Synergistic Effect of Zn with Ni on ZSM-5 as Propane Aromatization Catalyst: Effect of Temperature and Feed flowrate

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Abstract

This work shows how propane was catalytically converted to aromatic compounds over Zn-Ni/HZSM-5 to investigate the synergistic role of nickel as zinc stabilizer and promoter in propane aromatization. Co-impregnation method was employed for Zn-Ni/ZSM-5 synthesis fixed 2 wt. % of zinc and 1, 2 and 3 wt. % of nickel. Modified catalysts were fully characterized. Catalysts crystallinity, structure and microporosity were retained from analysis results. Propane aromatization process was conducted at 540 °C, 1200 ml/g-h gas hourly space velocity and atmospheric pressure. The presence of Ni with Zn improved catalytic performance for all Ni loading. Aromatic selectivity and propane conversion were improved with best performance to be Zn-Ni/ZSM-5 with 2 wt. % Zn, 2 wt. % Ni on ZSM-5 averaging 88 and 60 % for twelve hours’ time on stream. Aromatic selectivity on Zn-Ni/ZSM-5 is eight times better than the parent HZSM-5 and one and half times better than the Zn/ZSM-5 catalyst. The electronic interaction of zinc and nickel resulting from equality of oxidation state of +1 and +2 and metal binding energy change synergistically improved the catalytic performance of the bimetallic Zn-Ni/ZSM-5 over the HZSM-5 and Zn/ZSM-5. Flowrate increase from 6 to 35 ml min⁻¹ was found to decrease propane conversion from 80-40 % with increased aromatic selectivity from 55-80 %. Temperature increase from 500-580 °C favours both propane conversion and aromatic selectivity increase from 50-68 and 55-92 % respectively. The metallic interactions from H₂-TPR and XPS analysis revealed strong improvement on propane conversion, aromatic selectivity and product distribution.

1 Introduction

Transformation of natural gas, liquefied petroleum gases and other lower alkanes to aromatic compounds (BTEX) are receiving uncommon attention in research [1–3]. Currently, steam cracking, fluid catalytic cracking (FCC) and naphtha reforming are industrial processes for production of aromatic compounds as feedstocks for petrochemicals though not sufficient. [4–5]. Hence, light alkanes aromatization over zeolitic based catalysts is gaining grounds for the production of aromatic compounds. Aromatization being an energy intensive (endothermic) process requires high reaction temperature to achieve meaningful alkane conversion. The first stage in propane aromatization is protolytic cracking and protolytic dehydrogenation to alkenes which further undergo oligomerization-cracking reactions leading to higher hydrocarbon C₄–C₁₀ alkenes. The formed higher alkenes transfer hydrogen to other alkenes to form corresponding dienes and alkanes respectively. The dienes undergo cyclization (intramolecular oligomerization) to form cyclo-alkenes which are further transformed into cyclic dienes and which with through further hydrogen transfer yields aromatics [6–10].

Unique pore size and acidic properties of HZSM-5 makes it suitable for propane aromatization. Nevertheless, the process always records low aromatic yield and selectivity because of catalyst deactivation and enhanced cracking reaction leading to formation of lower alkanes, predominantly methane and ethane [11].
Many transition metals had been investigated for their catalytic properties and incorporated on HZSM-5 to improve aromatic yield. Molybdenum was reported to be highly effective for methane and methanol feedstock either as single metal or bimetallic with other metals [12–15]. Platinum is costly, deactivate easily and causes hydrogenolysis which is breaking down of propane and higher oligomers formed over platinum sites in the presence of hydrogen [16–17]. Gallium though highly dehydrogenating, it is very expensive and not safe at handling due to its poisonous nature [7, 18], zinc is highly dehydrogenating and readily available economically but unstable at operating temperature for aromatization [3, 7, 8, 19–24]. Report showed that hierarchical Zn/ZSM-5 improve zinc metal stability and hence aromatic selectivity [7, 18, 25]. Isomorphous substitution of metal in zeolite framework has also been reported to enhance catalytic performance [26]. Bimetallic impregnation of active metal with another as support have also been reported for alkane aromatization, among which are Zn-Fe/ZSM-5 [27], Zn-Cu/ZSM-5 [28], Zn-Co/ZSM-5 and Zn-Ni/ZSM-5 [29], dehydrogenation of propane over Pt-Zn/ZSM-5 [30], methanol transformation over La-Zn/HZSM-5 [31], ethane dehydroaromatization over Ga–Pt/HZSM-5 [32], methane dehydroaromatization over Zn-Mo/ZSM-5 and Fe-Mo/ZSM-5 [33], ethane aromatization over Pt and Pd reinforced Zn- and Mn-ZSM-5 [34] all of which had aided stability and catalytic performance.

This work focuses on co-impregnation of nickel metal with nearly same properties with zinc on HZSM-5 to enhance zinc stability, catalytic activity and overall aromatic selectivity. Comparative performance tests on propane aromatization, selectivity towards aromatics, effect of temperature and feed flow rate change on conversion, aromatic selectivity and products distribution were also studied.

2 Experimental Section

2.1 Catalyst preparation

HZSM-5 (Zeolyst International Si/Al = 50) was obtained from the calcination of ammonium-ZSM-5 at 550 °C (4 °C min⁻¹) for five hours. Mono and bimetallic catalysts of 2 wt. % of ZnO from Zn(NO₃)₂ 99.99% purity Sigma Aldrich analytical grade and 1 to 3 wt. % NiO (Ni(NO₃)₂) were synthesized using the procedures employed previously [27–28].

2.2 Catalyst Characterization

Regular FTIR, FTIR-pyridine spectra measurement, XRD, BET and textural properties, SEM, TEM, H₂-TPR and XPS were all used to characterize the catalysts using the same techniques in our previous studies [27–28, 35–36].

2.3 Catalytic activity test

Propane aromatization was carried out using the procedures in our previous studies in stainless-steel fixed bed reactor with propane (C₃) conversion and product selectivity calculated using same equations [27–29].
3 Results And Discussion

3.1 Catalysts characterization

FTIR spectra in Fig. 1 shows characteristic functional groups of ZSM-5 catalyst despite surface impregnation with Zn and Ni metals. 450 cm\(^{-1}\) and 550 cm\(^{-1}\) intensities depict T-O and double-5 ring bending stretches of ZSM-5 of good crystallinity respectively while 1100 and 1225 cm\(^{-1}\) correspond to internal and external asymmetric stretch respectively. 3400 and 1700 cm\(^{-1}\), which are the = stretching and hydroxyl (OH\(^{-}\)) group bending vibrations indicated physical absorption of water on HZSM-5. [1, 2, 37–38]. The presence of these characteristic groups showed that nickel co-impregnation with zinc did not destroy HZSM-5 structures [27–28].

Figure 2 displays the pyridine-FTIR of HZSM-5, mono and bimetallic catalysts with unique peaks at wavenumber of 1,450, 1,540, and 1,490 cm\(^{-1}\), which are allocated to Bronsted acid sites, Lewis acid sites and combined effect of the acid sites respectively. From the peaks, the amount of Lewis acid sites slightly increased after impregnation [9, 24, 39–41].

Figure 3 presents X-ray diffractograms for the catalyst samples. All catalysts possessed the typical ZSM-5 characteristic diffraction peaks at 2\(\theta\) = 10.83\(^\circ\), 14.82\(^\circ\), 23.04\(^\circ\), 23.86\(^\circ\), and 24.26\(^\circ\). However, with reduced intensity, indicating partial dissolution of crystalline structure during impregnation, the basic building structure of HZSM-5 are intact. In addition, no new peaks were detected on account of Zn and Ni impregnation on HZSM-5 [27–28, 42–45].

Figure 4 displays the surface morphology of the catalysts [parent ZSM-5 (A), Zn/ZSM-5 (B) and Zn-Ni/ZSM-5 (C) (2 wt. % Zn − 2 wt. % Ni) respectively]. Surface morphologies of modified catalysts showed sharp crystalline image of pure HZSM-5 due to low concentrations of impregnated dehydrogenating and stabilizing metals from B to C [27–28, 46].

Transmission electron microgram of the parent HZSM-5 (D), monometallic Zn/ZSM-5 (E) and bimetallic Zn-Ni/ZSM-5 (F) catalysts are shown in Fig. 5. The nickel co-impregnated with zinc reduced the dark coloration through the filling of the voids in the HSZM-5 and thus promoted dispersion of zinc on ZSM-5 [27–28, 46–47].

Nitrogen-sorption isotherms of ZSM-5 catalysts are shown in Fig. 6. All catalysts displayed Type-I isotherms without separate hysteresis loops [35–36]. This is a unique property of materials with micropores and lesser portions of mesopores. Table 1 shows textural properties obtained from of ZSM-5 catalysts. HZSM-5 displayed highest porosity proven by high surface area and pore volume [48]. Specific surface area and total pore width slightly reduced slightly with metal weight increase on HZSM-5 due coverage of zeolite surface. Zn-Ni/ZSM-5 microporous surface area and volume was slightly larger than that from Zn/ZSM-5 because of Zn and Ni metal species probably not been located as a single oxide phase, but co-existed on the surface of catalyst. This caused internal surface area to increase. Decreased
surface area inferred that the Zn and Ni species incorporated by impregnation were located both on the micropores and mesopores or on the outer surfaces of ZSM-5 crystals and thereby decreasing the catalyst surface area as compared the parent HZSM-5. Co-impregnation of zinc and nickel on HZSM-5 resulted in decrease in mesopore volume, pore size and increase microporous volume ($V_{\text{micro}}$) signifying that the metals mostly deposited on the external surfaces and partially blocked the catalyst pores [27, 48–51].

| Catalyst(s) | $S_{\text{BET}}$ ($\text{m}^2/\text{g}$) | $S_{\text{micro}}$ ($\text{m}^2/\text{g}$) | $S_{\text{mesoc}}$ ($\text{m}^2/\text{g}$) | $V_{\text{total}}$ ($\text{cm}^3/\text{g}$) | $V_{\text{micro}}$ ($\text{cm}^3/\text{g}$) | Pore width (nm) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| HZSM-5      | 373.22          | 333.36          | 39.87           | 0.26            | 0.11            | 2.79            |
| Zn/ZSM-5    | 361.08          | 323.10          | 37.98           | 0.25            | 0.14            | 2.78            |
| Zn-1Ni/ZSM-5| 371.52          | 324.72          | 37.30           | 0.27            | 0.15            | 2.76            |
| Zn-2Ni/ZSM-5| 362.02          | 324.45          | 34.73           | 0.25            | 0.15            | 2.72            |
| Zn-3Ni/ZSM5 | 362.94          | 324.09          | 38.85           | 0.26            | 0.15            | 2.71            |

Figure 7 presents the hydrogen-TPR analysis for the ZSM-5 catalysts. Sharp reduction peaks shown at 420 and 600 °C represented partial reduction of zinc present from [Zn–O–Zn]$^{2+}$ to ZnOH$^+$ on the ZSM-5 surface when compared with the parent HZSM-5. Zn-Ni/ZSM-5 showed reduction that could also be attributed to the presence of nickel from Ni$^{2+}$ to Ni$^+$ at 540 °C as against the reported peak for Ni/ZSM-5 at 350 and 490 °C [27–28, 52–53]. The strong interaction between zinc and nickel most probably led to the shift in reduction peak of the bimetallic catalyst when compared to the single metal counterpart. Thus, a more stable Zn-Ni/ZSM-5 catalyst has been formed. This could relate to the electronic interaction between Zn and Ni. Thus, the rearrangement of charge moved d-electrons from Zn into the interface region between Zn and Ni species [54]. Analysis of this result could indicate that some Ni species on the micropore interacted with Zn species in the microporous channels of the catalyst [49].

XPS was used to investigate the chemical state of the ZSM-5 catalysts. Zinc was 2+ both in bimetallic and monometallic catalysts by XPS analysis. The binding energy of the $2p_{3/2}$ and $2p_{1/2}$ Zn$^{2+}$ are 1025 and 1048 eV respectively as shown in Fig. 8. This increased as nickel was co-impregnated with zinc due to interaction between the metals to 1030 and 1054 eV which is believed to have aided in strengthening and improving zinc stability [27–28, 55–57]. Binding energy of nickel on bimetallic catalyst were 862 and 880 eV for $2p_{3/2}$ and $2p_{1/2}$, as against the reported values of 853 and 872 eV for nickel in Ni/ZSM-5, this suggests presence of new interface created on the catalyst surface via Zn-Ni interaction as also shown by hydrogen-TPR [10, 58].

### 3.2 Catalysts performance test
Light alkane aromatization over bifunctional ZSM-5 involves series of heterogeneous reactions. Bronsted acid sites had been reported to be responsible for oligomerization, cyclization, and cracking of olefins while Lewis acid sites principally aid the dehydrogenation of alkanes and cycloalkanes and recombination of $\text{H}^+$ to form $\text{H}_2$ in the hydride transfer steps [7, 10, 27–29, 59].

Figure 9–10 show the catalytic conversion of propane and aromatic selectivity over HZSM-5, Zn/ZSM-5 and Zn-Ni/HZSM-5 (2 wt.% of Zn, 1–3 wt. % of Ni) catalysts. It could be observed that similar conversions were recorded for HZSM-5 and Zn/ZSM-5 as reported in our previous works [27–29]. The Bronsted acid site of HZSM-5 is responsible for propane activation, oligomerization and aromatization [7, 27]. Propane conversion on Zn/ZSM-5 was low but increasing from 1 to 7 hours’ time one stream because of rich zinc on HZSM-5. Zn/ZSM-5 propane conversion was behaving like the parent HZSM-5 from 8–12 hours’ time on stream which depicted loss of zinc active site as evidenced in aromatic products distribution and undesired products as reported in our previous work [27–29]. Activity test on Zn-Ni/ZSM-5 (1–3 wt. % Ni) showed improved and stable propane conversion from average of 45% for parent HZSM5 and Zn/ZSM-5 to 60, 70 and 75% for Zn-Ni/ZSM-5 with nickel 2, 1 and 3% wt. respectively. The presence of Ni aided propane conversion. The equal metal loading of Zn and Ni promoted proper distribution of Zn over the surface of HZSM-5 thus enhancing its activity.

Figure 10 shows aromatic selectivity of the ZSM-5 catalysts. HZSM-5 as control 1 in this work had been reported to have low aromatic selectivity because of cracking of propane to $\text{C}_1$-$\text{C}_3$ and oligomerized alkanes [27–29]. Introduction of 2 wt. % Zn as control 2 to HZSM-5 by wet-impregnation method increased the aromatic selectivity. This was as a result of recombination of hydrides when zinc metal was used for dehydrogenation in converting alkenes or alkanes intermediates to aromatic hydrocarbons [7, 27–29, 43, 60–62]. Using Ni as second metal (Zn-Ni/ZSM-5) did not only improved selectivity but stabilized and sustained the activity and selectivity for the 12 hrs. time on stream investigated. Zn-Ni/ZSM-5 (2 wt. % Zn, 2 wt. %) displayed highest aromatic selectivity because of maximum synergistic interactions between zinc and nickel as shown in the XPS results and hydrogen-TPR analyses [10, 53–54].

The product distributions of propane conversions on ZSM-5 catalysts are clearly shown in Figs. 11–15. HZSM-5 had been reported from previous work to have low aromatic selectivity because of fast beta-scission side reactions producing $\text{C}_1$-$\text{C}_3$ and oligomerized alkanes (hexane, cyclohexane and heptane) as observed in Fig. 11. The introduction of zinc species on HZSM-5 was also reported to have increased aromatic selectivity by recombining hydrogen specie and inhibited beta-scission side reactions that usually lead to undesirable products [28]. The presence of Ni as stabilizer and promoter helped to sustain and improve selectivity towards aromatics as seen with 1, 2 and 3 wt. % loading of Ni with Zn on ZSM-5 in Figs. 12–14. The presence of Ni (1 and 3 wt. %) in Figs. 13 and 15 showed formation of more ethyl benzene and toluene, which was less seen in other catalysts. Ni aided alkylation of benzene to form more toluene and demethylation of o-xylene to form ethyl benzene which was not observed in the Zn/ZSM-5 monometallic catalyst. Equal weight percent of Zn with Ni (2 wt. %) on HZSM-5 (Fig. 13) showed similar
aromatic compound distribution like Zn/ZSM-5 only that C$_{9+}$ increased with increased TOS due to Zn instability.

3.3 Effect of temperature and feed flow rate on propane aromatization over Zn-Ni/ZSM-5

Propane aromatization catalyst of 2 wt. % Zn with 2 wt. % Ni on ZSM-5 gave the best aromatic selectivity, sustained product distribution and lowest C$_{9+}$. This formed the basis for choosing the catalyst for further performance test of effect of flow rate and temperature change on propane conversion, aromatic yield. Selectivity and product distribution.

Figure 15 shows the effect of temperature on propane conversion, aromatic yield and selectivity. Change in temperature plays a vital role as aromatization is an endothermic process. Increase in temperature from 500–580 °C favours endothermic reaction with high production of methane and other C$_1$-C$_2$ gases as a result of propane cracking to lower alkanes [63]. There was steady increase in activity and aromatic selectivity as displayed in Fig. 15, resulting from the improved propane conversion through stable Zn-Ni/ZSM-5 catalyst preventing cracking and reduction in aromatic formation. Temperature increase also aided cracking of C$_{9+}$ to lower aromatics which were clearly seen in toluene, benzene, o and m-xylene in Fig. 16. It could be observed that temperature increase favours dehydrogenation, oligomerization and cyclization [42].

Figures 17 and 18 show the effect of increase in feed flow rate on catalytic performance and product distribution respectively. Propane conversion from Fig. 17 reduced as feed flow rate increased from 6 to 35 ml min$^{-1}$ because propane had shorter time of contact with the surface of the catalyst for conversion. As feed flow rate increased, aromatic selectivity increased as C$_{9+}$ build up time of higher aromatics was limited. Figure 18 showed the product distribution as C$_1$-C$_3$ gases reduced because the contact time was short to favour cracking or any form of secondary reactions. Benzene was relatively stable among the aromatic compounds. The effect of flow rate increase was seen in toluene increase resulting from decrease in C$_{9+}$ because of limited build up time for higher aromatics formation, thus an overall increase in aromatic selectivity.

Conclusion

Zn and Ni species were co-impregnated on HZSM-5 to synthesize Zn-Ni/ZSM-5 bimetallic catalysts for propane conversion to aromatics in a fixed-bed reactor. Characterization analysis and performance test showed intermetallic interactions had strong influence on activity, aromatic selectivity and product distribution. Nickel was found to aid zinc stability on ZSM-5 with sustained and improved propane conversion and aromatic selectivity on the twelve hours’ time on stream (TOS). This increased and sustained aromatic selectivity minimized formation of lighter alkanes. Zn-Ni/ZSM-5 developed catalysts are highly selective towards toluene and ethylbenzene among other aromatic compounds. Conversion of propane decreased with increase in flowrate while the selectivity towards aromatics increased. Both
selectivity and conversion were steadily increasing with increase in temperature as naphthalenes crack to lower aromatics alongside alkylation of benzene to form more toluene.

**Declarations**

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**Conflict of Interest**

The authors of this paper declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Authors’ Contribution Statement**

Stated below are the contributions of the authors in this manuscript:

1. The manuscript text was written by me, Dr Gbenga Godwin Oseke as the corresponding author and catalyst testing while all co-authors reviewed the manuscripts severally.

2. The optimal operation of the fixed bed reactor, accompanying on-stream GC and other equipment were ensured in getting accurate research results by Dr Atta Abdulazeez Yusuf.

3. Professor Bello Mukhtar and Professor El-Yakubu Baba Jibril hugely contributed to linking catalyst performance to characterizations thereby giving its performance meaning.

4. Professor Aderemi Benjamin Olufemi contributed greatly in the catalyst synthesis, characterisation and discussions.

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**Figures**

![FTIR spectra of ZSM-5 catalysts.](image)

**Figure 1**

FTIR spectra of ZSM-5 catalysts.
Figure 2

Pyridine-IR of ZSM-5 catalysts.

Figure 3

X-ray diffractograms of ZSM-5 catalysts.
Figure 4
SEM image of ZSM-5 catalyst (A-HZSM-5, B-Zn/ZSM-5, C-Zn-Ni/ZSM-5).

Figure 5
TEM images of ZSM-5 catalysts (D-HZSM-5, E-Zn/ZSM-5, F-Zn-Ni/ZSM-5).

Figure 6
N$_2$-adsorption isotherms of ZSM-5 catalysts.
H$_2$-TPR of ZSM-5 catalysts.

**Figure 8**

XPS spectra survey analysis of ZSM-5 catalysts.

**Figure 9**

Propane conversions over ZSM-5 catalysts.

**Figure 10**

Selectivities to aromatics over prepared catalyst

**Figure 11**
Products distribution of propane aromatization over HZSM-5 at 540 °C

Figure 12

Products distribution of propane aromatization over Zn-1Ni/ZSM-5 at 540 °C

Figure 13

Products distribution of propane aromatization over Zn-2Ni/ZSM-5 at 540 °C

Figure 14

Products distribution of propane aromatization over Zn-3Ni/ZSM-5 at 540 °C

Figure 15

Temperature effect on catalytic performance

Figure 16

Temperature effect on product distribution
Figure 17
Flow rate effect on catalytic performance

Figure 18
Flow rate effect on product distribution