

Aromatization of Propylene on Pt-Cu / β -Al₂O₃ Nano-Catalyst

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Abstract

Aromatization of propylene was carried out on Pt-Cu/ β -Al₂O₃ bimetal catalyst at a temperature of $460 \pm 60^\circ\text{C}$ and the effectiveness of the catalyst was measured using the Gas to Liquid (GTL) product rate per single feed run. The observed mechanism was used to propose a kinetic that can be used to quantify the viability of the nano-catalyst presented here. From the kinetic analysis it was observed that adsorption of hexene-1 was responsible for isomerization reaction that produced methyl-cyclopentene. The methyl-cyclopentadiene served as electron pivotal at the catalyst centre where Pt-Cu/ β -Al₂O₃ was responsible for ring opening and subsequent cyclic formation and isomerization that produced benzene the final product with an observed suppression of cracked products.

Keywords: propylene, cyclopentene, nano-catalyst, methylcyclopentene, aromatization

Introduction

Catalysts that bring about chemical restructuring of hydrocarbon are called reforming catalysts. These catalytic materials are able to cause electron re-orientation of mother-feed hydrocarbon reagents to produce absolutely new hydrocarbon products. Such electron re-orientation may lead to carbon number elongation or stereo rearrangement of the mother carbon number. Prominent in the chemistry of reforming catalysts are materials and bimetallic derivatives of lithium (Li), platinum (Pt), rhodium (Rh), selenium (Ce) and palladium (Pd) which had been variously reported (Alexev et al, 2003; Choudhary, et al, 2001, and Davis, 1994). For any catalytic material to function as a reforming catalyst it must exhibit an acid centre. Such acid centre must be able to promote both isomerization and dehydrogenation reactions to effectively transform a feed hydrocarbon to another hydrocarbon product with or without carbon loss or cracking. Dehydrogenation reaction is a vital step in the electron re-orientation reaction that produces a reformed product. Also, the presence of excess hydrogen in the reactor may exhibit a dual function of catalyst regeneration on one hand and promoting hydro-cracking if not inhibited as often observed in platinum forming chemistry on the other hand.

For a catalyst material to achieve the expected goal and work for longer lifespan there is need for property-enhancing agents otherwise called co-catalysts, supports. Such material must show catalytic property by promoting specific reactions that facilitate or inhibit the reforming stage to stabilize the reformat. Such catalytic support can be materials dispersed on the surface of the base catalyst material either as in dual metal form or in a nano form (Adeyinka et al, 2013). Dual metal catalysts are called bimetal catalysts and these groups of catalysts are developed to promote electron pivotal and redistribution during reaction. They also serve as heat transfer agents from local hot spots thereby enhancing uniform electron distribution and promoting electron reformation to produce the catalyst-formed products. They also play the role as stabilizing metal aggregates, carbonaceous skeletal rearrangement especially when chlorinated alumina is involved (Adeyinka and Mugański, 1994). Although much work on alumina-promoted reforming catalyst exists, promoted alumina is not a good catalyst especially in gas to liquid (GTL) reaction where C₂ and C₃ are the main feedstock. This is primarily because alumina reacts with the dehydrogenate C₂ and C₃ which subsequently form ethyl/propyl alumina and promotes polymerization reaction rather than GTL reaction (Lui et al, 1999; Adeyinka et al, 2008). To produce a catalyst with high efficiency but which will work at low economic cost without trading-off the reactor life, metals that have higher promoting effectiveness are being experimented. Cu is a group II element and has proved its worth in oxychlorination reaction (Adeyinka and Mugański 1995; Papova et al, 1992, and

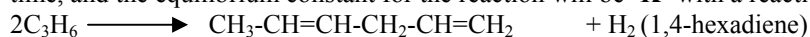
Adeyinka and Mamedov, 2000), also, Cu has catalytic ability in the synthesis of alcohols and had been proved as a high-active low- temperature operating catalyst. The synthesis of GTL on Cu nano-catalyst here is to validate the role of Cu as an electron pivoting site of the nano-catalyst especially where GTL is to be produced at lower temperature compared to other high temperature processes.

Experimental Procedure

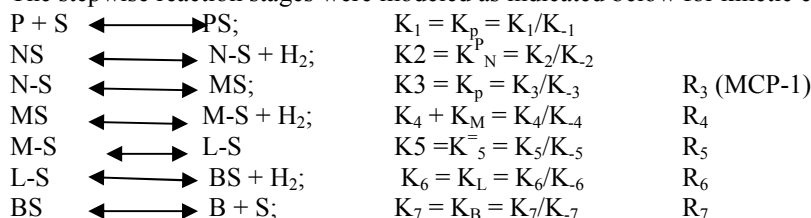
A pulse micro-catalytic reactor with an internal electrical heater was used to maintain the reaction temperature in this reaction. The Pt-Cu/ β -Al₂O₃ was loaded and heated to the reaction temperature prior to the feeding of the propylene gas. Cu in the catalyst was 0.5% and alumina was 0.6%. Catalyst preparation was as earlier reported (Adeyinka and Otaraku, 2012). Catalyst loading into the reactor (0.2g) was carried out under vacuum to avoid pressure drop in the 0.8mm diameter reactor following standard procedure (Adeyinka et al, 2008; Adeyinka and Umesi, 2002). The reaction of dehydrogenation and aromatization was carried out on the catalyst at varying contact time and concentration conditions (τ_c , C) at a constant pressure of 5.0kg/cm² and within the temperature range of 400°C and 540°C at a feed flow rate of 60ml/min.

Results and Discussion

Aromatization of propylene over Pt-Cu/ β -Al₂O₃ undergoes steps of dehydrogenation recombination and cyclicization with a subsequent dehydrogenation of the 1,4-cyclohexadiene to benzene, as the final product. Given that at any given time during the reaction, an equilibrium is maintained between dehydrogenation and isomerization, and assuming that a fraction of the catalyst active centre is covered by the reagent responsible for either dehydrogenation or isomerization, then ' Ω_i ' will be the fraction of the surface filled by i-species at a given time, and the equilibrium constant for the reaction will be ' K ' with a reaction rate of ' r '.



The stepwise reaction stages were modeled as indicated below for kinetic evaluation:



It was suggested that methyl-cyclopentene (MCP) was a transition product and served as electron pivoting during the isomerization stage. The methyl-cyclopentene (R₃) must undergo cyclic opening at the methyl-carbonyl, thereby creating electron imbalance and re-orientation. This observation suggested that electron pivoting ability of the catalyst was due to Cu abstracting H⁺ at the cyclopentene cyclic opening stage:

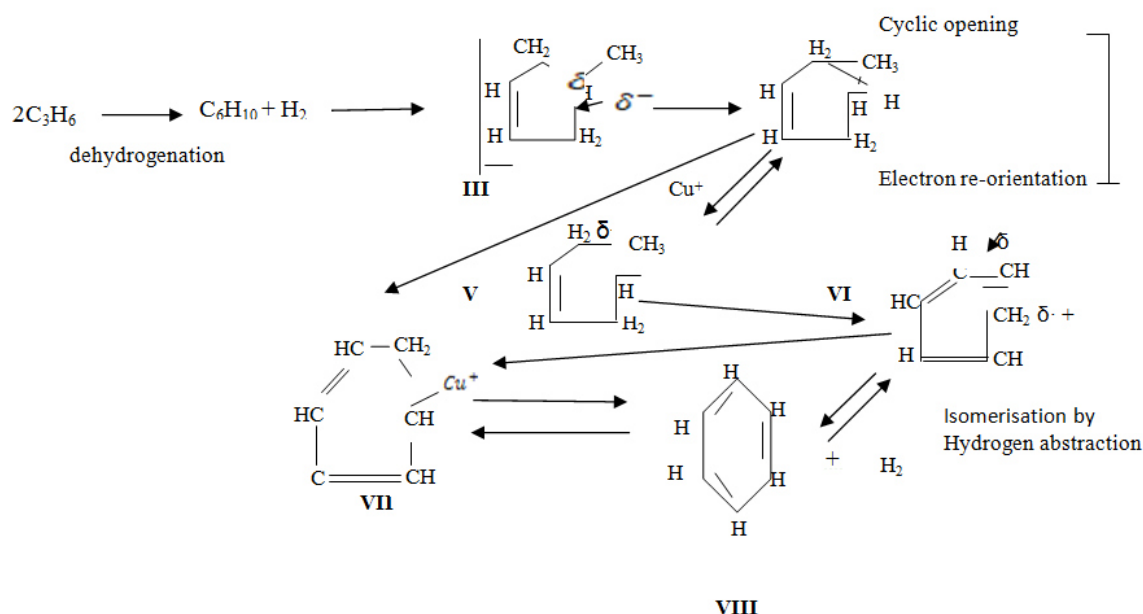


Fig. 1 Mechanism of aromatization reaction of C₃ hydrocarbon on Pt-Cu nano-catalyst

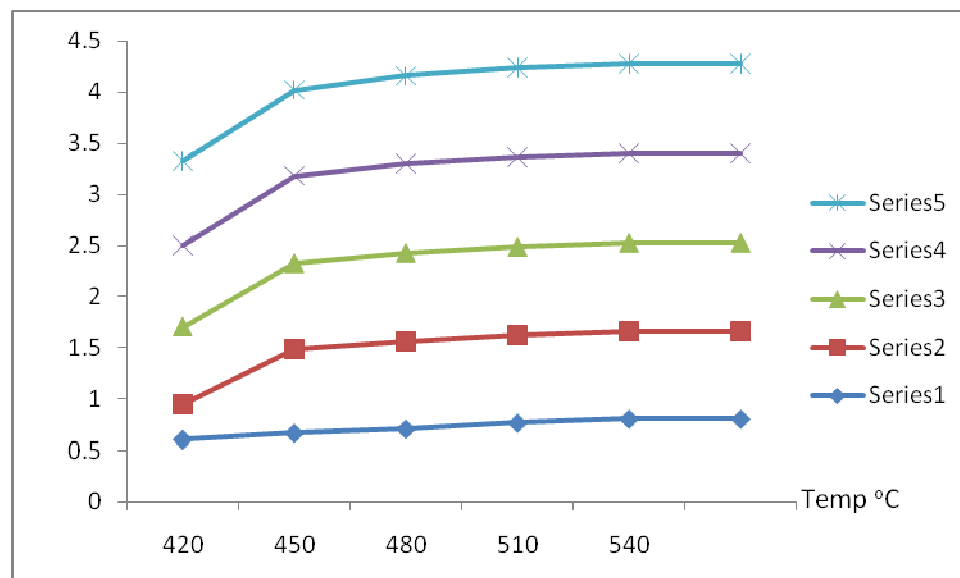


Fig. 2 Effect of temperature on MCP yield at constant contact time

Fig. 2 shows the yield of MCP at different temperatures. From the graph it will be observed that increase in temperature increased MCP yield. This is because evolution of hydrogen enhances the yield of benzene where the hydrogen evolved served as heat removing agent at the active site of the catalyst thereby promoting dehydrogenation with less effect on isomerisation. Also, the hydrogen gas served as a means of self regeneration for the catalyst during the reaction reducing cracking and coke formation. From the principle of propylene dehydrogenation and dimerization during the formation of hexane the reaction is promoted by the Pt-Cu/nano-catalyst. Pt/Al₂O₃ is a well noted catalyst for catalytic dehydrogenation with subsequent hydrocarbon reforming ability. Although, aromatization of n-hexane under hydrogen always produce cracked products, MCP-ene and benzene, formation of cracked product is dependent on temperature and residence time. Hexene in the presence of Pt-Cu does not undergo cracking reaction. This is because the hexene double bond in the presence of Cu-H encouraged methyl-cyclopentene formation at moderate temperature (480°C) than a cracking reaction. This is because dehydrogenation of MCP-ene produced hydrogen which is a product of aromatization reaction thereby displacing the thermodynamic equilibrium of the reaction (hydrogen abstraction stage) ((Davis, 1999; Nagamori and Kawase, 1998).

Formation of MCPene under hydrogen pressure showed that the mechanism of the bi-functional reaction of dehydro - isomerization of alkyl-cyclopentene produced methyl-cyclopentadiene. The presence of **Cu-H** produced the acid function required to produce ring enlargement of methyl-cyclopentadiene that finally dehydrogenated to produce benzene. From the mechanism of the reaction both the metal and acid function of the catalyst are required for formation of benzene from methyl-cyclopentene without a crack product (Trunschke et al 2000). From the mechanism of the reaction (Fig. 1), given that there was no carbon cracking as often characterized by low carbon numbered hydrocarbon at low temperature; also given that adsorption of hydrogen is negligible as a result of Cu⁺ at the active centre, then the overall reaction rates were assumed to be dependent on hydrogen abstraction, then the overall reaction for each of the stages can be summarized as:

Stage I: when propylene adsorption is the rate limiting reaction

$$-r_1 = \frac{k_1[P]}{1 + \left[\frac{k_4}{[H_2]} + \frac{k_4 k_5 k_6 (1+k_7)}{[H_2]^2} + \frac{k_4 k_5 k_6 k_7 k_8}{[H_2]^2} \right]} \quad (1)$$

Stage II: when adsorption of hexane-1 to MCP is the rate limiting reaction

$$-r_2 = \frac{k_5 k_1 [N] - \frac{k_5 [H_2]^3 [B]}{k_6 k_7 k_8 k_9}}{1 + k_1 [P] \left(1 + \frac{k_4}{[H_2]} + \frac{[H_2]^2 [B]}{k_5 k_6} \left(\frac{[H_2]}{k_5 k_7} + k_7 + 1 \right) \frac{[B]}{k_8} \right)} \quad (2)$$

Stage III: while when the adsorption and conversion of MCP to open ringed MCP in the formation of benzene is the rate limiting reaction

$$-r_3 = k_6[MS] - k_{-6}[M-S][H_2] = \frac{k_2 k_3 k_4 [N][S]}{[H_2]} - \frac{k_{-2} [H_2][B][S]}{k_7 k_8 k_9} \quad (3)$$

Fig. 3 shows the effect of contact time on the product yield. Contact time is a major factor in product yield during catalytic reaction. This is often affected by temperature of the reaction hence, a shift in temperature may negatively affect product stability and reduce yield (Rajesh et.al, 2005; Price and Kanazirev, 1991). Hydrogen gas produced was used to stabilize contact time and also used to reduce local hot spot on the Pt-Cu/Al₂O₃ surface. The hydrogen also served as a diluent to enhance conversion of MCPene to benzene. It can be observed that with increase in temperature there was a reduction in contact time as a result of the superficial velocity of the hydrogen thereby increasing hydrogen removal from MCPene to enhance electron rearrangement that produced a methyl-cyclopetadiene (MCPDene) which transformed to benzene.

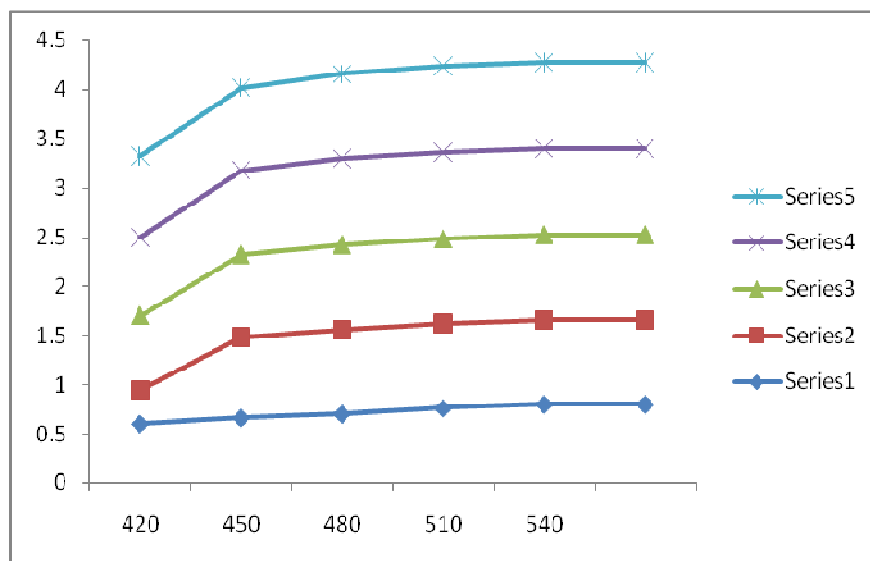


Fig. 3 Effect of residence time of multiple product yield on temperature

Our assumption from the mechanism of the reaction (Fig. 1) was that removal of hydrogen from MCP at the Cu-H complex will lead to formation of a stable cyclic aromatic ring. Fig.4 showed the yield of benzene from the conversion of MCPDene at reduced hydrogen pressure. It can be observed that with increased in temperature, there was an increase in benzene yield and the best yield was observed at 510°C in all the different runs with varying contact time studied. The best yield at 510°C suggest that at this temperature both dehydrogenation and isomerization reactions were favoured at the catalyst active site. This to some extent suggest that the advantage of Cu as nano material on Pt; firstly as a good heat conductor thereby reducing local hot spot and secondly, because of its ability to abstract hydrogen during MCPDene complex formation as indicated in Figure 1. Specifically, other Pt bimetal catalyst has not shown this transition complex (Sachtler, 1984; Smirniotis and Ruckenstein, 1995; Liu et.al 1999).

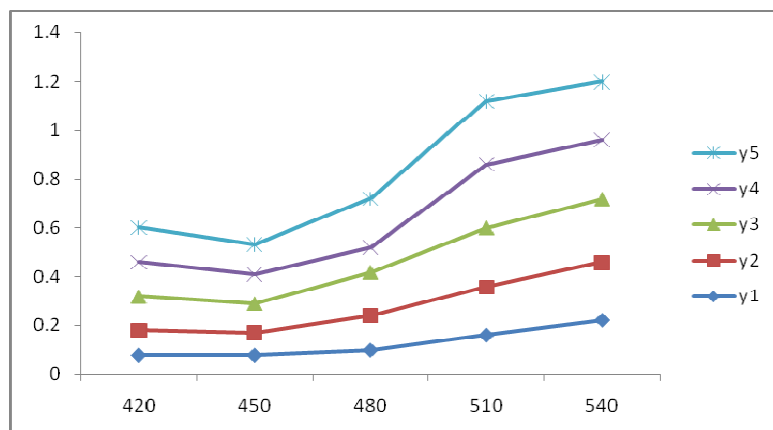


Fig. 4 Yield of benzene fom MCPDene

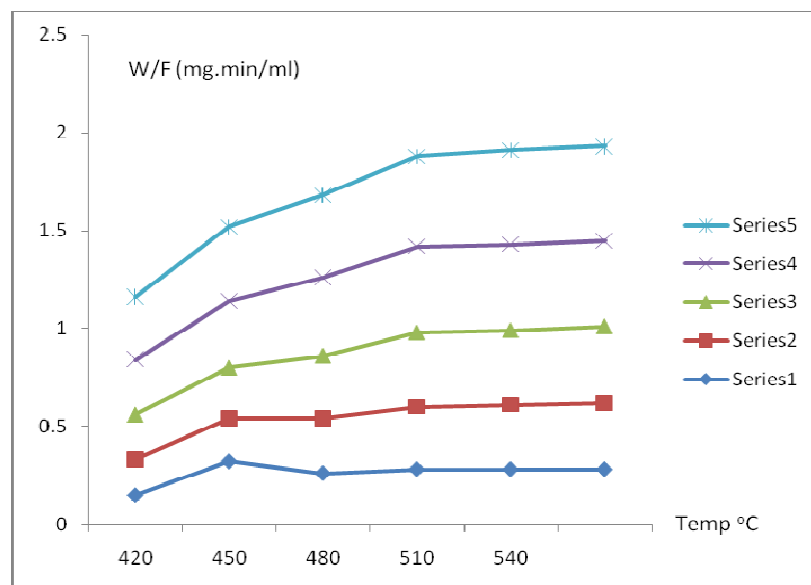


Fig. 5 Effect of temperature on product distribution of C₃ aromatization on Pt-Cu/Al₂O₃

Fig. 5 shows the effect of temperature on the yield of the products. The consistency in the molar ratio of the Low Molecular Weight (LMW) products suggested that cracking was inhibited as suggested in eq.3, while the heat transfer at the Cu-nano site favored hexene-1 adsorption which allowed high rate of MCP conversion to opened ring MCP in the formation of benzene ring with lower hydrogen pressure. From the mechanism of reaction, since the opened Cu-MCP ring transformed into the formation of benzene, the rate of benzene formation can be assumed to be dependent on the degree of freedom exhibited by the Cu-nano site which will determine the last dehydrogenation reaction. This operation, especially enhanced hydrogen removal, and redistribution of carbonaceous skeletal arrangements is the pivotal role of the aromatization reaction of the catalyst (Adeyinka, et al, 2011; Davis, 1999; Nagamori and Kawase, 1998). The role of Pt-Cu/Al₂O₃ as Nano material is the development of a new material in which current application is to ensure that catalytic promoter and support are materials that will enhance activity and participate in electron pivoting stage of the reaction.

Conclusion

Pt-Cu Nano catalyst reported here was produced to enhance gas utilization for GTL technology especially for ease of producing raw materials for the petrochemical industry. The success of Cu as a functional bimetallic catalyst is to sustain platinum accessibility because Pt-Cu is easier to produce and Cu is a heat transfer agent from local hot spots to Pt for uniform temperature at the catalyst sites. This operation especially enhanced hydrogen removal and redistribution of carbonaceous skeletal arrangements (Adeyinka, et al, 2011). The role of Pt-Cu/Al₂O₃ as Nano material is not a new development but current application is to ensure that promoter and support are materials that will enhance activity, ensure long operation time and possibly remove regeneration to reduce upload and down time activity of the reactor. It is also aimed at the reactor working at lower energy level to cut the unit cost of the product.

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Nomenclature

- N = propane
M = methyl cyclopentane
L = cyclohexene-1
BS = 1, 4-cyclohexadiene
P = propylene
S = active Surface
PS = adsorbed propylene at the active surface
NS = catalyst surface
N-S = methyl cyclopentene formation stage
B = benzene
K = equilibrium constant
k = rate constant
r = reaction rate
L-S = hexene-1
M' = methyl cyclopentene
Ω_i = catalyst active space per unit time
τ_c = contact time
C = concentration

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