Vol. 22, n.°1, pp. 25-34, 2023
Revista UIS Ingenierías
Página de la revista: https://revistas.uis.edu.co/index.php/revistauisingenierias

Toluene hydrogenation and ring-opening on bimetallic Pd-Pt/HY catalysts

Hidrogenación y apertura de anillo de tolueno en catalizadores bimetálicos Pd-Pt/HY

Trino Romero [1a, 4], Luis Melo [1b], María Esparragoza [1c], Rosarmy Ávila [1d], Alexander Moronta [2a], Gabriela Carruyo [2b], Luis García [1e, 3]

[1] Laboratorio de Refinación y Petroquímica, Escuela de Ingeniería Química, Universidad Central de Venezuela, Venezuela. Orcid: 0000-0002-1976-0873 [a], Emails: trinojavierromero@gmail.com [a], melol@ucv.ve [b], esparragoza1m@gmail.com [c], rosarmyav@ucv.ve [d], luisgarcía351@gmail.com [e]
[2] Instituto de Superficie y Catálisis, Facultad de Ingeniería, Universidad del Zulia, Venezuela.
Email: ajmoronta@gmail.com [a], gabcarruyo@gmail.com [b]
[3] Departamento de Química y Ciencias Exactas, Universidad Técnica Particular de Loja, Ecuador.

Received: 2 April 2022. Accepted: 15 September 2022. Final version: 31 December 2022.

Abstract

Bimetallic Pd-Pt/HY catalysts prepared by the co-impregnation method with an atomic variation of Pd/Pd+Pt were studied to convert toluene and methylcyclohexane. The catalysts were characterized by the BET method, chemisorption of CO by the pulse method, programmed temperature reduction (H_2-TPR), and programmed ammonia thermo-desorption (NH_3TPD). Results of chemisorption of CO and H_2-TPR for Pd-Pt/HY catalysts suggest the existence of a strong interaction between Pd and Pt. The NH_3-TPD showed that incorporating metals influences the percentage of relative distribution of weak/strong acid sites presented in decreasing order of acidity: Pd_0Pt_{100}/HY>$Pd_{100}Pt_0$/HY>$Pd_{33}Pt_{67}$/HY. Atomic composition Pd/Pd+Pt equal to 0.33, and relative distribution of weak/strong acid sites equal to 2, favor hydrogenation of toluene to methylcyclohexane in metal sites and subsequent skeletal isomerization in the acidic sites through dimethylcyclopentane intermediate and ring-opening in the metal sites, leading to increased formation of n-heptane relative to iso-heptane.

Keywords: toluene hydrogenation; ring-opening; platinum-palladium; HY zeolite.

Resumen

Catalizadores bimetálicos Pd-Pt/HY preparados por el método de co-impregnacion con variación atómica de Pd/Pd+Pt fueron estudiados en la reacción de conversión de tolueno y metilciclohexano. Los catalizadores se caracterizaron por el método BET, quimisorción de CO por el método de pulso, reducción programada de temperatura (H_2-TPR) y termodesorción programada de amoniaco (NH_3-TPD). Los resultados de la quimisorción de CO, la disminución de TOF de la reacción de tolueno a 110ºC por la adicción de Pd y el H_2-TPR de los catalizadores Pd-Pt/HY sugieren la existencia de una fuerte interacción entre Pd y Pt. El NH_3-TPD mostró que la incorporación de metales influye en el porcentaje de distribución relativa de sitios ácidos débil/fuerte que se presentan en orden decreciente de acidez: Pd_0Pt_{100}/HY> $Pd_{100}Pt_0$/HY> $Pd_{33}Pt_{67}$/HY. La composición atómica Pd/Pd+Pt = 0.33, y un porcentaje de distribución

ISSN Printed: 1657 - 4583, ISSN Online: 2145 - 8456.

How to cite: T. Romero, L. Melo, M. Esparragoza, R. Ávila, A. Moronta, G. Carruyo, L. García, “Toluene hydrogenation and ring-opening on bimetallic Pd-Pt/HY catalysts,” *Rev. UIS Ing.*, vol. 22, no. 1, pp. 25-34, 2023, doi: https://doi.org/10.18273/revuin.v22n1-2023003

relativa de sitios ácidos débil/fuerte igual a 2, favorece la hidrogenación del tolueno a metilciclohexano en los sitios metálicos y la posterior isomerización del esqueleto en los sitios ácidos a través del intermedio di-metilciclopentano seguido de la apertura del anillo en los sitios metálicos, lo que conduce a una mayor formación de n-heptano en relación con el iso-heptano.

Palabras clave: hidrogenación de tolueno; apertura de anillo; platino-paladio; zeolita HY.

1. Introduction

The environmental restrictions are becoming more demanding as regards the quality of diesel. The improvement of diesel fractions may be reached by (i) decreasing the sulfur content to less 50 ppm (ii) reducing the content of aromatics to less 10 vol.% and (iii) increasing the cetane number from 51 to 58 by hydrogenolysis/ring-opening reactions. The polyaromatic and naphthenic hydrocarbons in diesel produce more exhaust emission and poorer ignition properties due to low cetane number. To improve cetane number the ring opening is a solution [1], [2], [3], [4], [5], [6].

Wang et al. studied hydrogenation and selective ring opening of 1,2,3,4tetrahydronaphthalene (THN) on 0.3Pt/USY. The Pt reduced the total number of the acid sites, especially the strong acid sites of USY according to the results of NH_3TPD and Py-IR., high conversion of THN and the good selectivity of ring-opening were due to appropriate relation metal and acid sites [7]. Pérez-Guevara et al. studied the selective ring-opening of ethylbenzene on bifunctional catalyst Pt–Ir over Hierarchical USY Zeolite reported an adequate metal-acid balance in ring-opening of aromatic compounds, producing low branched paraffin and low cracking activity [6].

Arribas and Martinez have shown that Pt/USY catalysts have a very high methylnaphthalene conversion under the reaction conditions studied. They suggest a first step of the monomolecular mechanism for complete and or partial hydrogenation of 1-methylnaphthalene in the metallic sites of Pt and subsequent hydrocracking in the Brönsted acid sites of the USY zeolite in the bifunctional catalyst of Pt/USY [8]. Kubicka et al. demonstrated that the opening of the decalin ring is sensitive to temperature and reaction pressure in their studies on Ir/H-Beta catalysts [9].

Thomas et al. has shown on hydrogenation of toluene over Pt-Pd/FAU that Pd content substantially increases the sulfur tolerances. The effect of support acidity on S tolerances is observed only in high sulfur coverage [10]. Fujikawa et al. studied the hydrogenation properties of aromatic compounds in average distillates on Pt-Pd/$SiO_2Al_2O_3$, reported that for a weight ratio of Pd/Pt+Pd of 0.7 the hydrogenation of aromatics becomes maximal [11]. Navarro et al. analyzed the hydrogenation of toluene and naphthalene in the presence of dibenzothiophene on bimetallic Pt-Pd/SiO_2-Al_2O_3 catalysts. Using the TPR analysis, FTIR and XPS revealed the existence of a strong interaction of Pt-Pd, in which the electronic deficiency of Pt evidenced, attributing this as a contribution to the resistance of the bimetallic particles of Pt-Pd [12].

McVicker et al. investigated the selective ring-opening of naphthenic molecules of different metals supported on USY zeolite and showed that for the Ir/USY catalyst, it presents a higher activity and selective hydrogenolysis/ring-opening of methylcyclohexane with respect to the Pt/USY catalyst is present. In addition, they have suggested that ring-opening rates over iridium are directly proportional to the number of substituted, unencumbered C–C bonds and markedly decrease with increasing ring substitution [13].

Kustov et al. determined that acidity is essential for transforming multiple compounds such as decalin but not for simple rings such as cyclohexane that opened by a monofunctional metal catalyst [14]. Sugii et al. (2006) proposed for the conversion of methylcyclohexane in the Ir/H-β catalyst a bifunctional mechanism in which the contraction of the ring in a dimethylcyclopentane intermediate occurs at the acid sites of the zeolite and the hydrogenolysis/opening of the dimethylpentane ring occurs at the metal sites of Ir [15].

In this work, the hydrogenation and ring-opening of toluene and methylcyclohexane over bimetallic PdPt/HY catalysts were studied to understand the reaction scheme's opening monoaromatic hydrocarbon in linear and/or branched paraffin.

2. Experimental

2.1. Preparation of catalysts

The zeolite type Faujasita-H with a cell Unit $Na_{0.9}H_{43}Al_{44}Si_{148}O_{384}$, Si/Al ratio of 3.4, and specific surface area (SA) of 734m^2/g used to prepare the series of PdPt/HY by the method of co-impregnation. The metals incorporated to obtain catalysts with 0.4% weight of metal per gram of zeolite, with the different atomic proportions between the platinum and palladium: Pd/Pd+Pt equal to 0, 0.33, 0.50, and 1.0. The aqueous solutions of $[Pt(NH_3)_4]Cl_2.H_2O$ (Sigma-Aldrich, >99.9%) and $[Pd(NH_3)_4]Cl_2.H_2O$; (Sigma-Aldrich, >99.9%), were incorporated simultaneously in a 0.1 M solution of ammonium acetate (CH_3COONH_4, Sigma-Aldrich, 99.9%) as a competing agent containing the zeolite HY, followed by drying at 120ºC and calcination at 500°C overnight.

2.2. Characterization

The catalysts prepared, dried at 120°C calcined at 500°C, and analyzed by the atomic absorption technique to determine metals' content. Surface area (SA) data obtained by the N_2 adsorption BET method, using nitrogen a -196°C, in Micromeritics equipment, model 2010. The hydrogen temperature-programmed reduction experiments (H_2-TPR) carried out between 25°C and 850°C, using a flow of Ar/H_2 (30 cm^3/min, 5 vol. % H_2) and a temperature gradient of 10°C/min. The consumption of H_2 is controlled by an online chromatograph equipped with TCD.

Thermodesorption of ammonia (NH_3-TPD) was used to evaluate samples' acidity. The samples were heated at 100°C under flowing N_2 (30 cm^3/min) for an hour and then allowed to cool to room temperature. Then the sample was placed in-line, and pulses of ammonia injected at room temperature until saturation. Subsequently, the sample was subjected to a heating program from 25°C to 600°C with a rate of 10°C/min by performing desorption in nitrogen flow. The adsorption of CO in the catalysts measured by the pulse method and expressed in µmoles of CO/g-catalyst. The solids reduced in situ at 500°C for one hour under flowing hydrogen, then allowed room temperature and submitted to consecutive injections of pulses of 1.88 µmoles of CO to saturate the accessible metallic surface until no adsorption detected.

2.3. Activity measurements

Toluene and methylcyclohexane reaction carried out at 250ºC in a fixed-bed micro-reactor (Pyrex glass, 15 mm internal diameter) at atmospheric pressure, using toluene (HC) (Aldrich, 99.8% anhydrous) and methylcyclohexane (Aldrich,> 97 % anhydrous), injected around 2 ml/h employing compact pump, in a H_2/HC molar ratio of 9, spatial velocity of 6 h^{-1} and temperature of 250°C. The catalysts' reaction rate is determined by zero-time extrapolation of the conversion curves as a function of time. The rate calculated from Eq. 1:

$$r = F.\ \tau /N \qquad (1)$$

F is the feed rate of toluene (or methylcyclohexane) per hour, τ is the conversion extrapolated to zero time, and N is the total metal (Pd+Pt) catalyst sample. The conversion of toluene was also studied at 110°C, which was considered a sensitive reaction to the structure [16]. The rate constant for toluene conversion was calculated after one hour on stream (in h-1.g), assuming the pseudo-firstorder kinetics to toluene using the following expression: $k = -(F/m) \ln(1-x)$

Where k is the pseudo-first-order reaction constant for toluene, F is the molar flow of reactant (mol.h^{-1}), and m refers to the metal atoms per gram of catalyst (mol.g-1) [17]. The reaction products were analyzed by on-line-gas chromatography (HP 6890 model, with flame ionization detector) using a Chrompack Sil 5CB column (5% of methyl phenyl silicone, length 30 m, internal diameter 0.25mm). The reaction products for the conversion of toluene defined in hydrogenation (HT): methylcyclohexane, Ring-opening (RO): n-heptane and iso-heptane, and transalkylation (TAT): xylenes (ortho, meta, and para) and aromatic A_{8+}.

For the transformation of methylcyclohexane, the products defined in Ringopening (RO): n-heptane and iso-heptane and dehydrogenation (DH): toluene. It is important to note that benzene was not observed, so it presumed that it converted to toluene by transalkylation with xylenes and disappeared as a promoter of coke formation. Before carrying out the reaction, the catalysts reduced in situ to a hydrogen flow (30 cm^3/min) to a heating ramp of 10°C/min until reaching the temperature of 500°C, where it remained for one hour.

3. Results and discussion

3.1. Catalysts characterization

Table 1 summarizes the nominal composition and carbon monoxide chemisorption results obtained by the pulse method. The surface area (SA) results are 723±11 m^2/g, practically unaffected by the total content of 0.40% by weight of metals. The chemisorption of CO in the monometallic catalyst of Pd ($Pd_{100}Pt_0$/HY) is 3 times higher than Pt (Pd_0Pt_{100}/HY), which may be due to the strong metal-support interaction, which is in the Pt/HY higher than Pd/HY. Tri et al. demonstrated by the selective chemisorption of CO using the infrared technique, the existence of a strong interaction of the Pt with the surface of the zeolite HY evidenced by the displacement of the binding energy at higher frequencies υCO to the Pt/Al_2O_3 catalyst [18]. The atomic ratio CO/Pt and CO/Pd in Pt and Pd's monometallic catalysts are similar, respectively, 0.12 and 0.17 with an absolute difference of ± 0.05.

Table 1. Nominal composition and carbon monoxide chemisorption of catalysts

Catalysts^a	**Pt (wt.%)**	**Pd (wt.%)**	**CO**^{b} **(µmol/g)**	**CO/ Pd+Pt (mol/mol)**
Pd_0Pt_{100}/HY	0.40	-	2.4	0.12
$Pd_{33}Pt_{67}$/HY	0.34	0.09	14,3	0,55
$Pd_{50}Pd_{50}$/HY	0.25	0.14	18.9	0.73
$Pd_{100}Pt_0$/HY	-	0.40	6.3	0.17

^{a} Percentage of metal atoms: % Pd = (Pd/Pd+Pt) x100
^{b} Chemisorption of CO by Pulse method.

On the other hand, the atomic ratio of CO/Pd+Pt for the bimetallic catalyst $Pd_{33}Pt_{67}$/HY and $Pd_{50}Pt_{50}$/HY is equal at 0.55 and 0.73, respectively.

The result indicates that interaction with the support disappeared with concern for the monometallic catalysts Pd_0Pt_{100}/HY and $Pd_{100}Pt_0$/HY, which may be probably to the formation of bimetallic alloys of Pd-Pt [17], [19], [20], [21]. The H_2-TPR profiles of the Pd-Pt/HY catalysts are shown in Figure 1.

The $Pd_{100}Pt_0$/HY monometallic catalyst signals showed two low-intensity peaks at 196°C and 596°C and one more intense peak at 455°C.

The Pd_0Pt_{100}/HY monometallic catalyst showed three reduction peaks: a low-intensity peak at 511°C and two more intense peaks at 638°C and 674°C in which these signals are attributed to the reduction of Pt^{2+} and Pd^{2+} located in different positions in the zeolite Y. When the peak is formed at lower temperatures (α) cations are located in large cavities, while for the ones formed at higher temperatures, the cations are in sodalite (β) or hexagonal prism cavities (γ). For the Ni/HY catalyst, signals have been reported at 389ºC (α), 493ºC (β) and 772ºC (γ) and for Pt/HY at 240 ºC (α), 450ºC (β) and 500-600ºC (γ) [22]. Regarding the Pd/HY catalyst, the TPR signal at 145ºC and 414ºC and of Pt/HY 503ºC are attributed to the Pt^{2+}, and Pd^{2+} is located in large and sodalite cavities. For the Ir/HY catalyst, the higher reduction peak above 725 ºC is attributed to reducing those oxides in hexagonal prisms [23].

According to the TPR signals results for the Pt/HY catalyst, the signals of 511ºC, 638ºC, and 674ºC are attributed to Pt, preferably located in sodalite or hexagonal prism cavities.

For TPR signal at 196ºC, 455ºC, and 597ºC of Pd/HY are attributed to Pd^{2+} located in large and sodalite cavities.

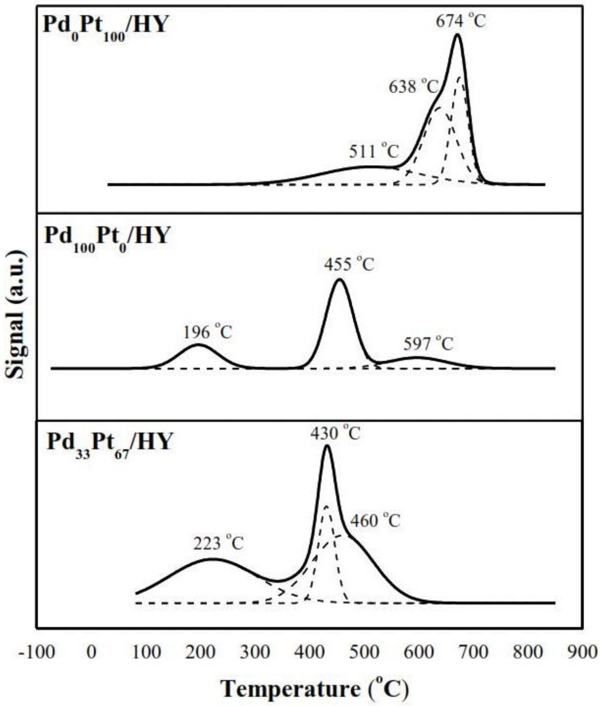


Figure 1. Hydrogen temperature-programmed reduction (H2-TPR) on Pd-Pt/HY catalysts.

H_2-TPR signals for the $Pd_{100}Pt_0$/HY and Pd_0Pt_{100}/HY catalysts evidence that there are different species of metallic Pd and Pt distributed on the surface of zeolite HY, with reduction and hydrogen consumption characteristics depending on the chemical environment in which they located, in the outer surface of the zeolite [24]. The H_2-TPR signal corresponding to the bimetallic catalyst Pd_{33} Pt_{67}/HY showed one peak of medium intensity at 430°C and two broad peaks of greater intensity at 223°C and 460°C. Besides, it observed that the presence of Pd inhibits hydrogen consumption of Pt, indicated by the disappearance of peaks at 511°C, 638°C and 674°C characteristics of Pd_0Pt_{100}/HY catalyst, showing that there is a strong interaction of Pd with Pt, where Pt less exposed in the surface of the solid [19], [20], [21]. The NH_3-TPD profiles of the Pd-Pt/HY catalysts were shown in Figure 2.

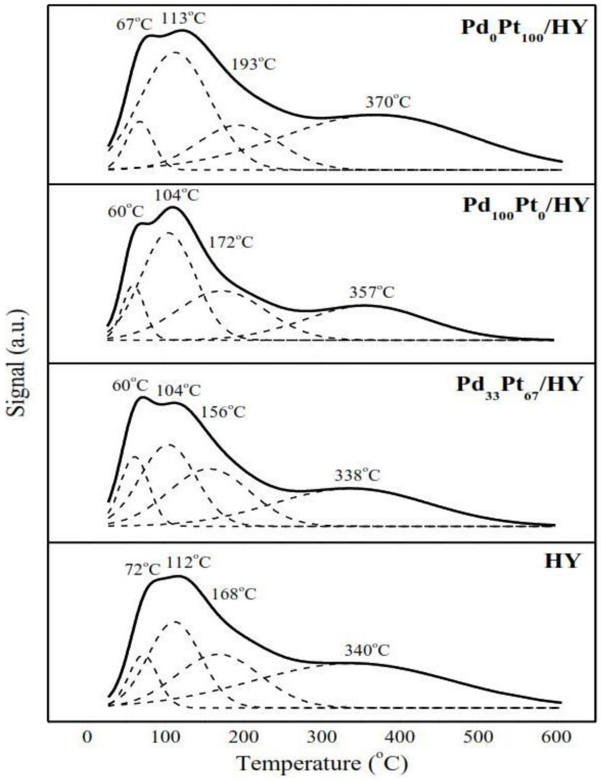


Figure 2. Thermodesorption of ammonia (NH3-TPD) on Pd-Pt/HY catalysts.

The percentage of weak and strong relative acidity distribution for the HY support and bimetallic Pd-Pt/HY catalysts are reported in Figure 3.

For TPR signal at 196ºC, 455ºC, and 597ºC of Pd/HY are attributed to Pd^{2+} located in large and sodalite cavities.

H_2-TPR signals for the $Pd_{100}Pt_0$/HY and Pd_0Pt_{100}/HY catalysts evidence that there are different species of metallic Pd and Pt distributed on the surface of zeolite HY, with reduction and hydrogen consumption characteristics depending on the chemical environment in which they located, in the outer surface of the zeolite [24].

The H_2-TPR signal corresponding to the bimetallic catalyst Pd_{33} Pt_{67}/HY showed one peak of medium intensity at 430°C and two broad peaks of greater intensity at 223°C and 460°C. Besides, it observed that the presence of Pd inhibits hydrogen consumption of Pt, indicated by the disappearance of peaks at 511°C, 638°C and 674°C characteristics of Pd_0Pt_{100}/HY catalyst, showing that there is a strong interaction of Pd with Pt, where Pt less exposed in the surface of the solid [19], [20], [21]. The NH_3-TPD profiles of the Pd-Pt/HY catalysts were shown in Figure 2. The percentage of weak and strong relative acidity distribution for the HY support and bimetallic Pd-Pt/HY catalysts are reported in Figure 3.

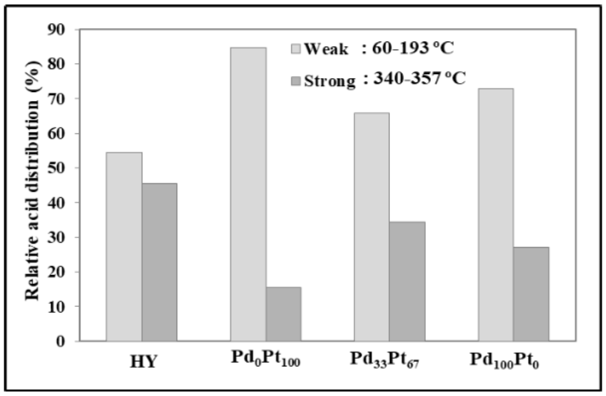


Figure 3. Relative Acid distribution (%) by NH3-TPD on Pd-Pt/HY catalysts.

It demonstrated that Pt and Pd's incorporation impacts the percentage relative of acid distribution in the Pd-Pt/HY catalysts during the catalyst preparation process. The calcined HY zeolite showed a relative distribution ratio of weak/strong acid sites of 1 and for the monometallic catalysts of Pt (Pd_0Pt_{100}/HY) and Pd ($Pd_{100}Pt_0$/HY) of 6 and 3, respectively. The bimetallic catalyst $Pd_{33}Pt_{67}$/HY exhibited a weak/strong acidity ratio of 2 [23], [26], [27].

3.2. Catalytic hydrogenation of toluene at 110°C

Constant kinetic (k) rate and TOF of the toluene at 110°C as a function of the atomic percentage of Pd in the Pd-Pt/HY catalysts was shown in Table 2.

Methylcyclohexane was the only product at 110°C, and the conversion of toluene was less than 5.0%. The reaction rate (k) of the toluene reaction was determined at 110°C, assuming a kinetic of pseudo-first-order for toluene. The rate constant for monometallic Pd_0Pt_{100}/HY catalyst is similar to bimetallic $Pd_{33}Pt_{67}$/HY to k = 0.54 ± 0.1 (s^{-1} g), then declines 50% of Pd and the monometallic Pd catalysts. The ratio of constant kinetic rate k_{Pt}/k_{Pd} equal to 15.4 is similar to those reported by Thomas for the ratio rate of intrinsic velocities of Pt/Pd equal to 15.5 [10]. Tri et al. (1982), studding the Pt catalysts supported on HY zeolite, demonstrated a high hydrogenation of toluene to benzene due to high electron deficiency Pt sites ($Pt^{\delta+}$) [18].

H_2-TPR for Pd_0/HY catalyst at 674ºC and high hydrogenation activity of toluene in methylcyclohexane evidence the electro-positive character of the Pt sites due to the strong interaction of the Pt with the support.

Table 2. The constant kinetic (k) rate and TOF of the toluene reaction at 110ºC on Pd-Pt/HY catalysts

Catalyts	k (s^{-1} g)	^{a}TOF (s^{-1})
Pd_0Pt_{100}/HY	0.43	19.3
$Pd_{33}Pt_{67}$/HY	0.64	5.5
$Pd_{50}Pd_{50}$/HY	0.07	0.7
Pd100Pt0 /HY	0.03	1.3

^{a} TOF = moles converted per mole-accessible metal by CO and per seconds.

However, it is observed that the $Pd_{33}Pt_{67}$/HY catalyst's turnover frequencies were lower than with the monometallic Pt (Pd_0Pt_{100}/HY) but higher than with Pd ($Pd_{100}Pt_0$/HY), for bimetallic $Pd_{50}Pt_{50}$/HY was observed a similar value than Pd catalyst. This dilution effect of Pt on bimetallic Pt-Pd particles formed was supported by the disappearance of TPR signal corresponding to the monometallic of Pt catalyst (Pd_0Pt_{100}/HY) concerning the signals observed in the bimetallic of $Pd_{33}Pt_{67}$/HY catalyst. Several researchers have evidenced this phenomenon, where crystalline Pt-Pd particles are supported by increasing the atomic % of Pd, the Pt atoms found inside the crystal, and Pd exposed on the outer surface [10], [11], [19], [25]. The turnover frequencies decrease for the bimetallic Pd-Pt/HY catalyst due to Pt atoms' strong interaction with the Pd because of Pt-Pd alloys' formation in which the electrophilic character of Pt increases, favoring the hydrogenation of toluene in methylcyclohexane.

3.3. Catalytic hydrogenation and ring-opening of toluene at 250°C

The reaction of toluene also performed at 250°C and space velocity (WHSV) of 6 h^{-1}. At this temperature, two main reactions occur in parallel: the hydrogenation and opening of ring of toluene, consecutive reactions, and transalkylation in xylene. It found that the overall rate decreases proportionally as the percentage of Pd increases. In Figure 4 the toluene rate at 250° C is represented as a function of the atomic % of Pd. Reaction rates of toluene into hydrogenation (r_{HT}) to methylcyclohexane, ring-opening (r_{RO}) to n- and isoheptane, and transalkylation (r_{TAT}) to xylene and aromatic A_{8+} shown in Figure 5. In the Pt (Pd_0Pt_{100}/HY) monometallic catalyst, the hydrogenation rate of toluene is higher than the ring-opening of methylcyclohexane because of consecutive reactions wherein the ratio of rates r_{RO}/r_{HT} is equal to 0.6. In contrast, in the monometallic Pd catalyst ($Pd_{100}Pt_0$/HY), the reaction rates in hydrogenation, ring-opening, and transalkylation are low and similar under the reaction conditions studied.

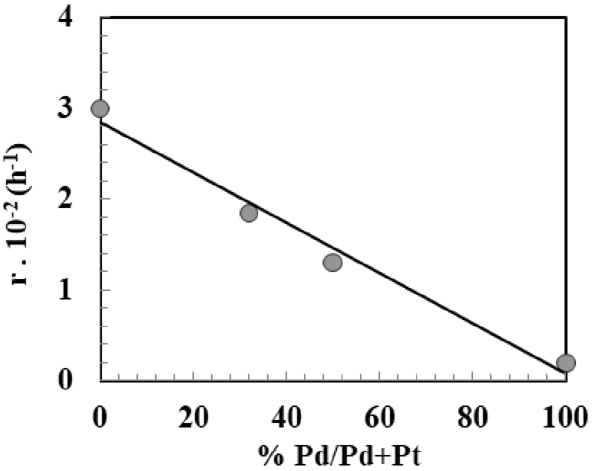


Figure 4. Rate of conversion toluene at 250 °C versus relative atomic % Pd.

The rate of ring-opening of the methylcyclohexane for $Pd_{33}Pt_{67}$/HY catalyst is similar to the monometallic Pt catalyst (Pd_0Pt_{100}/HY) and then decreases by 40% for $Pd_{50}Pd_{50}$/HY probably at the dilution effect of Pt on bimetallic PtPd particles formed on the surface [11], [12]. For the bimetallic $Pd_{33}Pt_{67}$/HY catalysts was observed that the ring-opening rate of methylcyclohexane (r_{RO}) is higher, by a factor of 2, than the hydrogenation of toluene (r_{HT}).

Hence, the determining step of this reaction for the monometallic Pt catalyst (Pd_0Pt_{100}/HY) is the transformation of methylcyclohexane, and it would be explained by the ratio of rates r_{RO}/r_{HT} equal to 0.6 in which the rate of hydrogenation of toluene is higher than the ring-opening of MCH. When comparing the relative distribution ratio of weak/strong acid sites of the monometallic Pt catalyst and the bimetallic $Pd_{33}Pt_{67}$/HY, values of 6 and 2 are obtained. This fact demonstrates that a metal composition of Pd/Pd+Pt between 0.33 and a relative distribution ratio of weak/strong acid sites about 2 is required, which favors the transformation of consecutive reactions of toluene to n- and iso-heptane according to Figure 6 of proposed response:

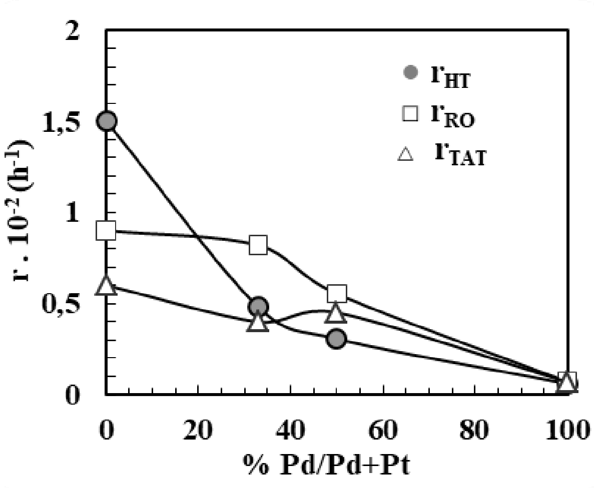
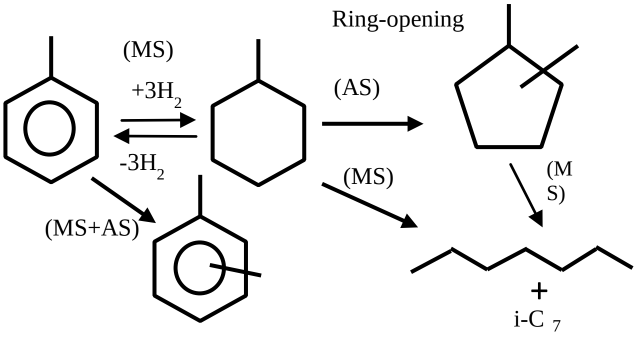


Figure 5. Rates of hydrogenation of toluene (r_{HT}), ringopening of methylcyclohexane (r_{RO}), and transalkylation of toluene (r_{TAT}) at 250 °C versus relative atomic Pd %.



AS: acid sites; MS: metal sites

Figure 6 he hydrogenation of toluene to methylcyclohexane in metal sites and subsequent skeletal isomerization.

In reaction scheme 1, the hydrogenation of toluene to methylcyclohexane in metal sites and subsequent skeletal isomerization in the acidic sites of the zeolite through a di-methylcyclopentane intermediate which is ringopening in the metal sites leading to the formation of nheptane and iso-heptane [9], [14], [15]. On the contrary, the monometallic Pd ($Pd_{100}Pt_0$/HY) with a weak/strong relative acidity ratio of 3 presented a different behavior. A decrease in the hydrogenation speed (r_{HT}) is evidenced by a factor of 20, in the ring-opening (r_{RO}) of 13, and the transalkylation (r_{TAT}) of 9. The transalkylation rate ratio r_{TAT}(Pt)/r_{TAT}(Pd-Pt) is equal to 1.5 ± 0.1, which shows that it is practically independent of the relative acidity of sites weak/strong.

3.4. Catalytic ring-opening of methylcyclohexane (MCH) at 250°C

The ring-opening of methylcyclohexane studied under the same conditions as the conversion of toluene at a temperature at 250°C and space velocity (WHSV) of 6 h^1. The reaction products for the conversion of MCH were n- and iso-heptane (82-93%) and toluene (7-18%). The results of the reaction rates in the transformation of methylcyclohexane (MCH) on the Pd-Pt/HY catalysts reported in Table 3.

The MCH ring-opening reaction rate of the Pt monometallic catalyst (Pd_0Pt_{100}/HY) is 2 times that $Pd_{33}Pt_{67}$/HY bimetallic and 3 times Pd monometallic catalyst. The ring-opening rate of MCH for the bimetallic catalyst $Pd_{33}Pt_{67}$/HY is well above dehydrogenation, in which the presence of Pd controls it.

Table 3. Rate ring-opening of methylcyclohexane (MCH) on Pd-Pt/HY catalysts at 250 ºC

Catalysts	**^{a}r. 10^2 (h^{-1})**	**$^b r_{RO}$. 10^2 (h^{-1})**	**$^c r_{DH}$. 10^2 (h^{-1})**	**n-C_7/ iso- C_7 (mol/mol)**
Pd_0Pt_{100}/HY	12,0	9,8	2,2	8
$Pd_{33}Pt_{67}$/HY	6,0	5,6	0,4	10
$Pd_{100}Pt_0$/HY	4,0	3,6	0,4	12

^{a}rate (h^{-1}) = moles of methylcyclohexane transformed/h/moles of total metal. ^{b}Ring-opening rate of MCH (r_{RO}). ^{c}Dehydrogenation rate of MCH (r_{DH}).

In the MCH ring-opening, the skeletal isomerization of MCH in a dimethylcyclopentane intermediate followed by the ring-opening in n-iso-C_7 paraffin is proposed as a reaction scheme (scheme 1) [15]. Results Table 4 shows that the ratio of the ring-opening/dehydrogenation rates (r_{RO}/r_{DH}) equals 14 of the MCH and the ratio of ringopening/hydrogenation rates (r_{RO}/r_{HT}) to toluene conversion equal 2 for $Pd_{33}Pt_{67}$/HY, concerning the monometallic catalysts of Pt (Pd_0Pt_{100}/HY) and Pd ($Pd_{100}Pt_0$/HY).

This result shows that for an atomic composition of 0.33 Pd in the Pd-Pt/HY bimetallic catalyst and relative distribution of weak/strong sites of 2, the MCH ring's opening is favored. It is evidenced in the opening of the ring aromatic of toluene, where the same composition favors the opening rate of the intermediate MCH ring to the hydrogenation rate.

Table 4. The ratio of ring-opening/dehydrogenation (r_{RO}/r_{DH}) of Methylcyclopentane reaction and the ratio of ring-opening/hydrogenation of the toluene reaction

Catalysts	$^a r_{RO}/r_{DH}$	$^b r_{RO}/r_{HT}$	**Relative distribution ratio of weak/strong acid sites (%)**
Pd_0Pt_{100}/HY	5	0.6	6
$Pd_{33}Pt_{67}/HY$	14	2	2
$Pd_{100}Pt_0/HY$	9	1	3

[a] ratio of the ring-opening/dehydrogenation of MCH reaction. [b] ratio of the ring-opening/hydrogenation rates of the toluene reaction.

The bifunctional condition (metal/acid) of the catalyst surface $Pd_{33}Pt_{67}/HY$ favors the hydrogenation of toluene to methylcyclohexane in metal sites and skeletal isomerization acidic sites to dimethylcyclopentane intermediary ring, which is ring-opening in the metal sites leading to a higher form of n-heptane concerning isoheptane.

4. Conclusions

The CO chemisorption, difference between H_2-TPR and decreased TOF toluene reaction at 110 ºC results observed on bimetallic Pd-Pt/HY catalysts suggest a strong interaction between Pd-Pt. The hydrogenation of toluene to methylcyclohexane is favored in metal sites and skeletal isomerization in the acidic sites to dimethylcyclopentane intermediary ring, which is ringopening in the metal sites leading a higher formation of n-heptane concerning iso-heptane, at a relative distribution of weak/strong sites of 2, for an atomic composition of 0.33 Pd in the Pd-Pt/HY bimetallic catalyst.

The proposal that appears at the end of the document arises from the need to predict the behavior of electrical energy consumption by analyzing a single voltage output that would allow establishing whether a given load complied with the operating limits.

Funding

This research received no external funding.

Autor Contributions

T. Romero: Conceptualization, Formal analysis, Investigation, Writing - Review & Editing. L. Melo: Methodology, Investigation, Writing - Original Draft. M. Esparragoza: Investigation, Writing - Original Draft. R. Ávila: Formal analysis, Investigation, Writing - Original Draft. A. Moronta: Investigation, Writing - Original Draft. G. Carruyo: Investigation, Writing - Original Draft. L. García: Investigation, Writing - Original Draft.

All authors have read an agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

References

[1] S. Lee, Y. Lee, J. Kim, S. Jeong, “Tactical control of ni-loading over w-supported beta zeolite catalyst for selective ring opening of 1-methylnaphthalene”. *J. Ind. Eng.Chem.*, vol. 66, 2018, doi: https://doi.org/10.1016/j.jiec.2018.05.042

[2] N. Catherin, E. Blanco, L. Piccolo, D. Laurenti, F. Simonet, C. Lorentz, E. Leclerc, V. Calemma, C. Geantet, “Selective ring opening of decalin over bifunctional RuS2/zeolite catalysts,” *Catal. Today* vol. 323, 2019, doi: https://doi.org/10.1016/j.cattod.2018.07.052

[3] N. Catherin, F. Blanco, D Laurenti, L. Piccolo, F. Simonet, C. Lorentz, E. Leclerc, V. Calemma, C.Geantet, “Transition metal sulfides on zeolite catalysts for selective ring opening” *Catal. Today*, 2020, doi: https://doi.org/10.1016/j.cattod.2020.10.012

[4] S.A D’Ippolito, A.D Ballarini, S.M. Rosas, L.Pirault-Roy, C. Especel, C. L Epron. “Influence of the Ir content and the support on the thiotolerance of the Ir/SiO2-Al2O3 catalysts for selective ring opening of decalin,” *Can. J. Chem. Eng.*, 2020, doi: https://doi.org/10.1002/cjce.23930

[5] X. Dong et al., "Noble-metal efficient Pt-Ir-Co/SiO2 catalyst for selective hydrogenolytic ring opening of methylcyclopentane," *Catal. Today*, vol. 316, pp. 162–170, 2018, doi: https://doi.org/10.1016/j.cattod.2018.03.059

[6] E. Pérez-Guevara, J. M. Molinillo, E. J. Martínez de la Ossac, J. Frontela, J. Lázaro, M. J. Franco, "Selective Ring Opening of Ethylbenzene on Bifunctional Catalyst Pt–Ir over Hierarchical USY Zeolite," *Petroleum Chemistry*, 2020, Vol. 60, pp. 104–112.

[7] Q. Wang et al., "Preparation of a highly efficient Pt/USY catalyst for hydrogenation and selective ring-opening reaction of tetralin," *Pet. Sci.*, vol. 15, no. 3, pp. 605–612, 2018, doi: https://doi.org/10.1007/s12182-018-0222-5

[8] M.A. Arribas, A. Martinez, "The influence of zeolite acidity for the coupled hydrogenation and ring opening of 1-methylnaphthalene on Pt/USY catalysts," *Appl. Catal.*, vol. 230, (2002) 203-217, doi: https://doi.org/10.1016/s0926-860x(01)01015-8

[9] Kubicka D., Kangas M., Kumar N., Tiitta M., Lindblad M., Murzin D. Yu. "Ring Opening of Decalin Over Zeolite-Supported Iridium Catalysts," *Top. Catal.*, vol. 53, pp. 1438-1445, 2010, doi: https://doi.org/10.1007/s11244-010-9604-7

[10] K. Thomas, C. Binet, T. Chevreau, D. Cornet, J. P. Gilson, "Hydrogenation of toluene over supported Pt and Pd catalysts: influence of structural factors on the sulfur tolerance," *J. Catal.*, vol. 212, pp. 63–75, 2002, doi: https://doi.org/10.1006/jcat.2002.3780

[11] T. Fujikawa, K. Idei, T.Ebihara, H. Mizuguchi, K. Usui, "Aromatic hydrogenation of distillates over SiO2-Al2O3-supported noble metal catalysts," *Appl. Catal.*, vol. 192, pp. 253-261, 2000, doi: https://doi.org/10.1016/S0926-860X(99)00403-2

[12] R. M. Navarro, B. Pawelec, J. M. Trejo, R. Mariscal, J. Fierro, "Hydrogenation of Aromatics on Sulfur Resistant PtPd Bimetallic Catalysts," *J .Catal.*, vol. 189, pp. 184-194, 2000.

[13] G.B. McVicker, M. Daage, M.S.Touvelle, W. Hudson, D.P. Klein, W.C. Baird Jr., B.R.Cook, J.G.Chen, S.Hantzer, D.E.W. Vaughana, E. S. Ellis O.C. Feeley, "Selective Ring Opening of Naphthenic Molecules," *J. Catal.*, 210, pp. 137-148, 2002, doi: https://doi.org/10.1006/jcat.2002.3685

[14] L. M. Kustov, A. Stakheev, T. V. Vasina, O.V. Masloboishchikova, E.G. Khelkovskaya-Sergeeva, P. Zeuthen, "Dual-function catalysts for ring opening of cyclic compounds," *Stud. Surf. Sci. Catal.*, vol. 138, pp. 307-314, 2001.

[15] T. Sugii, Y. Kamiya, T. Okuhra, "Conversion of methylcyclohexane over Ir/H-β zeolite in the presence of hydrogen," *Appl. Catal.*, vol. 312, pp. 45-51, 2006, doi: https://doi.org/10.1016/j.apcata.2006.06.022

[16] J., Chupin, N. S. Gnep, S. Lacombe, M. Guisnet, "Influence of the metal and of the support on the activity and stability of bifunctional catalysts for toluene hydrogenation," *Appl. Catal.*, vol. 206, pp. 43–56, 2001, doi: https://doi.org/10.1016/s0926-860x(00)00585-8

[17] A. S Rocha, E. L. Moreno, G. Da Silva, J.L. Zotin, A.C. Faro Jr, "Tetralin hydrogenation on dealuminated Y zeolite-supported bimetallic Pd-Ir catalysts," *Catal. Today*, vol. 133, pp. 394-399, 2008, doi: https://doi.org/10.1016/j.apcata.2006.06.022

[18] T. Tri, J. Massardier, P. Gallezot, B. Imelik, "Metal support and metal additive effects in Catalysis. Additives and support effects on Pt catalysts studied by the competitive hydrogenation of benzene and toluene," *Studies in Surface Science and Catalysis*, vol. 11, pp. 141-148, 1982, doi: https://doi.org/10.1016/S0167-2991(09)61385-9

[19] T. Matsui, M. Harada, K. K. Bando, M. Toba, Y. Yoshimura, "EXAFS study on the sulfidation behavior of Pd, Pt and Pd–Pt catalysts supported on amorphous silica and high-silica USY zeolite," *J. Catal.*, vol. 290, pp. 73-80, 2005, doi: https://doi.org/10.1016/j.apcata.2005.05.019

[20] L. Fiermans, R. De Gryse, G. De Doncker, P. A. Jacobs, J. A. Martens, "Pd segregation to the surface of bimetallic Pt–Pd particles supported on H-β zeolite evidenced with x-ray photoelectron spectroscopy and argon cation bombardment," *J.Catal.*, vol. 193, 2000, doi: https://doi.org/10.1006/jcat.2000.2868

[21] T. Rades. C. Pak, M. Polissetthfoin, R. Ryoo, J. Fraissard, "Characterization of bimetallic NaY-supported Pt-Pd catalyst by EXAFS, TEM and TPR," *J. Catal. Lett.*, vol. 29, pp. 91-103, 1994, doi: https://doi.org/10.1007/BF00814255

[22] C. M. N. Yoshioka, T. Garetto, D. Cardoso, “nHexane isomerization on Ni-Pt catalysts/supported on HUSY zeolite: the influence from a metal content,” *Catal. Today*, 2005, doi: https://doi.org/10.1016/j.cattod.2005.07.056

[23] P. Castaño, B. Pawelec, J.L.G. Fierro, J.M. Arandes, J. Bilbao, “Aromatics reduction of pyrolysis gasoline (pygas) over HY-supported transition metal catalysts,” *J. Appl. Catal. a: General*, vol. 315, pp. 101–113, 2006, doi: https://doi.org/10.1016/j.apcata.2006.09.009

[24] S. N. Gandhi, G. D. Lei, W. M. H. Sachtler, “Identification of Pd3+ ions in zeolite L by temperature programmed reduction and electron paramagnetic resonance spectroscopy,” *Catal. Lett.*, vol. 17, 1993.

[25] G. Lietz, H. Lieske, H. Spindler, J. Volter “Reactions of platinum in oxygen- and hydrogen-treated Pt/γAl2O3 catalysts: i. temperature-programmed reduction, adsorption, and redispersion of platinum,” *J.Catal.*, vol. 81, pp. 8-16, 1983, doi: https://doi.org/10.1016/0021-9517(83)90142-2

[26] Y. J. Lee, et al., “Ring Opening of Naphthenic Molecules Over Metal Containing Mesoporous Y Zeolite Catalyst,” *Nanoscience and Nanotechnology*, vol. 15, 5334-5337, 2015, doi: https://doi.org/10.1166/jnn.2015.10424

[27] S. A. D`Ippolito, L. B. Gutierrez, C.L. J. Pieck “Optimal Ir/Pt ratio for the ring opening of decalin in zeolite supported catalysts,” *Appl. Catal. A: General*, 2012, doi: http://doi.org/10.1016/j.apcata.2012.08.037