

# Hydrogenation of Naphthalene on Pt-Pd Catalyst

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*The hydrogenation of naphthalene was conducted on Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Characterization of the catalyst was carried out by determination of acidity and textural characteristics. The distribution of the acid strength of the prepared catalysts was determined by thermic desorption of diethyl amine and textural characteristics were determined by desorption of liquid nitrogen. Experiments were carried out on 1.5-6h<sup>-1</sup> and molar ratio hydrogen/ naphthalene of 10/1. The main compounds identified were tetralin, trans and cis-decalin. The naphthalene conversion was higher and grew up with temperature and pressure. Higher activity of Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is probably due to the appropriate distribution of textural and strength acid.*

*Keywords: catalyst, hydrogenation, acidity, naphthalene, tetraline*

Naphthalene shows a less pronounced aromatic character than benzene, as evidenced by the conjugation of naphthalene energy (61 kcal / mol), which is lower than the energy of conjugation of two benzene nuclei (2x36 kcal / mol). Electrons  $\pi$  of naphthalene are not uniform delocalized on all carbon atoms, as in the case of benzene [1]. Thus hydrogenation of naphthalene become easier in the first stage with formation of tetralin because it tends to turn into a compound whose nucleus has aromaticity equal to benzene. Catalytic hydrogenation of tetralin occur with a mixture of cis and trans isomers of decalin. Trans-decalin is more stable than cis-decalin by 2.1 kcal / mol (amount deducted from the heats of combustion) [2] because of the two links C - C that are equatorial oriented; cis-decalin can be isomerized in trans-decalin.

In the hydrogenation process of aromatic hydrocarbons, are used catalysts based on active metals deposited on a support, such as Ni-Mo, Ni-W, Co-Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [3], or noble metals on Y zeolites [4].

Catalytic hydrogenation of polynuclear aromatic hydrocarbons can be achieved by transition metals such as Pt, Pd, Mo, W, Ni or Ru, conventional catalysts being NiMo supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or and Pt-Pd supported on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [5-7]. Molybdenum concentration varies between 3-25% while Ni has a promoter role (concentration 0.5-5%) to prevent deactivation of the catalyst and coke storage. Texture control and efficiency of the catalyst involves choosing a suitable support, as well as the most efficient method for the preparation thereof. In the hydrogenation of aromatic hydrocarbons,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was found to be an effective support having a high stability and a large number of active sites. Achieving of naphthalene and tetralin high conversion (up to 80%) depends on the methods of preparation of the support and catalyst, of the metal concentration, of the support acidity and the operating conditions [8].

Hydrogenation of naphthalene at 280°C using Pt /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd / TiO<sub>2</sub> catalysts was studied by Montesinos et al [9]. In milder reaction conditions (280 °C and 30 atm) is obtained tetralin but the process can be accompanied by undesirable cracking reactions, after which there was obtained the low molecular weight compounds. However, by hydrogenolysis reactions may

be obtained the fragmentation compounds of the cyclical chain, as alkylcyclohexane, alkyl benzenes, spirodecane, which favors an increased value of cetane number.

Zhang X. [10] has studied the activity of the monometallic catalysts of Pt and Pd compared with the bimetallic Pt-Pd / SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, with mole ratio Pt-Pd 1: 1, 1: 4 and 4: 1. The conversion of naphthalene and its selectivity in decalin were 98.2% and respectively 93.6% for the bimetallic catalyst, giving greater values than in the case of the monometallic catalysts: Pd (97.5% and 59.1%), Pt (96.8% and 39.9%).

S. Albonetti and G. Baldi [11] have highlighted the influence of the type catalysts on the performance of naphthalene hydrogenation using Pd-Rh bimetallic catalysts and Pt-Pd on alumino-silica support. The best results were reported for a low metal content, 0.3%Pt-Pd catalyst having better performance. At a temperature of 340°C has registered a 88% conversion of naphthalene, this performance can be attributed to a large specific surface area due to the presence of bimetallic particles and acidic properties of the the catalytic support or promoters [12, 13].

Optimal operating conditions in the catalytic hydrogenation of aromatic hydrocarbons have been studied on metal catalyst on various acidic supports such as HY zeolites [14-17], MCM-41 [18, 24], mordenite [19], B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> [20-21] SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [22-23]. Fujikawa and his collaborators have determined the kinetic parameters, activity and selectivity of the Pt-Pd catalyst on the alumina-silica support. The data presented in the scientific literature highlights the complex mechanism of the polynuclear aromatics catalytic hydrogenation.

The use of noble metal at hydrogenation of aromatic hydrocarbons is advantageous because such catalysts are active at relatively low temperatures and can also minimize the thermodynamic limitations specific for the exothermic reactions carried out in high temperature conditions. The main disadvantage of noble metal catalysts is low tolerance to the sulfur and the higher cost.

In this work has taken into account testing of a Pt-Pd catalyst with increased activity in naphthalene hydrogenation whose support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) must be sufficiently acidic to modify the metal particles (Pt), so that it

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deficiency of electrons to disfavor formation metal-S bond, in the presence of sulfur compounds in petroleum fractions. The presence of the second metal, palladium, serves to increase catalyst activity and also proved a positive influence to sulfur resistance, because of changes in the electronic properties.

### Experimental part

The raw materials used in experiments were naphthalene 99% (Sigma-Aldrich), palladium chloride 99% (Sigma-Aldrich), hexachloroplatinic acid hexahydrate (Sigma-Aldrich),  $\gamma$ -alumina granulated and electrolytic hydrogen purity from Linde Company.

The synthesis of catalysts were achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the incipient wetting method. Concentration of catalyst precursor of the impregnation solution is calculated according to the proposed metal content (0.25%Pt-1%Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). Conditioning of the catalyst Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> between the steps of impregnating was achieved by drying at 120°C for 6 h and the final conditioning of catalyst was performed by drying at 120°C for 6 h and calcination at 450°C for 6 h. Activation of the catalyst prepared was carried out by treatment with an excess of sodium borohydride, followed by *in situ* reduction in a stream of hydrogen at 5 atm and 450°C for 6 h.

Chemical composition of catalyst used in the experimental program was determined by atomic absorption (Varian AA240FS). Catalyst characterization was performed by determining the acid strength and textural characteristics. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont Instruments *Thermal Analyst 2000/2100* coupled with a module *951 Thermogravimetric Analyzer*. Textural characteristics of the catalysts (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on a Autosorb 1 Quantacrome.

The experimental program was carried out in a continuous reactor, on a fixed bed catalytic. The process was carried out in isothermal conditions and the temperature was established with an automatic system by two thermocouples placed in the reactor jacket. Reaction conditions were:

- temperature: 230 - 270 °C;
- pressure: 30-60 atm;
- volume hourly space velocities of naphthalene (LHSV): 1,5-6 h<sup>-1</sup>;
- molar ratio hydrogen/ naphthalene: 10/1.

The composition of the reaction mixture was performed by the method of gas chromatography coupled with mass spectrometry, equipped with capillary column with a length of 30 m having a diameter of 0.250 mm, whose fixed phase was polyethylene glycol (PEG) and He as mobile phase.

### Results and discussions

The Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst contain a low concentration of strongly acid centers (0.136 meq./g) and a higher concentration of centers with medium acidity (0.147 meq./g). The concentration of strongly acid centers (0.525 meq./g) is over three times higher than the concentration with medium acidity; it can be appreciated that this type of catalyst contains mostly weakly acidic centers.

The isotherm of the adsorption / desorption for Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is type IV with hysteresis loop of H4 type (fig. 2). The isotherm shows a hysteresis loop in the relative pressure range of  $p / p_0 = 0.6$  to 0.9. For relative pressure below 0.6, the two curves for adsorption, respectively desorption, concur. The area between the loop between the two curves proves that the volume of mesopores is relatively large. The first concave part is assigned on a monolayer adsorption. Then, when the pressure becomes equal with the saturation pressure of the vapor, condensation leads to the formation of multi-layers.

The Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is characterized by a high value of the middle pore diameter of 6.254 nm and a relatively large surface area (approx. 437.032 m<sup>2</sup>/g), characteristics that situates it in the area of mesopore (fig. 3).

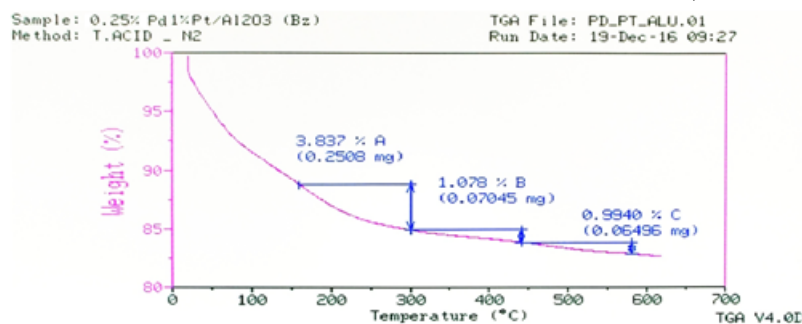


Fig.1. Diethylamine thermal desorption curve for Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

Table 1

DATA ON THE DISTRIBUTION OF STRENGTH ACID FOR Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CATALYST, DETERMINED BY THERMOGRAVIMETRIC ANALYSIS

Catalyst	Temperature range (°C)			
	150-300°C	300-450°C	450-600°C	150-600°C
	Weakly acids centers (meq/g catalyst)	Medium acids centers (meq/g catalyst)	Strongly acid centers (meq/g catalyst)	Total acidity (meq/g catalyst)
Pt-Pd/ $\gamma$ - Al <sub>2</sub> O <sub>3</sub>	0.525	0.147	0.136	0.808

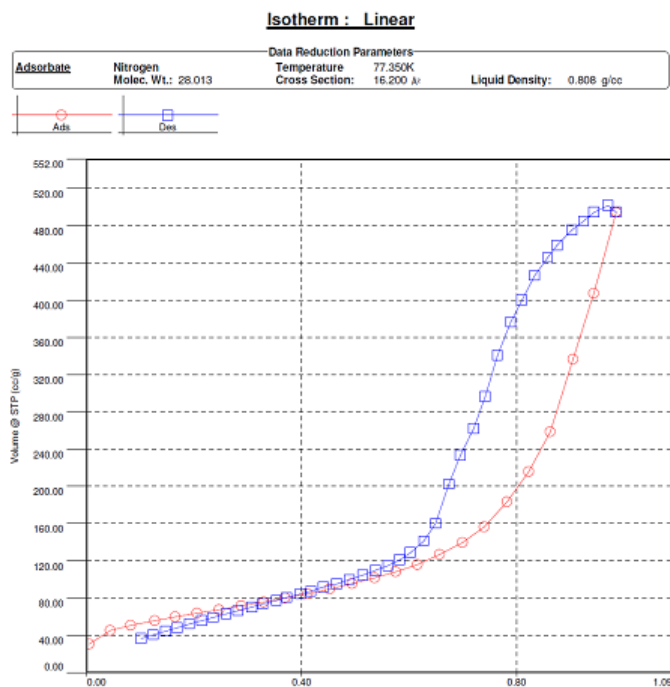


Fig.2. The adsorption / desorption isotherm for Pt-Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The textural characteristics for catalyst studied, obtained by BET and BJH methods are shown in table 2. Pore volume, pore size distribution and middle pore diameter were evaluated from desorption curve of isotherms with hysteresis by applying the BJH method.

Based on chromatographic analysis, were calculated the conversion of naphthalene (X<sub>i</sub>) and yields in the reaction products (ç<sub>i</sub>), using the following formulas:

$$X_i = \frac{\text{the amount of feedstock totally transformed}}{\text{the amount of feedstock introduced}} \times 100$$

$$\eta_i = \frac{\text{the amount of feedstock totally transformed in product } i}{\text{the amount of feedstock introduced}} \times 100$$

(1)

(2)

**BJH method Desorption dV(d)**

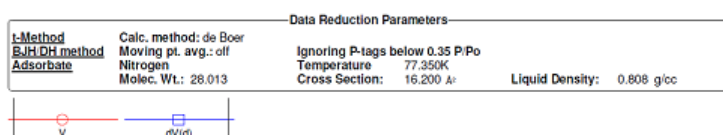
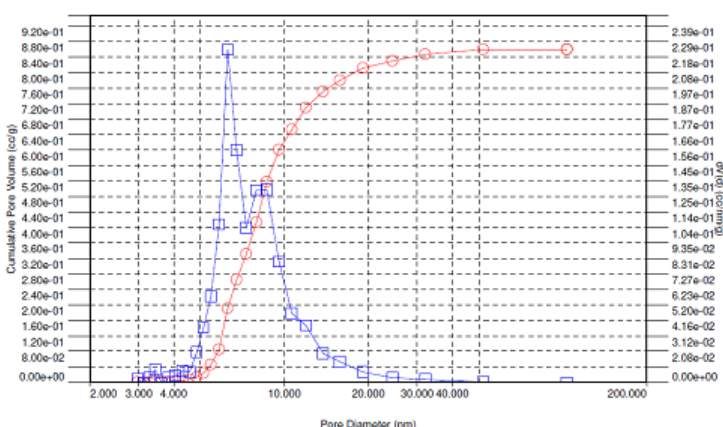


Fig.3. Pore volume distribution for Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst



Catalyst	Specific surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Middle pore diameter (nm)
Pt-Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	407.032	0.860	6.254

**Table 2**  
TEXTURAL CHARACTERISTICS OF CATALYST

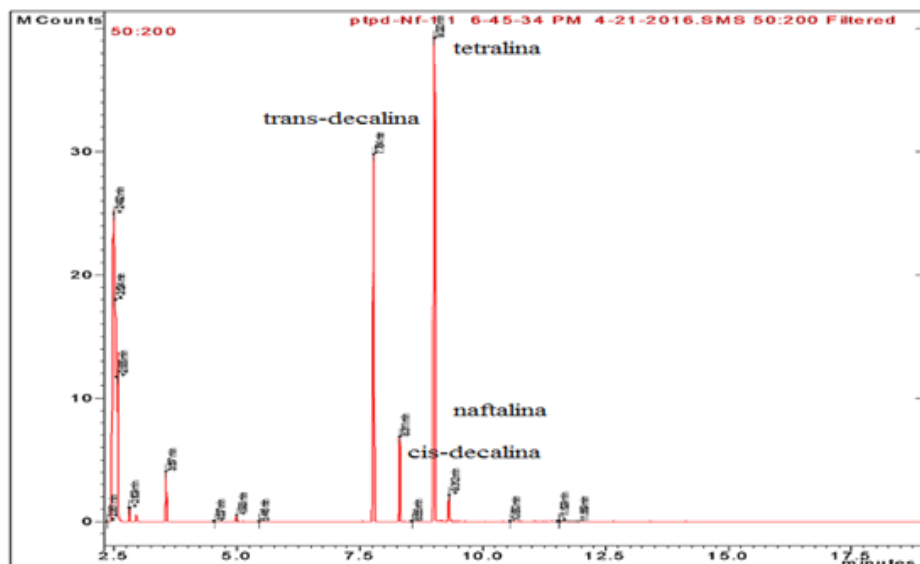


Fig. 4. GC-MS analysis of the reaction products at the naphthalene hydrogenation on the Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 30 atm, 230 °C, LHSV 1.5 h<sup>-1</sup>, molar ratio 10/1

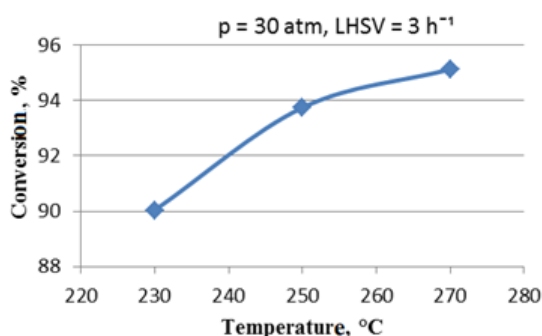


Fig. 5. Variation of naphthalene conversion with temperature on Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

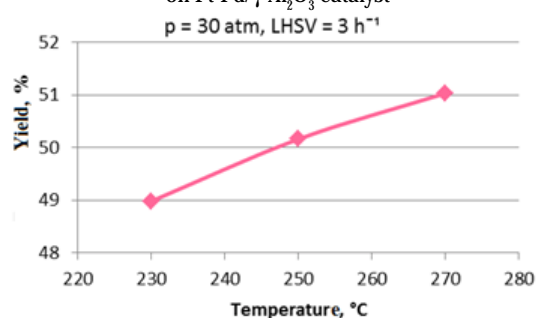


Fig. 6. Variation of the tetralin yield with temperature on Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

temperature, being more pronounced at lower temperature (fig. 5); thus, in 230-250 °C range, the conversion increases from approximately 90% to approx. 94% compared to the range of 250-270 °C where the conversion increases less, from 93.74 to 95.12%. This may suggest that for this catalyst, the reverse dehydrogenation reaction with formation of naphthalene is significant at temperatures greater than 250 °C.

The variation of the tetralin yield with temperature was investigated for various reaction conditions. The representative values were obtained for the lower values of pressure (30 atm), on the interval of temperature studied and is shown in figure 6. Increasing the temperature determines a small increase of the tetralin yield at the temperature range experienced. Thus, at 230 °C the yield in tetralin is 49% and increases with increasing the temperature up to approx. 51% at 270 °C (fig. 6).

In figure 7 are presented the variations of the trans and cis-decalin yield with temperature at 30 atm and LHSV of 3 h<sup>-1</sup>. It can be seen that the trans decalin is obtained in a higher proportion as compared with the cis isomer, trans-decalin yield is approx. 35%, while the yield in cis isomer is

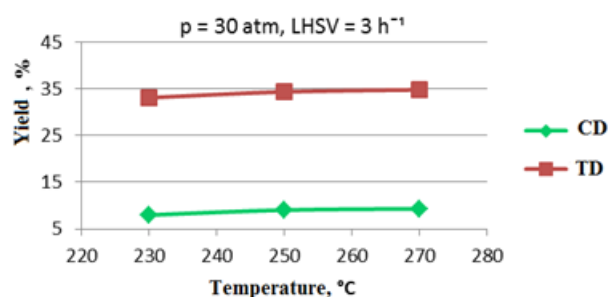


Fig. 7. The yield in trans-decalin and cis-decalin, according to temperature, on Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

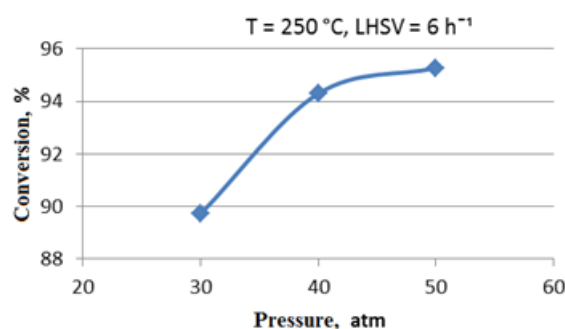


Fig. 8. Variation of naphthalene conversion with pressure on Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 250 °C and LHSV of 6 h<sup>-1</sup>

only 10%, at 250 °C. The yields in both decalin isomers increases with increasing temperature in the range 230-250 °C, but more trans, while at temperatures higher than 250 °C the yields in the two isomers are not influenced significant.

#### Influence of pressure

The variation of the naphthalene conversion with pressure in the hydrogenation reaction at 250 °C and 6 h<sup>-1</sup>, is shown in figure 8. The pressure increase in the range of 30-50 atm determines the conversion of naphthalene increase from 89.72% at 30 atm to 95.59% at 50 atm. The increase with approximately 6% of the naphthalene conversion with increasing of pressure from 30 to 50 atm, is probably due to the passing from gas-solid system, in gas-liquid-solid system and hence from kinetic regime in external diffusional regime. Increase of conversion with pressure increase is due to the fact that the high pressure positively influences the hydrogenation reactions and negative reactions of isomerization and craking.

In figure 9 is represented influence of pressure on the tetralin yield at 250 °C and LHSV of 6 h<sup>-1</sup>. The tetralin yield

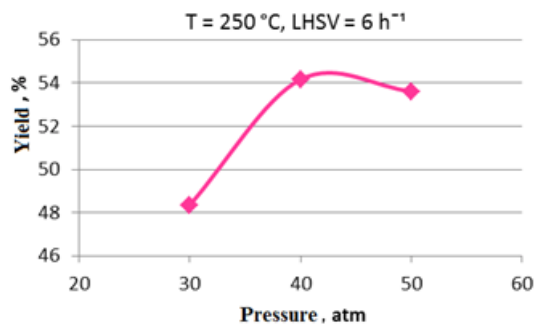


Fig. 9. Variation of tetralin yield with pressure on Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, at 250 °C and LHSV of 6 h<sup>-1</sup>

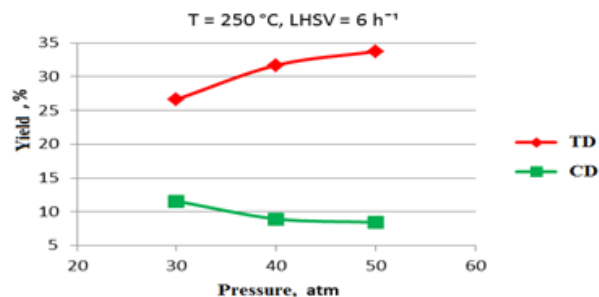


Fig. 10. Variation of the trans / cis-decalin yield with pressure on the Pt-Pd /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at LHSV of 6h<sup>-1</sup>

increase pronounced in the pressure range from 30 to 40 atm, but the pressure increase from 40 to 50 atm results in a relatively small decrease in the yield of tetralin (from approx. 54% to 53%).

The yields variations in cis and trans decalin isomers depending on the pressure are shown in figure 10. Over the pressure range investigated is obtained preferentially the trans isomer. From figure 10 is observed that the trans-decalin yield is not significantly influenced by pressure variation; thus, at 30 atm and 6 h<sup>-1</sup>, the yield in trans-decalin increase from around 27% at approx. 33%. Moderate variation of the trans-decalin yield with increasing the pressure from 30 atm to 50 atm is probably due to the occurrence of diffusional braking generated by occurrence of the liquid phase at higher pressure. The yield in cis-decalin decreases with increasing pressure from 10.57% at 30 atm, to 8.44% at 50 atm. The small values of yield in cis-decalin in comparison with trans-decalin yield is probably due to the higher thermodynamic stability of trans-decalin and implicitly to the isomerization of cis-decalin in trans-decalin favored by the acid function of the catalyst.

### Conclusions

The Pt-Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst led to high conversion of naphthalene at lower value of reaction temperature. The temperature increase favors tetralin yield increase in all temperature range studied (230 - 270°C). The yield in decalin is relatively high (15 - 60%, predominantly trans isomer), which proves the high capacity of the Pt - Pd catalyst to activate the total hydrogenation reaction of naphthalene, so implicitly the tetralin hydrogenation, the less reactive than naphthalene. Over the pressure range investigated (30-50 atm) is obtained preferential trans-decalin whose yield increases with the pressure increase, while the cis-decalin yield decreases. The small values of cis-decalin yield compared with trans-decalin is due by higher thermodynamic stability of trans-decalin and by isomerization of cis - decalin in trans-decalin, favored by the acid function of the catalyst.

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