirement for the formation of aromatics.²⁵ Although selectivity towards xylenes is reduced at lower temperatures, the catalyst produces only i-alkanes and aromatics, avoiding the production of unwanted by-products. The performance of this catalyst shows a notable preference to form same-carbon number aromatic and i-alkanes for *n*-octane conversion (xylenes and i-octanes).

XRD patterns of U-ZSM-5 and C-ZSM-5 (ESI,† Fig. S3) confirm the ZSM-5 crystal structure and MFI type frameworks of the catalysts. HRTEM images of U-ZSM-5 (ESI,† Fig. S4) and C-ZSM-5 (ESI,† Fig. S5) show uniform plate-like crystals and disordered, larger crystals, respectively. The support's bulk sizes are decisively decreased (>2.5× decrease) for U-ZSM-5 due to controlled synthesis accompanied by the same trend for particle size variations for the loaded metals, despite identical wetness impregnation procedures for the two supports. It has previously been shown that uniform support particle sizes can enhance the conversion and selectivity of different reactions because of reduced diffusion limitations.²⁶

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Fig. 3 SEM image of U-ZSM-5 support demonstrating the uniform particle sizes and a compact cylindrical morphology.

SEM imaging allows a 3-D inspection of the support particles (Fig. 3) and shows that U-ZSM-5 particles are highly uniform in size with unique, compact cylindrical forms.

The XPS spectra of the Pt 4f7/2 and Al 2p regions (ESI,† Fig. S6) show PtO and Pt metal species in all cases, typical of Pt loaded ZSM-5 materials.²⁷ There is a clear negative shift of Pt $4f_{7/2}$ peaks for U-ZSM-5 compared to Pt–Zn/CZSM-5 (72.2 eV and 71.4 eV) as the Pt²⁺ peak of Pt-Zn/C-ZSM-5 (72.2 eV) is convoluted with that of Al 2p. This is emphasized by the reduced broadening of the U-ZSM-5 Al 2p peaks compared to C-ZSM-5, complementing the Zn 2p spectra (ESI,† Fig. S7) where a stronger metal support interaction is the probable cause of such a shift for C-ZSM-5. Spent Pt-Zn/UZSM-5 catalyst shows an increase in metallic Pt species (Pt⁰) after the reaction (compared to Pt-Zn/ UZSM-5) demonstrating a slight reduction in Pt species during the reaction. This may be due to the mildly reducing atmosphere present during the reaction or separation of Pt nanoparticles from Zn species which has been observed for Pt alloys in the past.²⁸ The broadening of the Al 2p peak of Pt-Zn/C-ZSM-5 is attributed to the increased presence of Pt $4f_{5/2}$ contributions in that region.²⁹ Information on the Zn 2p_{3/2} region is accompanied by the XANES spectra (ESI,† Fig. S8).

Catalyst characterization has shown that a combination of increased external surface area (ESI,† Table S2), efficient diffusion, and presence of Pt–Zn intermetallic species could be responsible for the high selectivity displayed by Pt–Zn/U-ZSM-5 towards *n*-octane aromatization.

Analysis of the liquid and gas product distributions for Pt–Zn/U-ZSM-5 and Pt–Zn/C-ZSM-5 allows elucidation of potential reaction pathways. The pathway for Pt–Zn/U-ZSM-5 is assumed to proceed predominantly through isomerization, cyclization, and aromatization. This is supported by the product selectivity (ESI,† Table S1) which shows 83.6% selectivity towards products produced *via* isomerization, cyclization, and aromatization directly from *n*-octane. ESI,† Fig. S1 further supports this, showing a high molar concentration of hydrogen in the gas products, assumed to result from dehydrogenation of cycloalkanes, yielding aromatics. However, the presence of benzene and toluene in the product oil suggests two potential mechanisms. Dealkylation of xylenes could be occurring to form benzene and toluene but these species could also come from oligomerization of any alkanes and alkenes produced upon cracking. To provide more insight



Fig. 4 Effect of *n*-alkane chain length on Pt–Zn/U-ZSM-5 for the aromatization and isomerization reactions. [a] i-Alkanes of same chain length as their respective feedstocks.

it is prudent to assess the effect of lighter hydrocarbons over Pt-Zn/U-ZSM-5 (Fig. 4).

Upon reaction with n-heptane, a preference to toluene formation is observed, a similar trend with the n-octane reaction where xylene is the preferred product. n-Hexane allows the same observation although the selectivity towards benzene is less pronounced and with the formation of more i-hexanes. *n*-Pentane confirms that the catalyst performs cracking of the feedstocks as the product distribution is more varied with the production of benzene, xylene and i-pentane being the major products with reasonable amounts of gas. Thus, we confirm that production of benzene and toluene likely comes from cracked products as opposed to dealkylation of xylene. The importance of *n*-alkane carbon chain length is also shown, with C_6 - C_8 hydrocarbon feedstocks being preferable for the formation BTX. This is because direct aromatization can occur. For lower carbon chain *n*-alkanes, direct aromatization is not possible, and a broader product distribution is seen.

The suggested reaction pathway for both catalysts (Fig. 5) is shown above with Pt–Zn/U-ZSM-5 reactions following predominantly cyclization and subsequent dehydrogenation as well as isomerization. Pt–Zn/C-ZSM-5 produces polyaromatic hydrocarbons and a large amount of gas product, with no i-alkane formation.

Carbon deposition (coking) is the predominant deactivation mechanism of ZSM-5-based catalysts and causes issues with stability and reduced reaction performance.¹¹ TGA data (Fig. 6) shows that no coking occurs over the Pt–Zn/U-ZSM-5 catalyst, in contrast to Pt–Zn/C-ZSM-5 which produces 0.05 g coke per g cat. per h. These data evidence the incredible resistance to coking observed over the U-ZSM-5 support. As coke precursors are dominated by polycyclic aromatic hydrocarbons (PAHs) it's understandable that coke formation is witnessed when conventional ZSM-5 is employed as this catalyst is well known for over-aromatization and formation of coke.⁹ This evidence demonstrates the importance of avoiding cracking, oligomerization,



Fig. 5 Reaction pathways for U-ZSM-5 (blue) and C-ZSM-5 (red) supports when loaded with Pt–Zn during *n*-octane conversion.



Fig. 6 TGA profiles of Pt–Zn/U-ZSM-5 and Pt–Zn/C-ZSM-5 catalysts after reaction.

and the subsequent formation of polycyclic aromatic species during the aromatization of *n*-alkanes. Further deactivation studies are demonstrated in Fig. S9 (ESI \dagger).

In summary, a highly selective catalyst has been identified with a unique ability to convert *n*-alkanes to their respective i-alkanes and aromatic forms of the same carbon number. This performance has been attributed to two main factors: the uniform compact cylindrical aluminosilicate support (U-ZSM-5) and the bimetallic Pt–Zn. U-ZSM-5 shows uniform bulk particle sizes with less variance in available size ranges and increased external surface area. The bimetallic Pt–Zn nanoparticles promote positive electronic changes and exemplify different properties on the supports (C-ZSM-5 and U-ZSM-5). Importantly, no coking is observed when Pt–Zn/U-ZSM-5 is employed. Through controlled synthesis techniques, the realization of highly selective

catalysts for the direct aromatization and isomerization of undesirable *n*-alkanes has been achieved.

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Conflicts of interest

There are no conflicts to declare.

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