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Comparing the Performance of Heterogeneous Pd-Supported Catalysts: Pd/ZSM-5, Pd/13X and Pd/Al₂O₃ for the Hydrogenation of Benzene in a Mixture of Normal Heptane and Benzene

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ABSTRACT

In the presented research, the selective hydrogenation of benzene in a mixture of benzene and normal heptane (5 vol % of benzene) over different kinds of heterogeneous catalysts was investigated. For this purpose, a series of catalysts with various supports such as Pd/ZSM-5, Pd/13X and Pd/Al₂O₃ was developed. To prepare Pd supported catalysts, the modification of supports was conducted by a specified amount of palladium nitrate in the aqueous solution. Experimental catalyst evaluation tests were performed in the catalyst assessment set-up. The characterizations of the physicochemical properties of the prepared catalysts were performed by XRD, NH₃-TPD and BET. It can be found that the conversion of benzene was promoted under the optimized reaction conditions of 200 °C, 1 MPa, H₂/HC = 1.3 (molar ratio) and the weight hourly space velocity (WHSV) = 25 hr⁻¹. Among these catalysts, Pd/13X exhibited the maximum conversion of benzene (90 %) and the minimum light-cut production under the optimum conditions. The study on the stability of catalysts shows that, the decline activity of Pd/13X catalyst is more than that of the other catalysts (from 90 % to 81 %) in the specified 20 h time on stream, but so far the activity of this catalyst is the highest in comparison with that of other catalysts at the end of the defined time (20 h).

1. Introduction

Some of the refinery products contain toxic components which have detrimental effects on the human health. These harmful compounds are naturally present in the crude oil or can be created from reforming processes in the oil refineries [1].

Automotive gasoline is the main petroleum

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derivative of which the consumption is continuously increasing around the world. This oil cut is a complex mixture of different hydrocarbon groups, mainly, aromatics, paraffins and olefins. The major ingredients of the aromatic group are benzene, toluene and xylene, among which benzene is more flammable and volatile at the ambient temperature and pressure [2].

Because of the high vapor pressure, benzene molecules tend to escape from the liquid phase to the atmosphere and hence during contact with rich-benzene oils there is always benzene vapor present in adjacent air. Prolonged benzene vapor inhalation can cause serious permanent health problems [3]. Numerous studies have reported that the exposure to benzene in the long time can result in various diseases such as teratogenicity, carcinogenicity, and the destruction of the hematopoietic system [4, 5]. Therefore, to reduce the risk of the exposure to benzene, based on new environmental standards its concentration in gasoline, which is widely used as automobile fuel, should be less than 0.62 vol % [6].

The catalytic hydrogenation of benzene is one of the most effective methods that is vastly used in the refineries for reducing the content of benzene in gasoline. Because of higher efficiency, eco-friendly aspects and economic advantages compaired to the other techniques, the hydrogenation of benzene has attracted the attention of researches and refiners [7-9]. In this field a wide range of the different combinations of metals and supports are used as hydrogenating catalysts [10, 11]. The much favored noble metals (Pd, Pt and Ru) [12-14] and base metals (Ni, Co) [15-18] besides the bimetals (Pt-Co, Pt-Re) [19, 20], that are usually supported on different kinds of metal oxides, zeolites and other resistant porous materials are the most interesting catalysts for the process of removing benzene [21-23]. In comparison with other valuable metals, palladium is reasonable to be used due to the most important factor of its low cost.

The palladium supported catalysts, due to their high performance activity, thermal stability and plentiful depository, are significant topics of investigations for researchers and are broadly applied in catalytic reactions [24-28].

In particular, palladium catalysts play excellent roles in making the hydrogenation reaction progress fast. This effect is the result of a meaningful decrease of the H-H bond breakdown activation energy on the mentioned metal surface and also the easy mobility of the chemisorbed hydrogen [29, 30]. The effectiveness of palladium on the silica support (Pd/SiO$_2$), as the catalyst for the hydrogenation of benzene, and the impact of the metal loading and main reaction conditions (temperature and pressure) on the conversion improvement have been investigated [30, 31].

The experimental results indicate that multi-walled carbon nanotubes (MWCNT) filled with palladium bunches, exhibit higher activity than the other supports such as Y-zeolite, conventional active carbon and etc. in the hydrogenation of benzene [32].

The enhancement of the catalytic properties, including stability and sulfur resistance, of nickel on the silica-alumina support (Ni/ASA), with the incorporation of Pd elements in the base catalyst structure was confirmed for the hydrogenation of benzene in gasoline [11].

The higher selectivity toward the conversion of benzene was observed in the competitive hydrogenation of the benzene-toluene mixture for Pd/Al$_2$O$_3$ catalysts [33].

Catalyst supports not only support the metal catalyst, but also affect the catalytic activity of the metal sites. These amplify the catalytic reaction and decline side reactions. Subsequently, the effects of the support on the catalyst performance are jointly named as the "support effect". The support plays a key role in the creation of the unit morphology and metal dispersion. The catalysts prepared by using precious metal particles (Pt, Pd, Ru, Rh) doped onto various supports exhibited good performances. The nature of the support influences the dispersion of the active sites and the tendency to sinter and agglomerate the metal particles [34-36].

In studying the effect of temperature on the hydrogenation of benzene over Pd supported catalyst, it is found that the reaction order of benzene and hydrogen increased from 0 to 0.8 and from 0.5 to nearly 4 respectively by increasing the temperature from 80 to 200 °C [37].

For supported noble metal catalysts, after the first hydrogen molecule dissociates from the metal sites, next hydrogen atoms move to the catalyst surface. This phenomenon is named hydrogen spillover, and this effect will reinforce the interaction between the catalyst support and active particles and would result in improving the performance of the catalyst [38].

Due to the presence of the more active sites for the hydrogenation in acidic catalysts, their activity in the hydrogenation reaction is relatively high. For this kind of catalyst it is supposed that, aromatic compounds are adsorbed onto the acidic sites of the support and react with hydrogen atoms spilled-over from the metal sites [39].

Accordingly, the main goal in this project is to determine and compare the activity and stability of various Pd supported catalysts in the hydrogenation of benzene in a binary mixture of benzene and normal heptane. The most attractive porous materials (ZSM-5, 13X and Al_2O_3) that are usually applied as catalyst support in different catalytic processes are selected for supporting the active metal elements (Pd). In the continuation, the effect of the reaction temperature and pressure and also other variables as the hydrogen to hydrocarbon mole ratio and the weight hourly space velocity are evaluated and optimized. Furthermore, in this work the comparison of the performance of Pd/ZSM-5, Pd/13X and Pd/Al_2O_3, that are prepared as catalysts for the hydrogenation of benzene, is made for the first time. Additionally, we couldn't trace any preceding study in which the optimization of all major reaction conditions, that are most effective in this process, has been fulfilled in one time.

2. Experimental
2.1. Materials
Nearly pure benzene (99.8 vol %), normal heptane (99.3 vol %) and palladium (II) nitrate di-hydrate ($Pd(NO_3)_2.2H_2O$) were supplied from Merck Company. High purity (99.99 %) hydrogen and nitrogen gases were obtained from Mahan Gas. The γ-alumina (99 % pure Al_2O_3, GOPHIN CHEMICAL), high performance 13X zeolite (SiO_2/Al_2O_3=3, GOPHIN CHEMICAL) and ZSM-5 zeolite (SiO_2/Al_2O_3=25, NK CHEM) were employed as catalyst supports. The demineralized water was supplied locally.

2.2. Catalyst preparation
The monometallic catalysts of Pd/ZSM-5, Pd/13X and Pd/Al_2O_3 were prepared by the wet impregnation method. To obtain 0.5 wt % of Pd on various supports, a specified mass of the palladium (II) nitrate di-hydrate salt is

dissolved in an appropriate volume of demineralized water. Then the pre-treated catalyst support powder, that was heated already in 100 °C for 1 h, for evacuating moisture from the pores, is impregnated by adding the prepared salt solution to it. For the sake of reaching the equilibrium adsorption it is necessary that the obtained mixture of support and aqueous metal nitrate be stirred at room temperature for about 30 min with a magnetic stirrer. For drying the impregnated support, it is desiccated at 100 °C in an oven overnight. As the final step of the preparation of the catalyst, the calcination of the impregnated dried solid is conducted under the temperature of up to 450 °C for 3 h and air atmosphere, with temperature increasing rate of about 3 °C.min⁻¹.

2.3. Catalyst characterization

The different methods of analyzing were used to characterize the textural properties of the prepared catalysts. The specific area and structural details of each catalyst (S_{BET}) were investigated by the standard Brunauer-Emmet-Teller (BET) method using the obtained data of nitrogen adsorption-desorption (BET isotherms) at the temperature of 77 K using a BELSORP mini (Japan made). The sizes of Pore volume (V_p) and Pore diameter (d_p) were obtained from the corresponding nitrogen isotherm desorption branch by using the Barrett-Joyner-Halenda (BJH) method.

In order to evaluate the state of the impregnated Pd on catalyst supports, the metal dispersion degree, on catalyst supports, was measured by BELSORP max (Japan made) and in accordance with the universal oil products (UOP) 945 test method.

The structure of supported catalysts was studied with X-ray diffraction (XRD) patterns that has been taken by means of a diffractometer (Bruker AXS-D8) that uses the Cukα radiation and is operated at 40 kV and 40 mA. The scanning of the samples was done in the range of $5^0 < 2\theta < 40^0$ at the scanning speed of 0.02 s⁻¹.

To evaluate the acidic strength of the prepared catalysts, the ammonia temperature programmed desorption (NH₃-TPD) technique was utilized. In this procedure a TPD/TPR analyzer (2900 Micromeritics) that is equipped with a thermal conductivity detector was employed. First of all, the pre-treatment of catalyst samples (0.2 g) was done in the pure helium with the flow rate of 40 n-lit/min from the temperature range of 25 to 500 °C at a heating rate of 10 °C.min⁻¹ for 1 h. Then, the pre-treated samples were cooled to room temperature and were saturated with ammonia. To provide TPD profiles for the ammonia desorption, the sample temperature was raised from 25 to 750 °C by a ramp rate of 10 °C. min⁻¹. The total acidity of the the catalyst was found from its NH₃ desorption profile, by measuring the area under the corresponding curve using the integration method.

2.4. Catalyst evaluation

The process flow diagram (PFD) of the catalytic testing setup that used for the experimental evaluation of the catalyst is presented in Figure 1. As it is shown in the PFD file of the catalytic testing setup, two separate lines are considered for H_2 and N_2 gases and a single line for the liquid hydrocarbon as the feed (benzene and normal heptane) from the corresponding gas cylinders and liquid feed drum to the reaction section. The gas flow to the reactor is controlled accurately by means of a mass flow controller (MFC) that is placed for all

passes of gas lines. The required flow of the liquid feed is provided and controlled by using an ELDEX metering pump. The liquid and gas are mixed in a single transfer line to the reactor and then are preheated to the desired temperature through passing the unfilled part of the reactor. Also, the temperatures of the different zones of the reactor are maintained at an adjusted set point using a split type electrical auto-controlled furnace. In the center of the furnace, it is embedded a continuous tubular stainless-steel reactor. The reactor arrangement is down-flow with a fixed-bed of the catalyst at the middle of it. The length and internal diameter of the reactor are 50 cm and 1.2 cm respectively. For performing the catalyst evaluation tests, 1 g of the prepared catalyst was packed in the mid-section of the reactor. In order to send the free oxygen out of the reactor, vessels and all connecting pipe lines, the system was initially purged by flowing an inert gas (N_2) with the flow rate of 100 ml.min^{-1} for 30 min prior to introducing the feed mixture into the reactor. Before entering the liquid feed on the catalyst bed and starting the reaction, the catalyst sample was reduced

in a stream of hydrogen with the flow rate of 100 ml.min^{-1} for 1 h at the temperature of 350 °C. In the first section of the tubular reactor and before the feed arriving on the catalyst bed, the temperature of the feed mixture goes up and it changes from the vapor-liquid phase to the vapor phase passing the top heating region of the furnace. The benzene saturation reaction is performed under the specified conditions of temperature, pressure and the liquid-gas ratio on the packed catalyst bed in the reactor. For the separation of liquid and gas phases from the reactor effluent, this stream is sent to a vertical flash separator in which the liquid and gas are separated because of the difference in volatility. The collected liquid in the bottom of the separator was sampled after 2 h and analyzed by a Gas Chromatography (GC) analyzer (YL 6500) equipped with a flame ionization detector (FID) and HP Plot-Q capillary column (30 m × 0.32 mm × 1 μm). The reaction pressure was adjusted using a back-pressure regulator (BPR) installed in the gas stream stripped from the top of the separator.
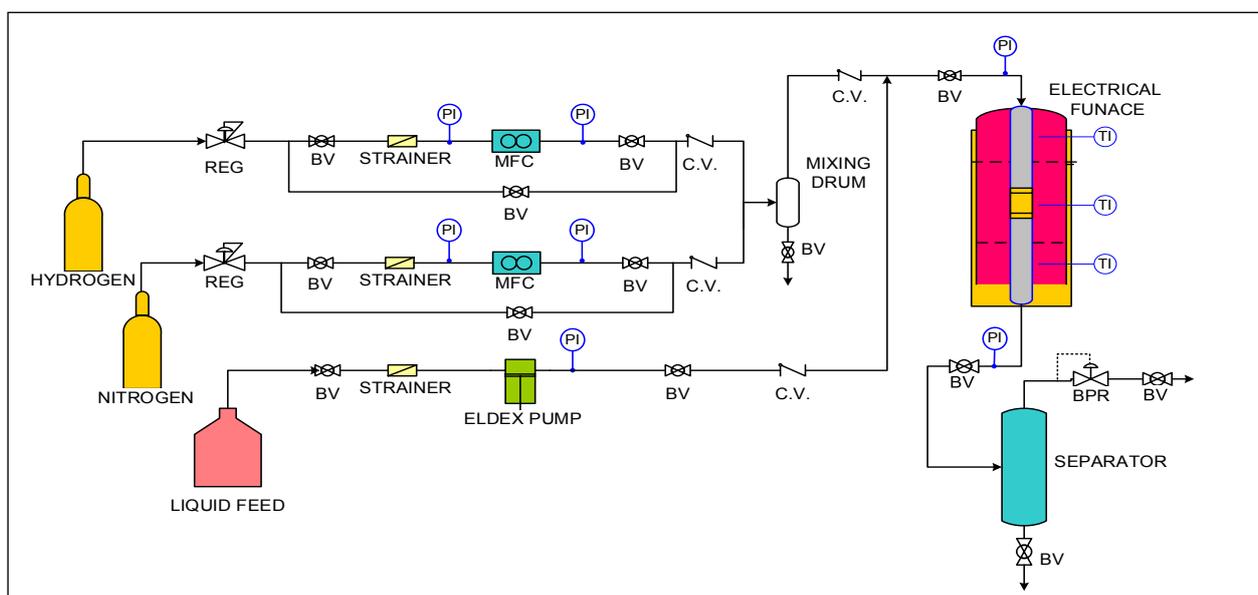

Figure 1. Schematic flow diagram of the catalytic testing setup for the benzene saturation test.

3. Results and discussion

3.1. Characterization tests

Figure 2 displays the adsorption-desorption isotherms of nitrogen for all prepared catalysts at 77° K. It is concluded that the isotherms almost similarly show a kind of IV shape and H4 hysteresis loop form that represent the monolayer-multilayer adsorption and capillary condensation in mesoporous substances with uniform cylinder-shaped pores. The capillary condensation takes place during two steps in these isotherms. The first condensation step appears in the P/P_0 range of 0.0-0.1 and it is associated with the filling of the intra-mesopores of the catalysts. The second condensation that is related to the larger mesopores and inter particle textural porosity, is shown in the P/P_0 range of 0.6-0.9. Since the gas evaporation and condensation process inside the pores are different, a slight hysteresis between the adsorption and desorption loops was observed. The difference in adsorption-desorption states is arisen from the slit-like pores formed by the aggregates, wide pore size distribution, asymmetrical-shape and plate-like particles.
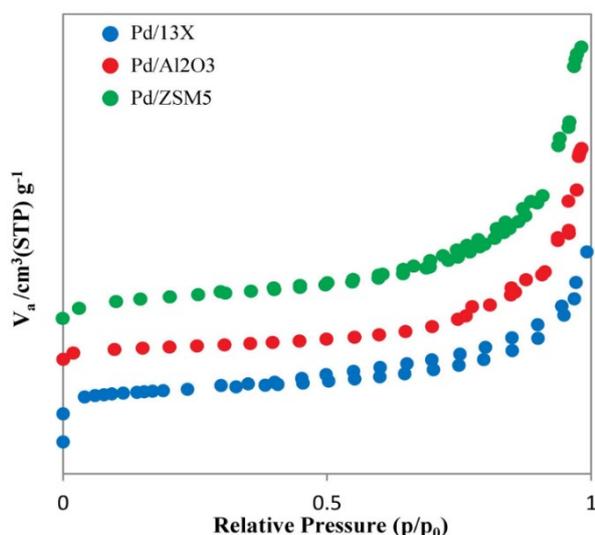

Figure 2. N_2 adsorption-desorption isotherms of Pd/Al$_2$O$_3$, Pd/13X and Pd/ZSM-5.

Table 1 provides the physical properties of the catalyst such as the surface area, pore volume and pore diameter obtained by the BET analysis. It can be observed that the specific surface area has decreased slightly for the modified samples, especially in the zeolite based samples, that could be related to the presence of Pd on the surface of the catalyst.

Table 1 reports the measurement results related to the metal dispersion on the catalyst supports. The largest degree of dispersion belongs to Pd/13X, in contrast with other ones, and this is a superior feature.

For studying the structure and degree of the crystallinity of the prepared catalysts after the calcination step, the X-ray Diffraction Technique was used and the results are shown in Figure 3. In comparison with unloaded supports [40-44], it is deduced that in the obtained XRD patterns of the prepared Pd loaded catalysts, the position of all peaks complies with the reported patterns for main supports and it was not distinguished any differences between them. In all spectra acquired for the modified catalysts the high intensity and low background lines of peaks show the superior crystallinity of catalysts and are convincing that the loading of palladium into the catalyst support by the wet impregnation method does not change the crystal structure of the support. Because of the low concentration and also good dispersion of the Pd oxide particles during the synthesis of the catalyst and the thermal treatment of prepared samples, it was found from X-ray diffractions that there was not any apparent peaks ascribed to the palladium oxide phase, so this implied that there was no discrete Pd-containing phase shaped through this modification procedure in the structure of the prepared catalysts.

Table 1
Physicochemical properties of prepared catalysts.

Data	Unit	Catalysts		
		Pd/Al$_2$O$_3$	Pd/13X	Pd/ZSM-5
V$_p$*	cm^{3}g^{-1}	0.87	0.17	0.57
r$_{p,peak}$*	nm	4.61	2.41	3.51
a$_{s, BET}$‡	m^{2}g^{-1}	200	224	182
Monolayer gas ads.†	(Cm^3(STP)g^{-1}) (V$_m$)	46.0	51.5	41.9
Metal dispersion††	%	53	75	71
Total acidity‡‡	mmol.g^{-1}	1.50	2.69	1.61

*Obtained from BJH desorption
‡Obtained from Brunauer-Emmett-Teller method
†Measured by Adsorption-desorption isotherms of N$_2$
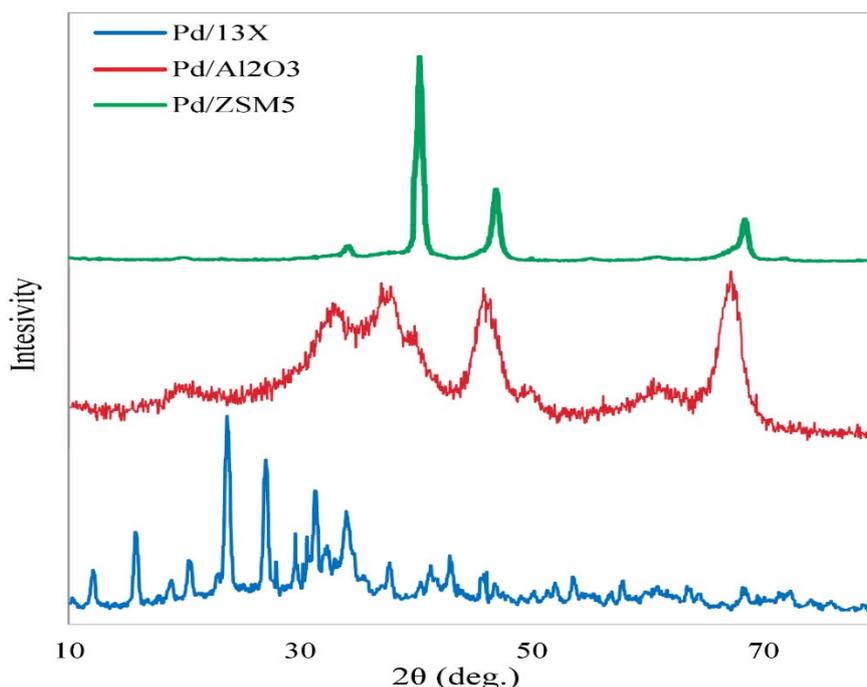††Determined by H$_2$ chemisorption
‡‡Measured by NH$_3$-TPD

Figure 3. XRD patterns of the catalysts: Pd/ Al$_2$O$_3$, Pd/ZSM-5 and Pd/13X.

To evaluate the acidic strength of the prepared catalysts, the ammonia temperature programmed desorption (NH$_3$-TPD) technique was utilized and the results have been illustrated in Figure 4 and Table 1. All of the catalyst samples show two/three desorption peaks that appear at the temperature range of 100-650 ºC and are related to weak, medium and rather strong acid sites respectively. In comparison, the largest peak area belongs to the Pd/13X catalyst, and therefore, the amount of

adsorbed ammonia on this catalyst is 2.69 (mmol NH₃.g⁻¹). The catalysts are ranked on
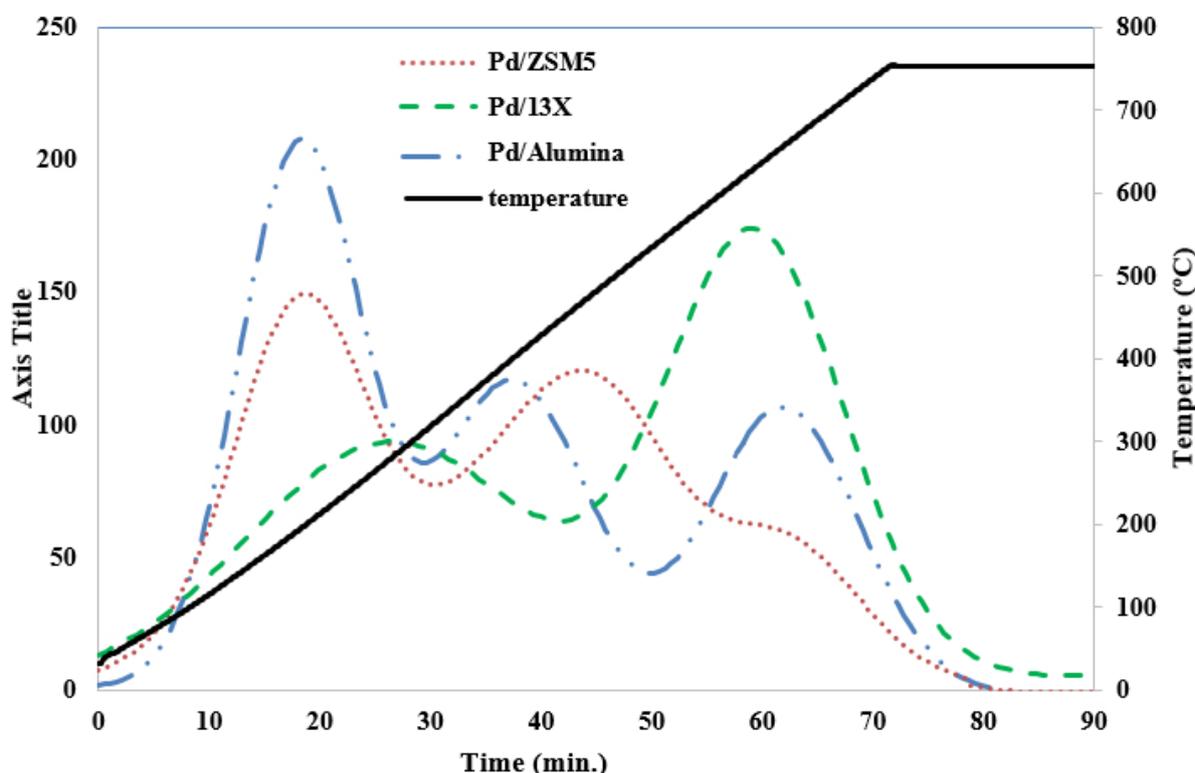
the basis of their acidic strength as follows:

$$Pd/13X > Pd/ZSM\text{-}5 > Pd/Al_2O_3$$

Figure 4. NH₃-TPD profiles of Pd supported catalysts.

3.2. Catalyst performance

In the reactor tests for optimizing the reaction conditions, the dependence of the conversion of benzene on various reaction factors such as temperature, pressure, the weight hourly space velocity (WHSV) of the liquid hydrocarbon feed and the molar ratio of hydrogen gas to total benzene in the feed (H₂/HC) were investigated. By doing plenty of experiments under various ranges of operating conditions the almost optimum point for each one was found, and here by the aim of shortening the discussion, only the changes of each parameters are considered with fixed amounts for other parameters. Since the used catalysts are in the powder shape and the reaction takes place in the gas phase, so for this reaction the mass diffusion limitations in the reactants path to catalyst

active sites are ignored. The rate of the conversion of benzene can be calculated as follows [5, 7]:

$$C_{BZ}(\%) = (V_{B0}\text{-}V_B)/V_{B0} \times 100 \qquad (1)$$

where, C_{BZ} is the conversion of benzene and V_{B0} and V_B are the volume percent of benzene in the feed and product respectively. The hydrogenation of benzene is an additional reaction in which hydrogen atoms are added all the way around to the benzene ring and as the result, cycloalkane is formed. These reactions destroy the electron delocalization in the original benzene ring, because these electrons are being used to form bonds with the new hydrogen atoms. Although, because of the formation of the new strong carbon-hydrogen bonds, the hydrogenation reaction is

exothermic overall.

Based on thermodynamics, since cyclohexane is more stable than cyclohexene in terms of the standard Gibbs free energy and entropy changes, the complete hydrogenation of benzene is more achievable [45]. So, the schematic reaction model for the hydrogenation of benzene is as follows:

$$\text{Benzene} + 3\ H_2 \xrightleftharpoons{\text{Catalyst}} \text{Cyclohexane} \tag{2}$$
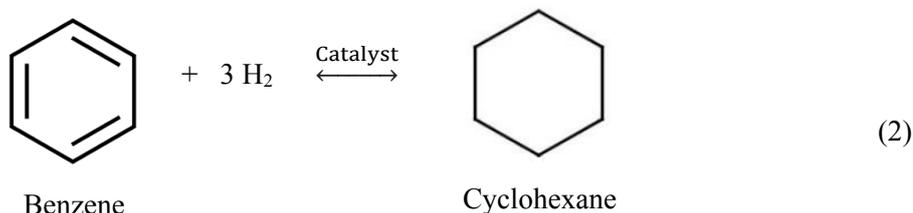
3.2.1. Effect of temperature

In order to save energy, all chemical industries tend to lower the reaction temperature for all associated processes. The effect of the reaction temperature on the hydrogenation of benzene over various catalysts was studied under the constant conditions of the pressure of 1 MPa, WHSV of 25 h^{-1} and H_2/HC of 1.3. Regarding Figure 5, it can be concluded that the conversion of benzene with the temperature of from 100 to 200 ºC increases and then declines slowly by increasing the temperature from 200 to 300 ºC. This matter comes from the thermodynamic equilibrium limitation in the hydrogenation of aromatics at low pressures and high temperatures [22]. The hydrogenation of benzene is an exothermic reaction, so lowering the temperature in a specified range helps the hydrogenation reaction progress [44]. Since the conversion of benzene reaches the maximum amount at 200 ºC for all types of catalysts, therefore in the succeeding tests, the preferred temperature for studying the effect of other parameters is set as 200 ºC. The same results were attained by previous researches [7], while the hydrogenation of benzene was conducted in different temperatures with the Ni metal loaded on ZSM-5 and Al_2O_3 supports Ni/ZSM-5 was more active than the Ni/Al_2O_3 catalyst.
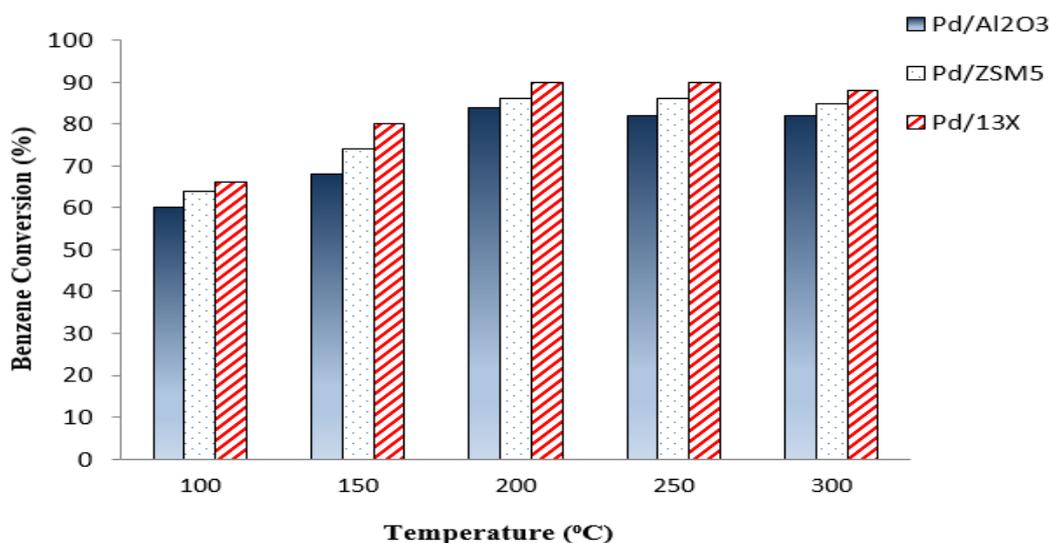

Figure 5. Effects of temperature on the conversion of benzene at P=1 MPa, WHSV= 25 h^{-1} and H_2/HC=1.3.

3.2.2. Effect of pressure

Running the processes in low pressures, in order to decrease the fixed and operating costs, is an excellent practice. By setting the temperature, WHSV and H_2/HC at the already found optimal values of 200 ℃, 25 h^{-1} and 1.3 respectively, a set of experiments was arranged for finding the desired pressure. It was observed that all catalysts especially Pd/13X showed an acceptable activity at P=1 MPa, so by increasing the pressure from 0.3 to 1.0 MPa a noticeable increment in the conversion of benzene (86-90 % for Pd/13X) was obtained in all samples. The further increase in pressure from 1 to 2 MPa led to a small rise (from 90 % to 92.5 % for Pd/13X) in the conversion of benzene (Figure 6). With regard to the stoichiometry of the reaction of the hydrogenation of benzene, the obtained results of the dependence of the conversion on pressure can be rationalized. Therefore, in this reaction four molecules of reactants convert to one molecule, for that reason this reaction is intensely reliant on pressure and under any equilibrium condition by increasing the pressure, the reaction shifts to the formation of more products.
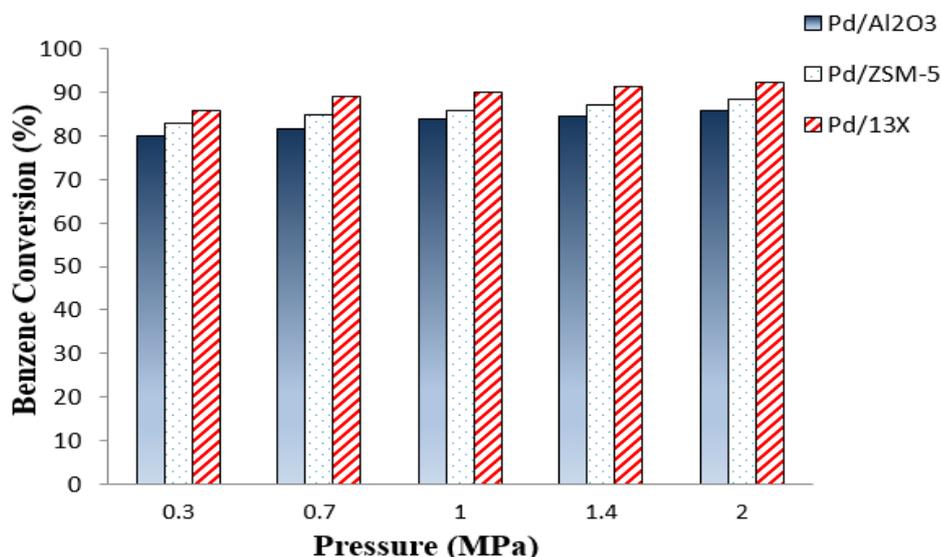

Figure 6. Effects of pressure on the conversion of benzene at T=200 ℃, WHSV=25 h^{-1} and H_2/HC=1.3.

3.2.3. Effect of the flow rate of reactants on conversion

Processing the maximum feed in a chemical unit generally is accompanied by more profits because of increasing the production rate without changing the fixed costs of the equipment. Figure 7 presents the effect of WHSV on the conversion of benzene. Under the conditions of the constant pressure, temperature and hydrogen to hydrocarbon molar ratio (H_2/HC) of 200 ℃, 1 MPa and 1.3 respectively, the conversion of benzene to cyclohexane on all catalysts declined by lowering the residence time of liquid and gas reactants which resulted from increasing WHSV to over a specified value. By increasing WHSV from 10 to 25 h^{-1} no significant change is observed in the conversion and it almost remains unchanged at a maximum level for all catalysts, but the conversion falls strongly by continuing the increment of WHSV from 25 to 40 h^{-1}. So, the WHSV of 25 h^{-1} is recommended to be considered as the optimum condition for this reaction parameter.
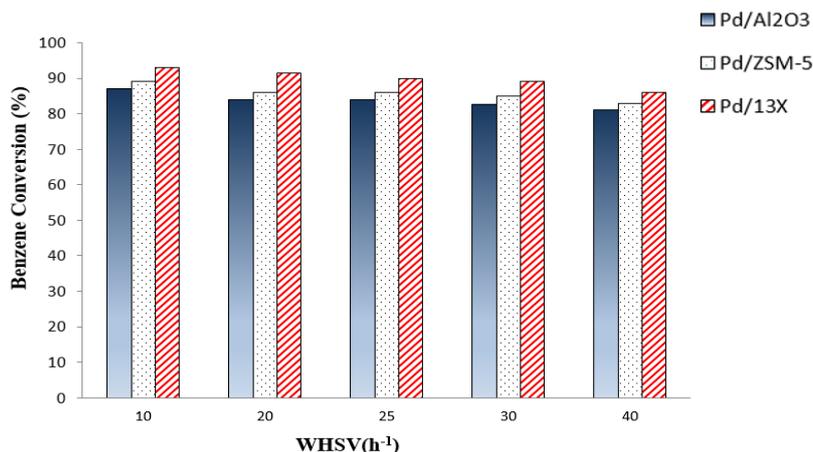
Figure 7. Effects of WHSV on the conversion of benzene at T=200 ºC, P=1 MPa and H_2/HC=1.3.

3.2.4. Effect of the hydrogen to hydrocarbon molar ratio (H2/HC)

The effect of H_2/HC molar ratio on the conversion of benzene is exhibited in the Fig. 8. Based on Le Chatelier's principle, the thermodynamic equilibrium moves toward the more conversion of benzene as the H_2/HC ratio is increased. As shown in Figure 8, the influence of increasing the H_2/HC ratio from 0.65 to 1.3 on the conversion of benzene is positive, but by further increasing from 1.3 the resistance time of reactants (all in gas phase) will decrease and so the conversion will decline accordingly. Thereby, a border limit can be considered for this parameter, in a way that in the lower quantities there is a deficiency in the required H_2 and in higher amounts, the excess H_2 will sweep the reactants from the catalyst surface.

Minimizing the flow rate of hydrogen in industrial units leads to lowering the cost of the compression and separation of products. Considering these reasons, the H_2/HC ratio can be considered as a process variable in the hydrogenation reaction. Therefore, by assuming a fixed amount for all other reaction parameters, the value of 1.3 was found to be a good condition for the H_2/HC ratio in conducting our experiments. The flow rates of the hydrocarbon liquid and hydrogen were adjusted at 0.6 and 250 ml.min^{-1} respectively, for the optimum value of 1.3 for the H_2/HC mole ratio.
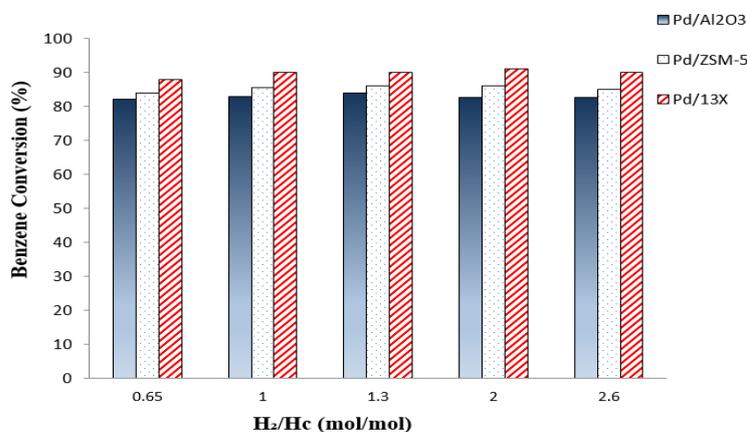

Figure 8. Effects of the H_2/HC mole ratio on the conversion of benzene at T=200 ºC, P=1 MPa and WHSV=25 h^{-1}.

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3.2.5. Time on stream, product yield and catalyst performance

In Figure 9 the deactivation rate of catalysts for a mixed feed (benzene + n-heptane) is shown. The deactivation rate is considered as decreasing the catalyst performance in the conversion of benzene with time and it arises from the coke formation on the catalyst surface.

The activity of catalysts is decreased by time on stream under the finalized conditions of the temperature, pressure, WHSV, mole ratio (H_2/HC) of 200 ºC, 1 MPa, 25 h^{-1} and 1.3 respectively. The conversion rate under specified conditions is descended by 7, 9 and 7 units for Pd/ZSM-5, Pd/13X and Pd/Al_2O_3 catalysts respectively over 20 hours of time on stream. However, the falling of conversion rate for the Pd/13X catalyst is the maximum between all samples. The faster deactivation of the Pd/13X catalyst can be arisen from the higher acidity of the 13X support as resulted from NH_3-TPD patterns.

Under the reaction conditions, some of the reactant components undergo undesirable reactions and crack to lighter products. Likewise, this matter can be caused by the acidic property of the catalyst supports. The volume percent of different components and the light cut hydrocarbon formed in the reactor outlet liquid in presence of all catalysts are represented in Figure 10. More light cut production because of more cracking by the Pd/13X catalyst is arisen from further and stronger acidic sites present in its support.

The liquid product yield (%) and conversion of benzene (%) are two important parameters in comparing the activity of catalysts. For considering the impact of these two parameters in the judgment of the performance of catalysts, the catalyst performance factor (CPF) is defined by the following equation:

$$CPF = [1 - V_{LC}/100] \times C_{BZ} \; (\%) \qquad (3)$$

V_{LC} is the volume percent of the light hydrocarbons produced by undesirable reactions and C_{BZ} is the value of the conversion of benzene . The values resulted from calculating the CPF for all catalysts are summarized in Table. 2. As it is shown, the CPF parameter for the Pd/13X catalyst is higher than the corresponding values of other catalysts and this result comes from the superior activity of the Pd/13X catalyst in the hydrogenation of benzene to cyclohexane.
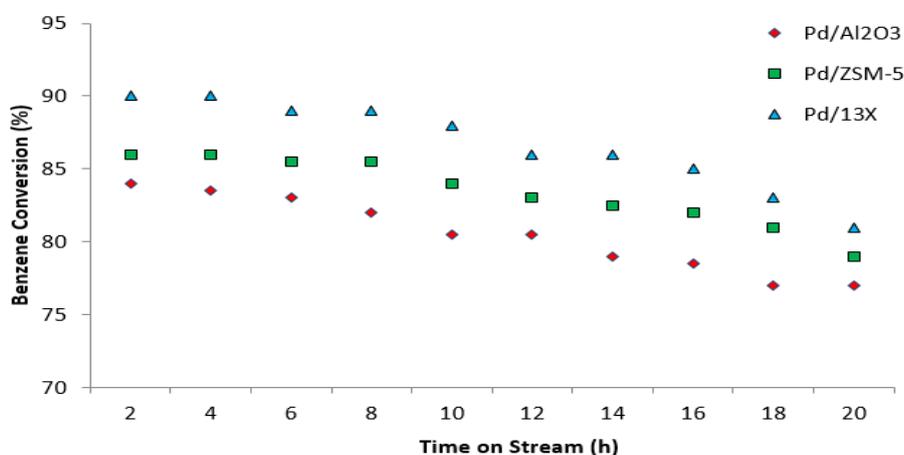

Figure 9. Conversion of benzene versus time on stream at T=200 ºC, P=1 MPa, WHSV=25 h^{-1} and $_{H2/HC}$=1.3.
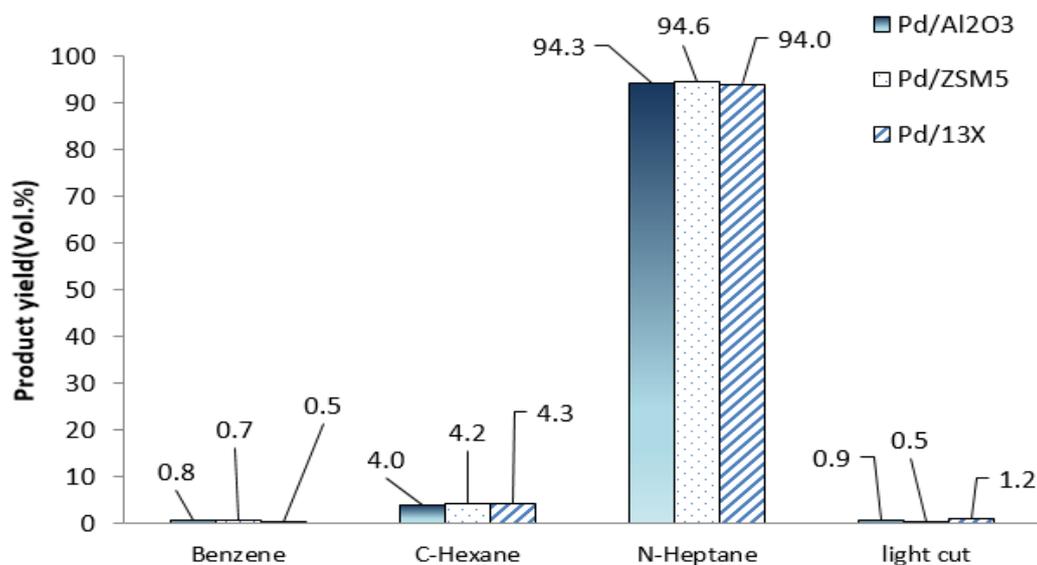
Figure 10. Products yield under the optimum conditions: T=200 ºC**,** P=1 MPa, WHSV=25 h^{-1} and H_2/HC=1.3.

Table 2

Catalysts performance factor, (T=200 ºC, P=1 MPa, WHSV=25 h^{-1}, $\frac{H_2}{HC} = 1.3$).

Catalyst	Pd/(Al$_2$O$_3$)	Pd/13X	Pd/ZSM-5
V$_{LC}$	0.9	1.2	0.5
C$_{BZ}$	84	90	86
[1 - V$_{LC}$/100]	0.991	0.988	0.995
Catalyst Performance Factor (CPF) = [1 - V$_{LC}$] × C$_{BZ}$	83.3	88.9	85.6

4. Conclusions

In the present study, the active sites of Pd on various supports such as ZSM-5, 13X and Al$_2$O$_3$ were synthesized by the dry impregnation method. Many tests for the hydrogenation of benzene in a mixture with n-C7 (5 Vol % of benzene in mixture with n-C7) were done on the prepared Pd supported catalysts in a tubular down-flow stainless steel reactor.

Physical and chemical characteristics of catalysts were studied with XRD, BET and NH$_3$-TPD analyzing methods. It was found from the characterization results that the metal loading on the supports with Pd precursors has no serious effect on the structure of the support.

The evaluation of the activity and stability of the catalysts in the hydrogenation of benzene was verified under different reaction conditions of temperature, pressure, WHSV and the molar ratio (H$_2$/HC). Almost in all experiments the highest activity in the conversion of benzene was obtained by the Pd/13X catalysts (∼ 90 % of conversion under the optimum conditions) and this can be attributed to the better physicochemical properties of this catalyst. The study of the stability of the catalysts during 20 hours shows that the activity of the Pd/13X catalyst is descended faster than that of other catalysts (from 90 % to 81 %), but so far, the activity

of this catalyst is the highest in comparison with those of other catalysts at the end of the defined time (20 hours). Additionally, it is found that the variety in the performance (activity, selectivity or stability) of catalysts can be illustrated in relevance to the properties of the corresponding catalyst.

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Nomenclature

BET	Brunauer-Emmet-Teller.
C_{BZ}	benzene conversion.
CPF	catalyst performance factor.
d_p	pore diameter [nm].
Ni/ASA	nickel on amorphous silica-alumina.
P	pressure [MPa].
Pa	pascal.
Pd	palladium.
$Pd(NO_3)_2$	nitrate di-hydrate.
PFD	Process Flow Diagram.
WHSV	Weight Hourly Space Velocity.
v_B	volume percent of benzene in the product.
v_{B0}	volume percent of benzene in the feed.
V_p	pore volume [cm^3/g].
V_{LC}	volume percent of light hydrocarbons.
XRD	X-ray diffraction.
ZSM-5	zeolite Socony Mobil-5.

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