Evaluation of transport processes in a catalytic reforming reactor with high performance nanocatalysts

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Abstract. Catalytic reforming reactors are the most important multiphase reactors in petroleum refineries producing high octane gasoline. The reforming process usually generates an unstable operation combined with catalyst activity loss due to the high levels of interaction between the heat transfer and mass transfer processes in the reactor and the specifications of the catalyst. In this investigation, n-heptane reforming reactions were investigated by preparing three types of nanocatalysts (Pt/HY, Pt-Ge/HY, and Pt-Re/HY). The reforming reactions were investigated at 440, 460, 480, 500, and 520 °C under atmospheric pressure in a reactor of dimensions 2 cm (inner diameter) by 30 cm (height) manufactured from stainless steel. The H2/n-heptane was selected to operate at a value of 2 with WHSV=2, and the effects of heat and mass transfer processes on the catalyst and reactor performance were thus evaluated. The results indicated that the Pt-Gr/HY catalyst showed the highest activity, selectivity, and stability at a reaction temperature of 480 °C. It was also noted that the heating rate and diffusional processes were severely affected by reaction selectivity during formation of the desired products as well as by the hydrodynamic parameters of the reactor. The activity of the prepared nanocatalysts demonstrated the sequence Pt-Ge/HY > Pt-Re/HY > Pt/HY, and the prepared nanocatalysts were able to offer high performance under controlled transport processes in terms of producing high-quality gasoline.

Keywords: Multiphase reforming reactor; Heat and mass transfer; Nanocatalyst; N-heptane.

1. Introduction
According to the principles of multiphase reactors, the catalytic naphtha reforming reactor is highly dependent on the interaction mechanism between the gaseous and solid phases of a catalyst. The heat and mass transfer rates on the catalyst surface thus plays a major role in controlling the overall reaction mechanism in the reforming reactor [1-4]. Usually, catalytic reforming includes a variety of different reactions, such as the dehydrocyclization of paraffins, isomerization of paraffins and naphthenes; dehydrogenation of naphthenes to aromatics; dealkylation of alkylaromatics; and hydrocracking of paraffins to light hydrocarbons [5-7]. All of these reactions significantly affect the bifunctional mechanism that occurs on metal sites and acid sites. The most common industrial catalysts for reforming reactions are Pt/Al2O3, Pt-Ru/Al2O3, Pt-Re-Sn/Al2O3, Pt/Zeolite, and Pt/Zirconia catalysts. From a heterogeneous reaction mechanism perspective, the operation of all these catalysts, as well as their deactivation rates, functions to affect the transport processes that occur inside solid catalysts [2,6,8].

The heat and mass transfer operations across a catalyst are highly dependent on the catalyst’s texture and pore size. Further, nanocatalysts are characterised by high surface area, high resistance to
deactivation, and high performance [3,6]. This means that the use of nanocatalysts in catalytic reforming reactions must lead to changes in the design approach of reactors due to reductions in the amount of catalyst required due to the high surface area of these nanocatalysts. As the external mass transfer resistance in nanocatalysts is generally minimal, high catalyst performance is thus achieved [9-14]. The influence of these processes on catalyst performance requires management of product distribution, gasoline quality, and the deactivation rate, however. Thus, an understanding of the effects of transport processes on the catalyst surface is required for efficient control of the reaction mechanisms in the reforming reactor.

Generally, the continuous enhancement of classical catalysts or nanocatalysts is focused on the production of high octane fuel with high quality aromatics and branched hydrocarbons [4, 15-19]. Usually, the formation of undesirable products leads to catalyst deactivation, which is especially true of coke formation. In this case, the catalyst performance is amended depending on the ability of the catalyst to resist the deactivation processes. Moreover, the catalyst’s crystalline structure, morphology, and performance are highly dependent on the reaction rate and the operating conditions. Additional metal types are usually utilised with platinum as promoter metals to enhance catalyst performance and stability [2, 9, 20]. Ponec and Bond [21] identified that the reason for coke formation on the catalyst surface is the appearance of a two-dimensional layer of coke precursors due to unsaturated hydrocarbon intermediates activity; they thus observed that the addition of another metal to platinum divides the metal surface into smaller areas that inhibit the polymerization of unsaturated hydrocarbons.

Blomsma et al. [2] evaluated the reaction mechanism of n-heptane reforming using Pt and Pd supported by beta-zeolite. The authors indicated that the reforming reactions of n-heptane can be achieved using a classical bifunctional mechanism and by adding a dimerization mechanism. Rahimpour [22] studied the catalytic reforming process using a comprehensive model and found that the reactor performance and the aromatics content in the reformate were significantly affected by the reaction inlet temperature. Mazzieri et al. [23] synthesised three types of reforming catalysts (Pt-Re/Al₂O₃, Pt-Sn/Al₂O₃, and Pt-Ge/Al₂O₃), and concluded that both metal and acid sites were improved by the addition of rhenium, tin, and germanium into a parent Pt/Al₂O₃ catalyst. These authors also noted that the presence of tin offered a clear reduction in the overall acidity of the Pt-Sn/Al₂O₃ catalyst. Vicerich et al. [24] investigated the effect of gallium on the performance of Pt-Re/Al₂O₃ catalysts in reforming reactions, observing that aromatic selectivity and stability were both increased in the presence of gallium for low cracking products. Zhang et al. [25] prepared three types of catalysts for reforming reactions by exchanging the Na⁺ of Y type zeolite with Mg²⁺, Ba²⁺, and Ce³⁺ ions. They noted that the Pt/CeY catalyst produced the highest activity when considered in comparison with a commercial Pt/Al₂O₃ catalyst, with a high rate of aromatization products and acceptable selectivity.

Based on this literature review, little work has focused on using nanocatalysts in the reforming processes [26-30]. A more general understanding of the effect of transport processes on the reaction mechanisms and catalyst performance is thus required, while the effects of the presence of other metals in the catalyst structure alongside platinum requires further exploration to determine the operation of catalytic reforming reactions. The main objective of the present study is thus to prepare high-performance bimetallic nanocatalysts and to observe their behaviours in reforming reactions to provide a deeper understanding of the effect of transport processes on reaction behaviours.

2. Materials and Methods
2.1 Materials
In this work, n-heptane was used as a feedstock (99.78%), as supplied by Sigma-Aldrich. Other chemicals used in this investigation, including Germanium tetrachloride (GeCl₄ 99.89%), Sodium silicate (Na₂SiO₃ 98.34%), and Sodium aluminate (NaAlO₂ 97.5%), were obtained from the Fluka Corporation, while perrenic acid solution (HReO₄, 70 % in water) was obtained from Sigma. Hexachloroplatonic acid (H₂PtCl₆ of 40% wt platinum, Riedel-De Haen AG) and hydrogen gas with a purity of 99.99% were also used in the reforming reactions.
2.2 Synthesis of nano Y-Zeolite
The preparation of crystalline nano Y-zeolite was achieved in the laboratory using the sol-gel chemical method under standard operating parameters. A mixture of NaOH solution and NaAlO$_2$ was then prepared as a seed-gel for the synthesis process. After that, the gel was mixed with Na$_2$SiO$_3$ solution using continuous stirring for 15 min before being aged for 32 hours at a temperature of 25 °C. A mixture of NaOH and NaAlO$_2$ was then synthesized from the gel feedstock. The mixture was stirred until all components in the mixture were fully dissolved, at which point a solution of Na$_2$SiO$_3$ was added as a supplement to the reaction mixture with continuous mixing at a high mixing velocity of 1,800 rpm. The final step of Y-zeolite preparation included the mixing of the aged seed-gel with the feedstock gel for 30 minutes at a mixing velocity of 1,800 rpm. The final product was crystallised at a constant temperature of 95 °C for 24 hours, then the semi-solid precipitate was filtered using a Buchner funnel. This was flowed by washing with deionized water three times, until a pH value of 9 was achieved for the produced filtrate solution. The synthesized nano Y-zeolite was then dried at 110 °C overnight and subjected to a calcination process at 500 °C for 4 hours in presence of air.

The prepared nano Y-zeolite was using multiple characterisation methods. The morphology of the zeolite was tested using scanning electron microscopy (SEM type VEGA). The crystalline structure of the prepared nano Y-zeolite was then measured using an XRD diffractometer of type 6000 (Shimadzu) while the catalyst total surface area and pore volume were measured using an N$_2$ adsorption device (BET technique).

2.3 Catalyst preparation
Three nanocatalysts were synthesised using nano zeolite Y as a support (Pt/HY, Pt-Ge/HY, and Pt-Re/HY). The structure of the prepared nano NaY zeolite was enhanced by exchanging sodium ions with ammonium ions; the sodium form nano NaY zeolite was then treated with a 3 N concentration of NH$_4$Cl solution, with 151.5g of NH$_4$Cl dissolved in 1 L of distilled water treated with 100g of zeolite. The mixture was subjected to a reflexing condition for 3 hours at a temperature of 100 °C, after which the percentage of exchanged Na$^+$ ions in NH$_4^+$ was measured to be 92.3 %. At this stage, the HY zeolite was filtered and washed twice with deionized water to remove the Cl$^-$ ions. The HY zeolite was then dried at 110 °C overnight in an electrical oven before being calcined in the presence of air at a calcination temperature of 500 °C for 6 hours.

The Pt/HY catalyst was prepared using an impregnation technique, in which the HY support was impregnated with 0.5 wt% of platinum (hexachloroplatinic acid H$_2$PtCl$_6$ containing 40% platinum). The platinum acid solution was added dropwise to the HY support with continuous stringing for 6 hours at a temperature of 30 °C. The catalyst mixture was then dried at room temperature for 24 hours with continuous mixing, which was followed by a slow evaporation process developed during 6 hours at 80 °C. The produced catalyst was then dried overnight at 110 °C before being calcined in the presence of air at 500°C for 6 hours. The prepared Pt/HY catalyst was then reduced using hydrogen gas at 450 °C for 4 h to convert the platinum from ionic form into a metallic form.

The Pt-Ge/HY and Pt-Re/HY catalysts were synthesised using the co-impregnation technique. Each metal salt was thus added separately into the Pt/HY catalyst. In the preparation of Pt-Ge/HY, a germanium tetrachloride GeCl$_4$ salt was used in the preparation process, with a weight of 1.6 mg of germanium per mL forming a solution added into the Pt/HY catalyst. The Pt-Re/HY was prepared similarly by adding the perrhenic acid solution into the Pt/HY. Each bimetallic catalyst was dried at 120 °C for 12 h, then subjected to a calcination process in the presence of air at 500 °C for 8 h. The prepared bimetallic catalysts were reduced using hydrogen gas at 400 °C for 6 hours. Thus, bimetallic Pt-Ge/HY and Pt-Re/HY catalysts were prepared with metal concentrations of 0.5 wt% for Pt, Ge, and Re, respectively.

2.4 Experimental apparatus
The evaluation of catalyst activity and selectivity was achieved using catalytic reforming pilot plant apparatus constructed from stainless steel. Figure 1 illustrates the catalytic reforming apparatus and Figure 2 shows the schematic diagram of the apparatus. The reactor length was 30 cm, with internal and external diameters of 2 and 4 cm. The catalyst bed bulk temperature was measured at the reactor centre using a temperature control system consisting of a calibrated thermocouple temperature sensor of iron-constantan (type K) ±2°C. An electrical furnace was utilised to supply the required heating rate to the reactor at a uniform distribution with constant operating temperature. The reactor pressure was measured using accurate pressure gauges, and the pressures at the gas and hydrocarbon lines were also controlled. The flowrates of n-heptane and H₂ gas were controlled using calibrated flow meters.

Figure 1. Catalytic reforming apparatus.

Figure 2. Schematic diagram of the experimental work pilot plant.

2.5 Experimental procedure
From a reaction mechanism perspective, the measurement of catalyst performance at real reforming conditions offers the clearest picture of the process. The experimental procedure was conducted in the catalytic reforming pilot plant for each catalyst type. A weight of 10 g of fresh dry catalyst was charged into the reactor to be reduced with hydrogen gas at a temperature of 400 °C for a reduction time of 4 hours. The reforming process was tested at reaction temperatures of 420, 460, 480, 500, and 520 °C. All reaction runs were carried out at atmospheric pressure with a hydrogen to n-heptane molar ratio of 2, and a weight hourly space velocity of 2. Preheating was used to raise the temperature of the feed mixture to 150 °C before it was placed in the reactor. The output products from the reactor were then analysed using gas chromatography (Shimadzu GC-2014, FID), with capillary column (ZB-FFAP) dimensions of length=30 m, I.D.= 0.32 mm, FD=0.50 μm. N₂ gas was used as a carrier for the measuring process.

3. Results and discussion

3.1 Characterisation of synthesised nano Y-Zeolite

To determine the crystallinity of the synthesised nano Y-zeolite, an XRD test was performed. Figure 3 reveals the XRD pattern of the nano Y-zeolite synthesised using the sol-gel method. All of the archived peaks in the XRD results accord with the corresponding planes of standard Y-zeolite [8,17]. Figure 3 thus illustrates that the synthesised nano Y-zeolite was highly crystalline with high purity. Moreover, the XRD results show that no impurities existed in the zeolite structure, as the general peaks that characterise pure nano Y-zeolite crystal were located within the standard structure of the nano Y-zeolite [21]. These XRD results were in compliance with the work of Ahmedzeki and Al-Tabbakh [17] and Lane et al. [20].

![Figure 3. XRD pattern of nano Y-zeolite synthesised using the sol-gel method.](image)

Additionally, during the chemical analysis of the prepared nano Y-zeolite, the SiO₂/Al₂O₃ ratio was found to have a value of 3.52. Figure 4 presents the SEM photograph of the prepared nano Y-zeolite at two magnifications, clearly showing spherically shaped particles of nano Y-zeolite. The particle size was determined by particle size analysis to have an average diameter of about 84 nm, while the BET test showed the total surface area of the prepared nano Y-zeolite to be 620 m²/g, with a pore volume of 0.46 cm³/g. Based on these results, the synthesised nano Y-zeolite displayed the standard properties of nano Y-zeolite [1,8,28].
Figure 4. SEM photographs of synthesised nano Y-zeolite at two magnifications.

3.2 Influence of temperature on catalyst performance

Catalyst activity, selectivity, and lifetime are the main criteria underlying reaction mechanisms and transport process interactions with chemical reactions. Table 1 illustrates the general specifications of the three types of synthesised catalysts. The results indicate that the total surface area of the Pt/HY, Pt-Ge/HY, and Pt-Re/HY nanocatalysts were 622, 648, and 631 m²/g, respectively. The use of nano Y-zeolite as a support thus improved the total surface area of the mono (Pt/HY) and the bimetallic (Pt-Ge/HY and Pt-Re/HY) nanocatalysts. This high surface area is important for enhancing chemical reactions as well as to meet high dispersion metal requirements. According to Blomsma et al. [2], Li et al. [9], and Lin et al. [15], the advantage of the presence of additional metals in a catalyst structure to form a bimetallic catalyst may be related to maintaining the high dispersion of platinum without aggregation where the other metal combines with platinum to prevent sintering or coke formation from reducing the catalyst surface area.

Table 1. General properties of synthesised nanocatalysts.

| Specifications          | Pt/HY | Pt-Ge/HY | Pt-Re/HY |
|------------------------|-------|----------|----------|
| Metal Weight (%)       | 0.5% Pt | 0.5% Pt and 0.5% Ge | 0.5% Pt and 0.5% Re |
| Surface Area (m²/g)    | 622   | 648      | 631      |
| Pore Volume (cm³/g)    | 0.46  | 0.44     | 0.44     |
| Pore Size (Å)          | 22    | 21       | 21       |
| Content of Cl⁻(wt%)    | 0.5   | 0.5      | 0.5      |

The influences of reaction temperature on the production of aromatics, iso-paraffins, and cracking gases over the three types of nanocatalysts are shown in Figures 5, 6, and 7, respectively. A fixed-bed reforming reactor was operated at a hydrogen/n-heptane ratio of 2 and WHSV of 2 for all experimental runs. The catalyst performances were evaluated at temperatures of 440, 460, 480, 500, and 520 °C. As shown in Figure 5, the reaction temperature played a major role in governing the production of aromatic hydrocarbons. The results clearly indicate that the best n-heptane reforming temperature in terms of highest aromatics yield was 480 °C. Moreover, the results indicate that the reformate produced at 480 °C showed octane values of 84, 91.5, and 87 for Pt/HY, Pt-Ge/HY, and Pt-Re/HY, respectively. The Pt-Ge/HY catalyst showed the highest octane number at this reaction temperature, and this enhancement in octane number is attributed to the high reaction rate of the dehydrogenation of naphthene, thus
generating more aromatic hydrocarbons. These results agree with the work of Aberuagba and Susu [6] and Tregubenko et al. [10].

The nano-bimetallic catalysts produced more of the desired products than the mono Pt/HY nanocatalyst. Many authors have highlighted the importance of the other metal in bimetallic catalysts in terms of supporting a greater volume of produced aromatic hydrocarbons in the reformate. Ahmedzeki and Al-Tabbakh [17] and Olah and Molnár [27] pointed to the operating temperature as the main factor in reforming reactions; by increasing or decreasing reactor temperature, the quality of produced reformate can thus be easily varied. Based on the catalytic reforming mechanism, reformate products can be initiated from three chemical reactions, the aromatization reaction, isomerization reaction, and cracking reaction. All tests indicate that the process temperature is a highly significant parameter in determining the quality of produced reformate, however. The main constituent of the produced aromatics was toluene, which formed about 53% of the total produced aromatics at 480 °C. It is thus important to mention that new environmental regulation requirements restrict the percentage of aromatics in gasoline fuel due to human health requirements, so these should be minimised [25,30].

![Figure 5](image-url)

**Figure 5.** Produced aromatics (mole %) from the n-heptane reaction at different reaction temperatures over three types of nanocatalysts.

The concentrations of produced iso-paraffins over the three types of prepared nanocatalysts as a function of reforming temperature is shown in Figure 6. This figure shows that the produced reformates contain high quantities of isomers of high octane number. The production of branched paraffin by n-heptane reactions is usually subjected to a bifunctional mechanism. Here, the produced branched isomers were produced quickly and appeared at all reaction temperatures and conversions [18,26]. The maximum number of branched isomers was noted using the Pt-Ge/HY nanocatalyst. The production volumes of branched isomers over the three catalysts at the best reaction temperature (480 °C) were 18, 16.5, and 14.2 mole% for Pt-Ge/HY, Pt-Re/HY, Pt/HY nanocatalysts, respectively, suggesting the following sequence for nanocatalyst activity among isomers: Pt-Ge/HY > Pt-Re/HY > Pt/HY. The production of high octane number branched isomers in a reforming reaction is a good indication of the creation of a high quality and safe gasoline fuel that meets the requirements of internal combustion engines [5,7,15]. In addition, the number of branched isomers produced was reduced with an increase in reforming temperature due to the initiation of cracking reactions [16,22].
The influence of reforming temperature on cracking product (C$_1$-C$_4$) distribution over Pt/HY, Pt-Ge/HY, and Pt-Re/HY nanocatalysts is shown in Figure 7. The cracking gases were produced in minimal quantities over the nano-bimetallic catalysts at all tested reaction temperatures. The results in Figure 7 indicate that the activity of the cracking reaction is highly affected by the reforming temperature. Pt/HY is the most active nanocatalyst for cracking reactions, providing the highest selectivity for C$_1$-C$_4$ gases. Generally, all cracking products resulting from the reforming reactions at a given temperature over the three types of nanocatalysts showed low values in comparison with other reactions such as aromatization or isomerization. This behaviour can be attributed to the low selectivity of nanocatalysts toward cracking reactions. Furthermore, high reaction temperatures produce higher levels of cracking products, as shown in Figure 7.

The distribution of produced gases is thus an outcome of the complex mechanisms underlying the n-heptane hydrocracking reactions. These mechanisms are highly dependent on a high reaction level of conversion and the applied temperature of the reforming reaction. Thus, the recombination of propane intermediates with n-heptane produces more cracking products in the gasoline produced in this process [2,9], in accord with Iranshahi et al. [11], Peyrovi et al. [13], and Rahimpour [22].
3.3 Catalyst deactivation

Reforming catalyst activity usually undergoes a clear decrease due to the deactivation processes that appear on the catalyst surface as operating time increases. These processes include coke formation on the catalyst surface, poisoning of active catalyst sites by contaminants, and sintering of catalyst surface area [23,26]. Figure 8 illustrates the conversion of n-heptane as a function of reaction time for the three synthesised catalyst types at the best reaction temperature of 480 °C, with WHSV=2, and a hydrogen/n-heptane ratio of 2. The results in Figure 8 indicate that the highest n-heptane conversion was noted at the initial reaction time and that this decreased slowly with reaction time due to deactivation processes, particularly coke formation. It was observed that the Pt/HY, Pt-Ge/HY, and Pt-Re/HY catalysts showed total initial conversions of 53, 85, and 66%, respectively. Many authors, such as Burghardt [14], Beltrami et al. [16], and Vicerich et al. [24], have pointed out that the presence of coke formation on active sites creates a major deactivation problem in reforming units by reducing catalyst activity. The same conclusion was noted by Raouf et al. [26] and Hamoule et al. [29].

Shakor et al. [18] used a kinetic model to predict results in a real industrial naphtha reforming plant using a Pt/Al2O3 catalyst. They observed that catalyst activity decreased after an operating time of for years by 58.8% as compared to original activity. Borgna et al. [20] investigated the effects of coke and sulphur content on the performance of Pt and Pt-Re supported on alumina catalysts and using n-hexane as a reforming reaction feedstock, observing that the sulphur and carbonaceous compounds were precipitated on the metallic sites and reduced catalyst activity. All these studies highlight the importance of careful evaluation of deactivation problems in catalytic reforming processes due to their direct effect on catalyst performance.

![Figure 8. Conversion of n-heptane with reaction time at 480 °C, WHSV=2, and H2/n-heptane =2.](image)

Based on the catalytic reforming reaction, the dehydrocyclization and aromatization reactions are dependent on the bifunctional catalyst mechanism. The dehydrogenation and hydrogenolysis reactions are thus usually achieved on metallic sites, while the reaction of isomerization appears on acid sites. Many authors have pointed to the importance of careful management of the reactions of hydrogenation and dehydrogenation (metal sites) and zeolite (acid sites) to produce high-quality gasoline [2,7,17]. Moreover, it is clear that as carbon wastes are deposited inside the catalyst surface area, the reforming reaction mechanism will cease the production of desired products.

Figure 9 illustrates the results of desired product selectivity (aromatics and iso-paraffins) as a function of reaction time over 14 hours on-stream using Pt/HY, Pt-Ge/HY, and Pt-Re/HY catalysts. Pt-Ge/HY and Pt-Re/HY (bimetallic catalysts) showed the highest selectivity at initial operation, with values of 95% and 83%, respectively in comparison with the 69% seen for the Pt/HY catalysts. Further, the prepared nanocatalyst type Pt-Ge/HY represented a more stable catalyst for reforming reactions over reaction time, which can be attributed to the effect of Ge, being characterised by high stability with lower coke formation. The decreasing behaviour in terms of desired product selectivity is related to the reduced catalyst surface reaction area caused by coke formation. The deposition of such material on the catalyst
surface reduces the availability of catalyst active sites and thus the quantity of Lewis and Brønsted acid sites in the catalyst. These results agree with Zhang et al. [19] and Mazzieri [23]. The problem of carbon formation is thus the chief challenge in selecting catalytic reforming catalysts as it reduces the catalyst activity, selectivity, and stability with reaction time.

![Figure 9](image.png)

**Figure 9.** Variation of product selectivity (aromatics and isomers) with reaction time at 480 °C, WHSV=2, and H₂/n-heptane = 2.

### 3.4 Effect of heat and mass transfer processes on nanocatalyst performance

The temperature effect is the key factor in determining the quality of gasoline fuel produced. The results of the present work demonstrate that the aromatics yield was improved by 11% for the Pt-Ge/HY nanocatalyst as the reforming temperature increased from 460 to 480 °C, while the production of iso-paraffins was also clearly enhanced at 480 °C. Similar behaviour was noted for the other two prepared nanocatalysts, with smaller improvements. From a catalytic reforming reaction thermodynamic perspective, dehydrogenation and dehydrocyclization reactions are highly endothermic reactions which lead to a clear decrease in reactor temperature. A continuous heat supply to the reaction mixture inside the reactor is thus required. This case further emphasises the importance of heat transfer operations to keep reactions stable in terms of thermodynamic requirements [4,8]. Moreover, the dehydrogenation reactions achieved on the metallic sites of the catalysts were characterised by very fast mechanisms in comparison with other reactions in the reforming units, while the slowest catalytic reforming reaction was the hydrocracking reaction, characterised by exothermic behaviour. These results indicate that the bimetallic Pt-Ge/HY and Pt-Re/HY nanocatalysts showed the highest values of selectivity and stability with low deactivation rates at the optimal reaction temperature of 480 °C. This can be attributed to the metals working as reducing agents for hydrogenolysis reactions on the nanocatalyst surface [1,28,30].

Rahimpour [22] noted that reactor performance is highly affected by the reactor input temperature, with produced aromatics in the reformate increased with increasing reaction temperatures. The quality of produced reformate fuel is mainly determined by catalyst activity, selectivity, and stability, however, and these are significantly affected by the transport processes on the catalyst surface as well as other reaction parameters such as reaction kinetics, reaction temperature, pressure, and type of catalyst deactivation mechanism [6,9,11,25]. In this study, the Pt-Ge/HY catalyst provided higher stability at a reaction temperature of 480 °C in comparison with the other two catalysts, Pt/HY and Pt-Re/HY. This excellent activity can be attributed to the high surface area of the nanocatalyst and to the high dispersion of both noble metal (Pt) and promoting metal (Ge). The high dispersion of platinum in the catalyst micropores and the intensive interaction of Pt with the HY zeolite provided high nanocatalyst activity with a long life time [3,7].
The results also demonstrate that Pt and Ge metals play a key role in the reaction of dehydrogenation by converting n-heptane into 1-heptene. According to Xu et al. [5], the presence of stable platinum clusters alongside another metal in the zeolite channels works by converting the 1-heptene to aromatics using a dehydrocyclization reaction. The results of this work indicate that the product distribution in the reforming reaction is highly affected by the reaction temperature, type of the used bimetallic, high surface area of nanocatalyst, and mass transfer operation inside the texture of the nanocatalyst, however. An understanding of the influence of the Ge and Re particles on catalytic performance and stability was the main target of this study, and the performance evaluation process (Figures 8 and 9) indicated that the Pt-Ge/HY and Pt-Re/HY nanocatalysts offered the highest catalytic activities due to their high metal dispersions and the low catalyst deactivation rates. Accordingly, the high performance of bimetallic nanocatalysts was attributed to the influence of Ge and Re metals as promoter agents on the catalyst surface.

4. Conclusions

The reactor performance is a function to heat transfer and mass transfer processes. Then, the use of fixed-bed reactors as a multiphase reaction system for the reforming process requires a more in-depth understanding of the relationships between transport processes and catalyst surface area. Three types of nanocatalysts (Pt/HY, Pt-Gr/HY, and Pt-Re/HY) were synthesised successfully and used in n-heptane reforming reactions. The monitoring of the produced gasoline quality showed that mass transfer mechanisms and heating processes are the chief factors offering these nanocatalysts the ability to operate at high performance levels. The results indicated no chlorine addition or loss was required, minimising the problem of corrosion of the reforming unit. The best reaction temperature was noted to be 480 °C, which offered high aromatization and isomerization products for all three types of catalysts, with low cracking gases. The activity of the prepared nanocatalysts flowed in the sequence of Pt-Ge/HY > Pt-Re/HY > Pt/HY. It was also observed that the hydrogenolytic activity of the reforming reaction reduced significantly in bimetallic catalysts; both the metal and acid sites of the catalyst were improved dramatically by the combination of Ge and Re to form bimetallic catalysts. These bimetallic nanocatalysts also provided higher stability than the mono-metal nanocatalyst (Pt/HY) due to a decrease in the polymerization reactions of unsaturated hydrocarbons that can generate coke formations.

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