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Original Research Article

Enhancing Octane Number via n-Paraffin Reforming over Modified Pt/γ-Al_2O_3-Sn Catalyst

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Abstract

Catalytic reforming upgrades low-octane hydrocarbons into high-octane gasoline, yet conventional Pt/γ-Al_2O_3 catalysts suffer from hydrocracking, coke deposition, and limited selectivity. This study investigated the effect of tin (Sn) promoter loading (0.1-0.5 wt%), incorporated during the sol–gel synthesis of γ-Al_2O_3 supports, on the physicochemical properties, n-paraffin reforming performance, and Research Octane Number (RON) enhancement over Pt/γ-Al_2O_3-Sn catalysts. Supports prepared using $SnCl_2.2H_2O$ were extruded, dried (150 °C, 1 h), calcined (550 °C, 5 h), and impregnated with 0.3 wt% Pt from $H_2PtCl_6.6H_2O$. Catalysts were characterized via XRD, WDXRF, N_2 physisorption, H_2-TPR, and NH_3-TPD, and evaluated in a fixed-bed reactor (17 bar, H_2/HC = 50, LHSV = 1 h^{-1}) at 500-510 °C using an *n*-paraffin feed analyzed by GC-DHA. XRD confirmed γ-Al_2O_3 peaks (2θ ≈ 37°, 45 °, 67 °) without SnO_2 or Pt crystallites, indicating high dispersion, while crystallinity decreased from 41.18% to 39.87% with Sn addition. Increasing Sn raised the reduction temperature (388 to 430 °C) and acidity (0.106 to 0.115 mmol/g), maintaining mesoporous textures (~ 163 m^2/g surface area; 86-88 Å pore diameter). Pt/γ-Al_2O_3-Sn1 achieved the optimal metal–acid balance. Raising the temperature from 500 to 510 °C increased n-paraffin conversion from 10.30% to 14.92%. At 510 °C, selectivities reached 63.08% iso-paraffins, 26.32% olefins, 6.67% aromatics, and 3.01% naphthenes, while RON increased from 20 feed to 29.17 at 500 °C and 32.94 at 510 °C. Furthermore, Pt/γ-Al_2O_3-Sn1 exhibited 72 hour time-on-stream stability (27.6 wt% carbon deposit), demonstrating strong potential for high-octane gasoline production.

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Keywords: Catalytic Reforming; Pt Catalyst; octan number; Metal-Acid Balance; n-Paraffin

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1. Introduction

The increasing global demand for cleaner and higher-performance transportation fuels has encouraged the petroleum refining industry to continuously improve gasoline quality while complying with strict environmental regulations. One of the most important parameters of gasoline quality is the octane number, which determines the anti-knocking characteristics of fuel during combustion in spark-ignition engines. Fuels with higher octane numbers provide better combustion efficiency, improved engine performance, and lower exhaust emissions. Consequently, catalytic reforming has become one of the most important refining processes for upgrading low-octane hydrocarbons into valuable high-octane products, such as isoparaffins, naphthenes, and aromatic compounds [1].

Among various hydrocarbon feedstocks, n-paraffins are considered suitable precursors for octane enhancement because their straight-chain

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structures can undergo isomerization, cyclization, and aromatization reactions to produce branched hydrocarbons and aromatics with significantly higher octane values [2]. Catalytic reforming of n-paraffins involves a complex network of reactions, including dehydrogenation, hydroisomerization, hydrocracking, cyclization, and dehydrocyclization reactions [3]. The effectiveness of these reactions strongly depends on the bifunctional properties of the catalyst, where metallic sites facilitate hydrogenation–dehydrogenation reactions and acidic sites promote isomerization and cyclization pathways [4].

Platinum supported on γ-alumina (Pt/γ-Al_2O_3) has long been utilized as a commercial reforming catalyst because of its excellent hydrogenation–dehydrogenation activity, thermal stability, and resistance to catalyst poisoning [5]. However, conventional monometallic Pt/γ-Al_2O_3 catalysts exhibit several limitations, such as excessive hydrocracking, coke deposition, metal sintering, and insufficient selectivity toward high-octane products [4]. These drawbacks can reduce the catalyst lifetime and reforming efficiency during the n-paraffin conversion [6]. Therefore, catalyst modification through the incorporation of promoter metals has attracted considerable attention for improving catalyst performance and stability [7].

Tin (Sn) is one of the most widely studied promoter metals for Pt-based reforming catalysts because of its ability to modify the electronic and geometric properties of the active sites of platinum [3]. The incorporation of Sn into Pt/γ-Al_2O_3 catalysts can improve metal dispersion, suppress coke formation, reduce undesired hydrogenolysis reactions, and enhance catalyst stability [8]. In addition, Sn can regulate the acidity of the γ-Al_2O_3 support, thereby minimizing excessive cracking reactions and promoting the selective formation of isoparaffins and aromatics that contribute to octane enhancement [9]. Previous studies have demonstrated that Pt–Sn catalysts exhibit superior aromatization activity and stability compared with monometallic Pt catalysts. For example, Yan *et al.* reported that Sn-modified Pt catalysts exhibited excellent n-octane reforming performance with an aromatic selectivity of 92.7%, which was attributed to the synergistic interaction between electron-deficient and electron-rich Pt species induced by Sn modification [9].

Furthermore, several studies have reported that Pt–Sn catalysts can significantly suppress carbon deposition and thermal sintering, leading to improved catalyst durability during hydrocarbon reforming and dehydrogenation [10]. The interaction between Pt and Sn creates alloy-like structures that alter the adsorption behavior and reduce coke precursor formation on platinum sites [11]. These characteristics are highly desirable in catalytic reforming processes, where catalyst deactivation is a major industrial challenge.

Despite numerous studies on Pt–Sn catalysts, the relationship between catalyst modification, physicochemical properties, and octane enhancement during n-paraffin reforming is unclear [12]. Most previous studies have focused on catalyst conversion and dehydrogenation activity, whereas limited attention has been devoted to understanding how Sn incorporation influences the product distribution of high-octane compounds in reforming systems [13]. In addition, differences in the synthesis methods, metal loading, reduction treatments, and support characteristics may significantly affect the catalyst acidity, metal dispersion, reducibility, and catalytic selectivity [14].

This study aimed to develop and assess a modified Pt/γ-Al_2O_3-Sn catalyst to enhance the octane number by reforming n-paraffins. Unlike conventional approaches, where Sn is introduced through post-impregnation onto the support surface, in this study, Sn was synthesized directly with γ-Al_2O_3 during support preparation to form an Sn-modified alumina structure prior to Pt incorporation. This approach is expected to generate a stronger interaction between the Sn species and alumina matrix, resulting in improved metal dispersion, modified acidity, enhanced thermal stability, and better resistance to coke formation. Furthermore, incorporating Sn into the alumina framework may create a more uniform distribution of acidic and metallic functionalities that can promote the selective conversion of n-paraffins into high-octane iso-paraffins and aromatic hydrocarbons while suppressing undesirable hydrocracking reactions.

Catalyst characterization techniques such as XRD, XRF, BET, and H_2-TPR were employed to investigate the influence of Sn incorporation into the γ-Al_2O_3 structure on physicochemical properties, including surface area, pore characteristics, reducibility, and metal-support interactions. Evaluating the catalytic activity in n-paraffin reforming provides insights into the correlation between the catalyst structure and octane enhancement. The results of this study are expected to contribute to the development of more efficient and selective reforming catalysts through support modification strategies, offering an alternative pathway for producing cleaner gasoline with higher octane numbers. This study investigates the influence of tin (Sn) promoter concentration on the physicochemical properties and catalytic performance of Pt/γ-Al_2O_3 catalysts in the reforming of n-paraffins.

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2. Materials and Methods

2.1. Materials

The materials used to synthesize the catalyst were boehmite (AlOOH, Chalco, Basis alumina >70%), Tin(II) chloride dihydrate ($SnCl_2.2H_2O$, Merckmilipore, 98%), hydrochloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$, Sigma-Alderich, ≥ 37,50% Pt basis), hydrochloric acid (HCl, Merckmilipore, 37%), ammonium hydroxide solution (NH_4OH, Merckmilipore, 25%), n-pentane (C_5H_{12}, Fulltime, ≥ 99%), n-hexane (C_6H_{14}, Fulltime, ≥ 99%), and n-heptane (C_7H_{16}, Fulltime, ≥ 99%).

2.2. Methods

2.2.1. Synthesis of γ-Al_2O_3-Sn

γ-Al_2O_3-Sn was prepared via the sol–gel method. In short, 100 g of boehmite (AlOOH) mixed with Sn at concentrations 0.1; 0.3; and 0.5 wt% ($SnCl_2.2H_2O$ as a promoter) and 100 mL of 1.5 M HCl were added and stirred until a homogeneous sol was formed. Subsequently, 10 mL of 13 M NH_4OH was added and stirred until homogeneous. The mixture was then extruded into a trilobate shape using an extruder. The extrudate γ-Al_2O_3-Sn was subjected to a drying process at 150 °C for a duration of 1 h, followed by calcination at 550 °C for 5 hours.

2.2.2 Preparation of catalyst

The Pt/γ-Al_2O_3-Sn catalyst was prepared using the incipient wetness impregnation method. Platinum 0.3 %(b/b) impregnant solutions were prepared 0.796 g of $H_2PtCl_6.6H_2O$ precursor, which was dissolved in 90 mL of distilled water and stirred until dissolved.

2.2.3. Catalysts characterizations

The physicochemical properties of the support and Pt/γ-Al_2O_3-Cl catalysts were characterized using X-Ray Diffraction (XRD; Miniflex 200, Rigaku), X-ray fluorescence (WDXRF; Axios, PANalytical), Surface Area Analyzer (SAA; Autosorb iQ-6S), H_2-Temperature Programmed Reduction (H_2-TPR; Chembath Pulsar, Anton Parr) and NH_3-Temperature Programmed Desorption (NH_3-TPD; Chembath Pulsar, Anton Parr). Prior to characterization, all samples were ground into fine powder. XRD analysis was performed using Cu-Kα radiation ($\lambda =$ 0.15406 nm) operated at 40 kV and 35 mA over a 2θ range of 5–90° to evaluate the crystalline phases, crystallinity, crystallite size, and metal dispersion of the catalysts. The elemental composition and Pt loading were determined using XRF analysis at an operating voltage of 40 kV and a current of 45 mA.

The textural properties, including the specific surface area, pore volume, and average pore diameter, were analyzed using SAA through N_2 adsorption – desorption measurements. Approximately 0.3 g of the sample was degassed under vacuum at 100 °C for 1 h, followed by treatment at 300 °C for 5 h, prior to analysis. The reducibility of the catalysts was evaluated by H_2-TPR using 0.1 g of sample heated from room temperature to 600 °C at a heating rate of 10 °C/min under a 4% H_2/Ar gas flow, while the hydrogen consumption was monitored using a thermal conductivity detector (TCD). The acidity was investigated using NH_3-TPD. Approximately 0.1 g of the sample was pretreated under He flow at 500 °C for 1 h, followed by NH_3 adsorption at room temperature and desorption under He flow from 21 °C to 800 °C to determine the acidity characteristics and acid strength distribution of the catalysts.

2.2.4. Catalyst activity analysis

The catalytic performance test was conducted using a fixed-bed continuous pilot-plant reactor (Xytel) (Figure 1). The experimental procedure consisted of catalyst preparation, activation, and

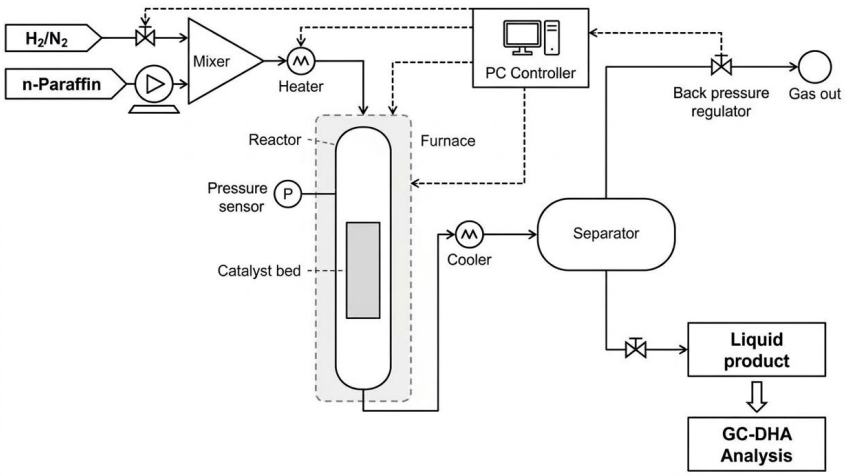


Figure 1. Schematic flow diagram of the Xytel reactor.

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catalytic reforming reactions. Approximately 60 g of catalyst was loaded into the reactor tube prior to the reaction. Before activation, N_2 gas was introduced into the reactor system to remove residual oxygen from the reactor pipelines via a purging process. Subsequently, the catalyst was activated under H_2 flow.

The catalytic reforming reaction was carried out at a Liquid Hourly Space Velocity (LHSV) of 1 h^{-1}, hydrogen pressure of 17 bar, and H_2/HC ratio of 50. The reaction temperature was varied between 500 and 510 °C. After the desired operating temperature and pressure were achieved, the n-paraffin feed was introduced into the reactor using a micropump at a predetermined flow rate. Liquid product samples were collected every 4 h after sufficient product accumulation in the collectors. The reaction products were analyzed using Gas Chromatography–Detailed Hydrocarbon Analysis (GC-DHA; Agilent 7890B, Agilent Technologies) equipped with a Flame Ionization Detector (FID) and a methyl silicone capillary column (HP-1 PONA, $100\ \text{m} \times 0.25\ \text{mm} \times 0.5\ \mu\text{m}$). The n-paraffin feed used in this study was modelled to contain 20 vol% n-paraffin. % n-pentane (C_5H_{12}), 35 vol.% n-hexane (C_6H_{14}), and 45 vol.% n-heptane (C_7H_{16}), representing a light naphtha fraction rich in straight-chain paraffinic hydrocarbons suitable for catalytic reforming reactions.

2.2.4. Feed and product analysis

The hydrocarbon compositions of the feed and liquid products were analyzed using Gas Chromatography-Detailed Hydrocarbon Analysis (GC-DHA). Approximately 2 mL of the sample was placed in a vial and injected into the instrument for analysis. The injected sample was vaporized at 100 °C prior to separation in a chromatographic column. The separated compounds were subsequently detected using a flame ionization detector (FID). The analysis generated chromatograms, peak integration data, and hydrocarbon composition results, which were reported as weight percentages (%wt).

The catalytic reforming performance was evaluated in terms of n-paraffin conversion, hydrocarbon product selectivity, and product yield based on the weight percentage (wt%) compositions obtained from GC-DHA analysis, calculated according to Equations (1-3):

$$Conversion\ (\%) = \frac{W_{n\text{-paraffin, feed}} - W_{n\text{-paraffin, product}}}{W_{n\text{-paraffin, feed}}} \times 100\% \quad (1)$$

$$Selectivity_i\ (\%) = \frac{W_{i,\text{ product}} - W_{i,\text{ feed}}}{W_{n\text{-paraffin, feed}} - W_{n\text{-paraffin, product}}} \times 100\% \quad (2)$$

$$Yield_i\ (\%) = \frac{W_{i,\text{ product}} - W_{i,\text{ feed}}}{W_{n\text{-paraffin, feed}}} \times 100\% \quad (3)$$

where, $W_{n\text{-paraffin, feed}}$ and $W_{n\text{-paraffin, product}}$ represent the weight fractions (wt%) of n-paraffins in the feed and reformate product, respectively, while $W_{i,\text{ feed}}$ and $W_{i,\text{ product}}$ denote the weight fractions (wt%) of each hydrocarbon group i (iso-paraffins, olefins, naphthenes, and aromatics) in the feed and product streams.

3. Results and Discussion

3.1. Catalyst Characterizations

The synthesized catalysts were characterized to evaluate their physicochemical properties, including the crystalline phase, crystallinity, crystallite size, elemental composition, textural properties, reducibility, and acidity. The catalyst samples consisted of Pt/γ-Al_2O_3-Sn catalysts with various Sn loadings.

3.1.1. Effect of Sn concentration on catalyst crystal structure (XRD)

XRD analysis showed that all the supports and catalysts exhibited three main diffraction peaks at approximately 2θ = 37 °, 45 °, and 67 °, which are characteristic peaks of γ-Al_2O_3. These results confirm that the synthesized support maintained the γ-Al_2O_3 phase after Sn incorporation and Pt impregnation. No additional diffraction peaks corresponding to SnO_2 or Pt species were observed (such as Pt at 2θ = 81-82°). This absence suggests that both Sn and Pt species are highly dispersed on the alumina matrix or exist as sub-nanometer crystallites below the detection limit of XRD, rather than forming large bulk crystalline agglomerates [15].

The crystallinity of the catalysts slightly decreased with increasing Sn concentration, from 41.18% for Pt/γ-Al_2O_3-Sn1 to 39.87% for Pt/γ-Al_2O_3-Sn3. This minor decrease suggests that Sn incorporation introduced slight structural disorder into the γ-Al_2O_3 lattice owing to the strong interactions between the Sn species and the alumina matrix. Furthermore, no diffraction peaks associated with Pt agglomeration were detected in the range of 2θ = 81–82° [Figure 2A], corresponding to the characteristic Pt (311) reflection at 81.3°. In accordance with UOP Method 905 (Standard Test Method for Platinum Agglomeration by X-Ray Diffraction) [16], the absence of a distinct diffraction peak at 81.3° 2θ confirms that platinum agglomeration is below 1% (< 1% Pt agglomeration) and that the Pt crystallites remain smaller than 3.5 nm (< 3.5 nm). This absence indicates that Pt species are highly dispersed across the γ-Al_2O_3 support without forming large crystalline agglomerates during catalyst preparation. Additionally, the

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lack of peak shifting in this region rules out the formation of segregated bulk Pt–Sn metallic alloys, supporting the conclusion that Sn interactions remain highly dispersed or amorphous within the alumina matrix.

3.1.2. Effect of Sn addition on catalyst

XRF analysis demonstrated that the Sn content in the supports and catalysts was close to the target loadings. The Sn concentration increased from 0.08% in Pt/γ-Al_2O_3-Sn1 to 0.58% in Pt/γ-Al_2O_3-Sn3, whereas the Pt content remained relatively constant at approximately 0.34% (Table 1). This result indicates that the synthesis and impregnation methods successfully maintained the Pt loading across all catalyst variations.

BET analysis demonstrated that the incorporation of Sn did not significantly affect the specific surface area, pore volume, and pore diameter of the catalysts. This indicates that Sn modification preserved the mesoporous structure of the γ-Al_2O_3 support across all Sn loadings. The synthesized catalysts exhibited surface areas of approximately 163 m^2/g, with pore diameters ranging from 86 to 88 Å (Table 1). These textural properties are considered suitable for catalytic reforming applications because they facilitate the diffusion of n-paraffin molecules and reforming products toward active sites [17]. The decrease in the surface area and pore characteristics after metal incorporation is associated with the deposition of Pt and Sn species within the pore structure, which partially blocks the pores and reduces the accessible surface area [18]. Similar behaviors have been commonly reported for supported metal catalysts after their impregnation and calcination. Despite the reduction in textural parameters, the catalysts maintained relatively high surface areas and mesoporous structures, indicating that the incorporation of Sn into the γ-Al_2O_3 framework did not significantly damage the pore structure [17]. The preservation of mesoporous characteristics is important because adequate pore accessibility enhances reactant diffusion and improves catalytic performance during n-paraffin reforming [19].

H_2-TPR analysis (Table 1 and Figure 2B) showed that increasing Sn concentration resulted in higher reduction temperatures, shifting from 388 °C for Pt/γ-Al_2O_3-Sn1 to 430 °C for Pt/γ-Al_2O_3-Sn3. This temperature shift reflects modified reducibility of the platinum species, which is attributed to stronger metal–support interactions between the metal species and the Sn-modified alumina matrix [18]. The higher reduction temperatures suggest that Sn incorporation stabilizes the oxidized Pt species, making them more strongly anchored to the support surface. While higher reduction temperatures are often associated in the literature with intimate Pt–Sn contact or modified Pt–Sn interactions [20], the absence of distinct alloy peaks in XRD implies that any Pt–Sn interactions remain highly dispersed or amorphous. Importantly, all

Table 1. Compositions, BET surface area, and chemisorption characterizations of catalyst.

Catalyst	Compositions			BET Surface Area			Chemisorption	
	PtO (%)	SnO (%)	Cl (%)	SA (m^2/g)	PV (cm^3/g)	PD (Å)	H_2-TPR (°C)	NH_3-TPD (mmol/g)
Pt/γ-Al_2O_3-Sn1	0.345	0.08	0.73	163.688	0.350	87	388	0.106
Pt/γ-Al_2O_3-Sn2	0.341	0.23	0.73	163.718	0.360	88	409	0.110
Pt/γ-Al_2O_3-Sn3	0.344	0.58	0.91	163.881	0.350	87	430	0.115

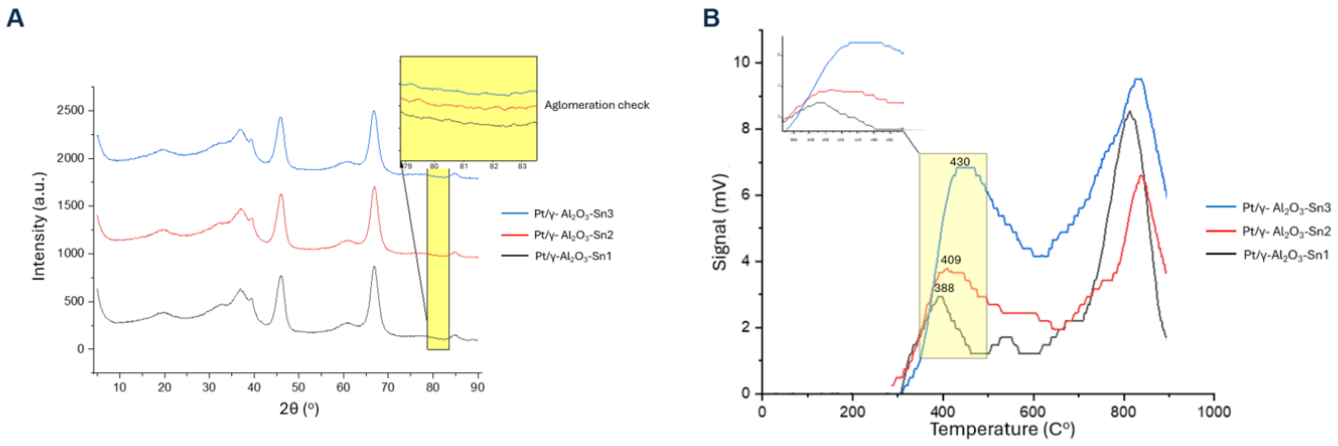


Figure 2. X-Ray Diffraction (A) and H_2-Temperature Programmed Reduction (H_2-TPR).

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observed reduction temperatures (388–430 °C) remain well below the catalytic reforming operating temperatures (500–510 °C), confirming that full activation to active metallic Pt species occurs effectively prior to or during the reaction process [21].

The increase in acidity (NH_3-TPD) indicates that the Cl content in the catalysts compared to the supports was attributed to chloride ions originating from the $SnCl_2$ and H_2PtCl_6 precursors (Table 1). Chlorine plays an important role in enhancing the acidity of catalysts, which promotes isomerization reactions during catalytic reforming [22]. A higher acidity indicates that the combination of Sn and Cl successfully enhanced the number of acidic sites on the catalyst surface [23]. Acidic sites play an important role in the isomerization and cyclization of n-paraffins into iso-paraffins and aromatic hydrocarbons. The presence of chloride species on alumina is also known to enhance Brønsted acidity, thereby improving hydrocarbon rearrangement reactions [22]. An increase in the number of acidic sites generally enhances the catalytic activity because more active sites become available for the hydrocarbon conversion. However, excessive acidity may promote undesirable hydrocracking reactions; therefore, an appropriate balance between metallic and acidic functions is essential [22].

3.2. Catalytic Activity in n-Paraffin Reforming

Among all the synthesized catalysts, Pt/γ-Al_2O_3-Sn1 was selected as the optimum catalyst because it exhibited the best balance between the physicochemical properties and catalytic performance in n-paraffin reforming reaction. XRD analysis showed that Pt/γ-Al_2O_3-Sn1 possessed a relatively small crystal size and no indication of Pt agglomeration, indicating good Pt dispersion and a high availability of active sites for reforming reactions [15]. BET analysis also demonstrated that the catalyst maintained a high surface area and mesoporous structure, which are important for enhancing reactant diffusion and accessibility to active sites [17,18]. In addition, H_2-TPR analysis revealed a lower reduction temperature than that of the higher Sn-loaded catalysts, indicating that the Pt species in Pt/γ-Al_2O_3-Sn1 were more easily reduced to their active metallic forms [21].

The catalytic reforming performance of the synthesized Pt/γ-Al_2O_3-Sn1 catalysts was evaluated in a continuous fixed-bed reactor at temperatures of 500-510 °C under 17 bar pressure, H_2/HC ratio of 50, and LHSV of 1 h^{-1}. The reaction products were analyzed using GC-DHA (Gas Chromatography – Detailed Hydrocarbon Analysis) to determine the hydrocarbon distribution and octane enhancement performance.

The reforming activity increased with increasing reaction temperature owing to the acceleration of the dehydrogenation, isomerization, and cyclization reactions. Higher temperatures promoted the conversion of linear n-paraffins into branched isoparaffins and aromatic hydrocarbons, which are known to possess higher octane values [24].

The hydrocarbons obtained from the catalytic performance evaluation indicates that the synthesized Pt/γ-Al_2O_3-Sn catalyst exhibited favorable activity toward the conversion of naphtha into higher-octane hydrocarbons. As presented in the Figure 3, increasing the reaction temperature from 500 °C to 510 °C significantly influenced the composition of the reformate products, particularly the formation of iso-paraffins and olefins. This behavior confirms the bifunctional nature of the catalyst, where the metallic function facilitates dehydrogenation reactions while the acidic sites promote isomerization and cyclization pathways. Similar catalytic behavior has been widely reported for Pt-Sn reforming catalysts supported on chlorinated alumina [1,25].

Among all hydrocarbon groups, iso-paraffins represented the dominant product fraction and increased substantially from 7.53% at 500 °C to 9.76% at 510 °C. The increase in the iso-paraffin concentration suggests that the higher reaction temperature enhanced the isomerization of normal paraffins to branched hydrocarbons. Branched paraffins possess significantly higher-octane numbers than straight-chain paraffins, making them highly desirable for catalytic reforming [24]. The incorporation of Sn into Pt/Al_2O_3 catalysts has been reported to improve isomerization selectivity while suppressing excessive hydrogenolysis and hydrocracking reactions by modifying the metallic function and acid site distribution [26].

The olefin content also increased markedly from 1.80% at 500 °C to 3.92% at 510 °C. This trend indicates that the dehydrogenation reactions became more pronounced at elevated temperatures. Olefins are important intermediate compounds in catalytic reforming because they can undergo cyclization and dehydrocyclization reactions to form aromatic hydrocarbons [27]. Previous studies on Pt-Sn catalysts have demonstrated that metallic Pt sites effectively catalyze paraffin dehydrogenation, whereas Sn improves catalyst stability and reduces coke formation during hydrocarbon transformation reactions [13,25].

Aromatic hydrocarbons were detected in relatively small amounts but remained stable at both operating temperatures, with concentrations close to 1%. The presence of aromatic compounds confirmed that the catalyst

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was capable of facilitating dehydrocyclization reactions, which are among the principal reactions responsible for octane enhancement during naphtha reforming [23,24]. The aromatization activity in Pt-Sn/Al_2O_3 systems has been associated with the synergistic interaction between Pt and Sn, which improves the selectivity toward valuable aromatic products while minimizing coke deposition and catalyst deactivation [1,28]. Meanwhile, the naphthene fraction remained relatively low throughout the reaction. This observation suggests that naphthenic compounds were continuously converted into aromatic hydrocarbons through dehydrogenation reactions on metal active sites. This behavior is characteristic of Pt-based reforming catalysts, in which naphthenes serve as important intermediates for aromatic production [29].

The quantitative catalytic performance and evaluate the catalytic efficiency of Pt/γ-Al_2O_3-Sn1, the *n*-paraffin conversion, hydrocarbon product selectivity, and product yield at 500 °C and 510 °C are presented in Figure 3B-D. As shown in Figure 3B, elevating the reaction temperature from 500 °C to 510 °C substantially enhanced the *n*-paraffin conversion from 10.30% to 14.92%. This 4.62% increase in conversion confirms that higher thermal energy accelerates the activation of straight chain paraffins over the bifunctional active sites, particularly favoring endothermic dehydrogenation and skeletal isomerization pathways [24].

The corresponding product selectivities are illustrated in Figure 3C. At 500 °C, the catalyst exhibited high selectivity toward iso-paraffins 69.73%, followed by olefins 17.52%, aromatics 9.93%, and naphthenes 2.15%. When the temperature was raised to 510 °C, iso-paraffin selectivity decreased slightly to 63.08%, whereas olefin selectivity increased markedly from 17.52% to 26.32%, accompanied by a modest rise in naphthene selectivity to 3.01% and a decrease in aromatic selectivity to 6.67%. This shift in selectivity distribution indicates that while skeletal isomerization remains the predominant reaction pathway at both temperatures, higher operating temperatures thermodynamically favor endothermic paraffin dehydrogenation over exothermic isomerization, thereby driving olefin formation [4,24,30].

Consequently, the overall product yields Figure 3D reflect the combined effects of enhanced conversion and shifting selectivity. Raising the temperature from 500 °C to 510 °C increased the iso-paraffin yield from 7.18% to 9.41% and more than doubled the olefin yield from 1.81% to 3.93%. Meanwhile, the naphthene yield rose from 0.221% to 0.449%, and the aromatic yield remained nearly constant at 1.023% 500 °C and 0.995% 510 °C. These quantitative yield improvements confirm that operating at 510 °C effectively maximizes the generation of high-octane branched paraffins and reactive olefin intermediates over the Pt/γ-Al_2O_3-Sn1 catalyst [31,32].

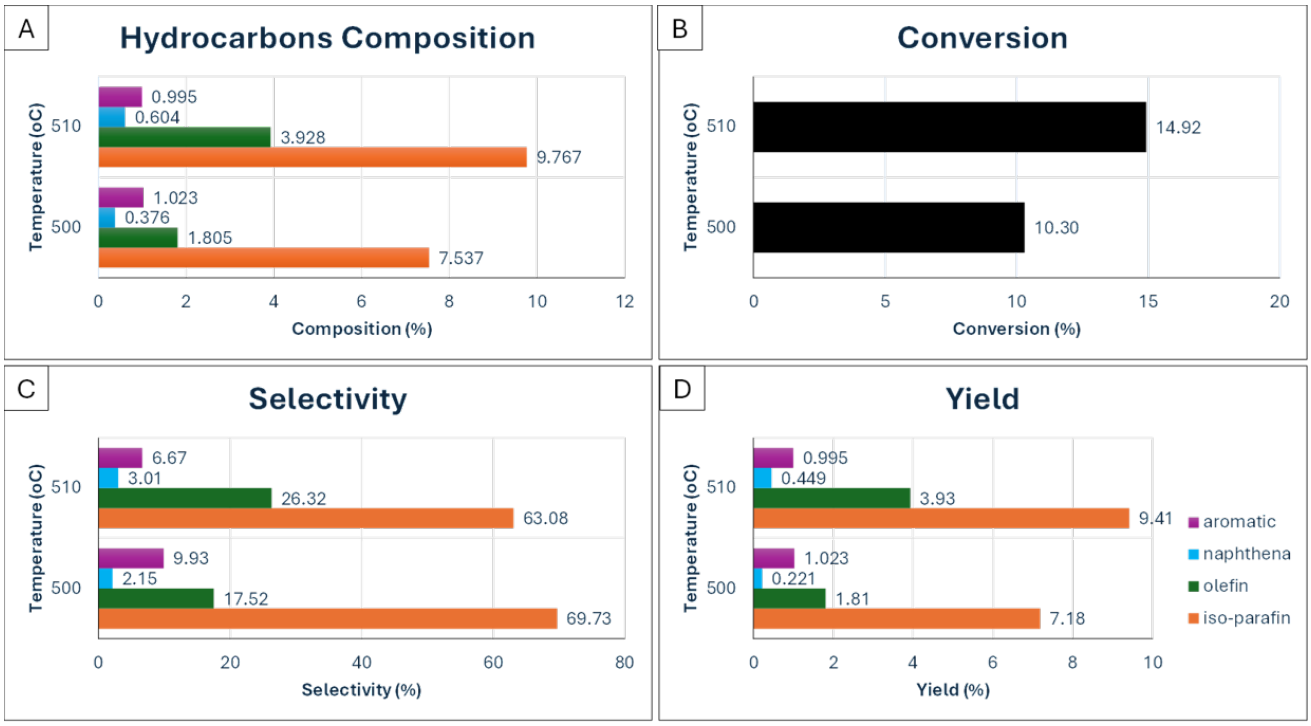


Figure 3. Hydrocarbon compositions (A), conversion (B), selectivity (C), and yield).

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The primary objective of catalytic naphtha reforming is to upgrade low-octane paraffinic feedstocks into high-octane reformate fractions to satisfy modern fuel quality standards [23]. Figure 4 illustrates the Research Octane Number (RON) of the initial feed and the reformate products obtained over the Pt/γ-Al_2O_3-Sn1 catalyst at reaction temperatures of 500 °C and 510 °C. The raw *n*-paraffin feed exhibited a very low RON of 20.00, characteristic of straight-chain light naphtha components. Upon catalytic reforming at 500 °C, the RON increased substantially to 29.17. Elevating the reaction temperature further to 510 °C led to an additional enhancement in fuel quality, achieving a maximum RON of 32.94.

This progressive enhancement in RON with increasing operating temperature directly correlates with the shift in hydrocarbon distribution. As the temperature increased, the formation of branched iso-paraffins and unsaturated olefins was markedly accelerated. Iso-paraffins, olefins, and aromatic hydrocarbons possess significantly higher intrinsic octane numbers than straight-chain normal paraffins; thus, their cumulative enrichment in the product stream effectively elevates the overall anti-knocking properties of the reformate [4,23].

Furthermore, the higher operating temperature provides the necessary thermal activation energy for endothermic dehydrogenation and acid-catalyzed isomerization pathways over the tuned metallic and acidic sites of the Pt/γ-Al_2O_3-Sn1 catalyst [5,7]. The incorporation of Sn plays a critical role in optimizing the metal–acid site balance, thereby promoting selective skeletal rearrangement while suppressing non-selective hydrocracking reactions that typically lead to yield loss [1,25]. These results substantiate the primary claim that Sn modification effectively enhances catalytic reforming selectivity toward high-octane hydrocarbon synthesis. Overall, the hydrocarbon distribution demonstrates that the synthesized Pt/γ-Al_2O_3-Sn1 catalyst exhibited effective reforming activity, particularly toward the production of isoparaffins and aromatic compounds, which contribute to a higher gasoline octane number [33].

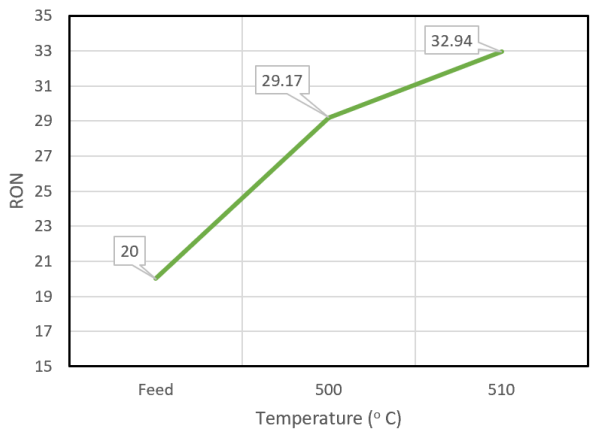


Figure 4. Reseacrh Octane Number (RON).

The catalytic performance of the synthesized Pt/γ-Al_2O_3-Sn1 catalyst, our findings were compared with previously reported bimetallic Pt-Sn/Al_2O_3 reforming systems evaluated under similar *n*-paraffin reforming conditions [34]. Gonzale-Marcos *et al.* investigated industrial-type Pt-Sn/Al_2O_3 catalysts in *n*heptane reforming at temperatures up to 510 °C and demonstrated that Sn addition substantially suppresses undesirable hydrogenolysis reactions while promoting skeletal isomerization and dehydrocyclization pathways. Consistent with their observations, our Pt/γ-Al_2O_3-Sn1 catalyst exhibited a pronounced increase in *n*-paraffin conversion from 10.30% to 14.92% and high selectivity toward high-octane branched iso-paraffins 63.08% and olefin intermediates 26.32% at 510 °C. Whereas conventional impregnated Pt-Sn/Al_2O_3 catalysts often suffer from partial Pt site blockage at elevated Sn loadings [32], incorporating Sn during the sol-gel synthesis of the γ-Al_2O_3 support in the present work effectively preserved high metallic Pt dispersion and tailored the metal–acid balance, thereby sustaining high isomerization efficiency and octane number enhancement.

3.3. Proposed Reaction Pathways and Bifunctional Site Contributions

The observed product distribution over the Pt/γ-Al_2O_3-Sn1 catalyst can be interpreted through a classic bifunctional catalytic framework, where metallic Pt sites and support-derived acidic sites act synergistically to facilitate *n*-paraffin upgrading [24]. Rather than presenting a single deterministic pathway, the overall performance reflects competing parallel and consecutive reaction routes governed by the metal–acid site balance and thermal activation [2].

Characterization by H_2-TPR confirmed that Pt/γ-Al_2O_3-Sn undergoes reduction to active metallic Pt^0 species at a relatively low temperature (388 °C), ensuring complete activation under the reforming conditions (500-510 °C). Metallic Pt sites primarily catalyze endothermic dehydrogenation of straight-chain *n*-paraffins to form mono-olefins. The prominent increase in olefin concentration, provides direct evidence for the strong temperature dependency of this metal-catalyzed dehydrogenation pathway. Olefins serve as key reactive intermediates that readily migrate to neighboring acid sites for subsequent chemical transformation [2,5].

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The acidic functionality of the catalyst, quantified at 0.106 mmol/g (NH_3-TPD) is generated by Brønsted and Lewis acid centers on the chlorinated alumina surface. Once olefins are generated on metallic Pt, they undergo protonation at these acidic sites to form secondary or tertiary carbocation intermediates. These carbocations undergo skeletal rearrangement via 1,2-hydride and alkyl shifts, leading to the formation of branched iso-paraffins upon subsequent hydride transfer or re-hydrogenation on Pt sites [4,25].

At elevated reaction temperatures, the increased availability of olefinic intermediates facilitates secondary cyclization over acidic sites to form naphthene. Subsequently, these naphthenic intermediates undergo rapid metal-catalyzed dehydrocyclization on Pt sites to yield aromatics (Figure 3D).

3.4. Catalyst Stability and Spent Catalyst Carbon Analysis

The operational stability and carbon deposition behavior of the optimized Pt/γ-Al_2O_3-Sn1 catalyst were evaluated via a 72-hour time-on-stream (TOS) reforming test at 500 - 510 °C. Following the reaction run, the spent catalyst was collected and analyzed using a Carbon Analyzer to quantify the total carbon accumulation. Elemental analysis revealed a total carbon deposition of 27.6 wt% on the spent Pt/γ-Al_2O_3-Sn1 catalyst after 72 h TOS. This progressive carbon accumulation is attributed to the extended exposure (72 h) to severe endothermic reforming conditions, wherein dehydrogenated and cyclized intermediates gradually undergo oligomerization and condensation on the catalyst surface [1,13,27]. Notably, despite the accumulation of 27.6 wt% carbon over the extended run, the catalyst exhibited sustained reforming performance without catastrophic activity loss. This operational durability is associated with the Sn-modified metal–acid site balance and the geometric ensemble dilution of active Pt sites [1,10,20], which enhances coke tolerance by retarding severe graphitic carbon growth directly on metallic Pt sites [6,35].

Consequently, similar to commercial catalytic reforming units in petroleum refineries such as semi-regenerative or continuous catalyst regeneration (CCR) systems periodic oxidative regeneration is required to restore catalytic activity after extended operation [24,36]. During industrial regeneration, accumulated carbonaceous deposits are removed via controlled carbon burn off, followed by oxychlorination and reduction steps to re-disperse platinum species and restore the optimal metal acid balance [3,8,14]. Pt/γ-Al_2O_3-Sn1 catalyst is well-suited for cyclic regeneration protocols in industrial reforming applications.

4. Conclusions

The modified Pt/γ-Al_2O_3-Sn catalyst exhibited favorable physicochemical properties and catalytic performance for n-paraffin reforming, enhancing the octane number. Among the synthesized catalysts, the optimal Sn-modified formulation Pt/γ-Al_2O_3-Sn1 retained a mesoporous γ-Al_2O_3 structure with high metallic Pt dispersion, moderated surface acidity, and stronger metal-support interaction as confirmed by XRD, N_2-physisorption, H_2-TPR, and NH_3-TPD analyses. These structural modifications optimized the metal–acid balance and suppressed undesired hydrogenolysis and cracking reactions. In catalytic performance evaluations, increasing the reaction temperature from 500 °C to 510 °C enhanced *n*-paraffin conversion from 10.30% to 14.92%. At 510 °C, the Pt/γ-Al_2O_3-Sn1 catalyst achieved product selectivity of 63.08% toward iso-paraffins, 26.32% toward olefins, 6.67% toward aromatics, and 3.01% toward naphthenes, corresponding to product yields of 9.41%, 3.93%, 0.995%, and 0.449%, respectively. As a result, the Research Octane Number (RON) increased from 20 feed to 29.17 at 500 °C and 32.94 at 510 °C. Furthermore, the catalyst maintained stable operation over a 72-hour time-on-stream (TOS) test with a total carbon deposition of 27.6 wt%. Overall, the synthesized Pt/γ-Al_2O_3-Sn1 catalyst demonstrated promising potential for industrial catalytic reforming applications to produce high-octane reformate products.

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CRediT Author Statement

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Declaration of Conflict of Interest

The authors declare no conflict of interest. While PT Pertamina facilitated the research infrastructure and materials, the study was conducted independently, and the company had no role in biasing the data interpretation or the decision to publish the results.

Declaration of Generative AI Use

The authors confirm that generative AI tools were used solely to refine the linguistic quality and text clarity during manuscript preparation. Every section was subsequently inspected and validated by the authors, who bear full accountability for the scientific content presented herein.

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