Hydrogenation of Naphthalene on Ni-Co-Mo-Re/γ-Al_2O_3 Catalyst

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The hydrogenation of naphthalene was conducted on catalyst based on Ni-Co-Mo-Re /γ-Al_2O_3. The distribution of the acid strength of the prepared catalysts was determined by thermic desorption of diethyl amine in the temperature range from 20 to 600°C. Experiments were carried out on a fixed bed catalytic reactor at 280-350°C, 60-80 atm, naphthalene volume hourly space velocities of 1,5-6 h^{-1} and molar ratio hydrogen/ naphthalene of 10/1. The main compounds identified were tetralin, cis-decalin and trans-decalin, reaction arising mainly with forming of tetralin.

Keywords: catalyst, hydrogenation, acidity, naphtalene, tetralin

Polyaromatic hydrocarbons from the fuel can be removed by chemical methods, but limits imposed by the current standards, highlights the need to use catalytic hydrogenation. Hydrogenation of aromatics hydrocarbon occurs in the presence of various metal catalysts on supports like g-alumina. The active component and support acidity influences the performance of the hydrogenation process.

The limitation of the aromatics in diesel for exhaust gas pollution reduction favors the improving of characteristics such as smokeless flame height, the cetane index etc. Hydrogenation of polynuclear aromatic hydrocarbons requires optimal conditions for reaction and suitable catalysts. Depending on the severity of the process, the reaction may devolve with formation of tetralin in the first step, and to form cis and trans-decalin in the second stage. The performance of the hydrogenation process depend on the catalysts and operating parameters such as pressure and temperature.

Usually, in the hydrogenation of aromatics mono and bi-metallic catalysts are used. Thus the tetralin hydrogenation was studied on three mono-metallic catalysts based on Ni at different reaction temperatures (275-375°C). The catalysts were prepared by impregnating with aqueous solution of nickel nitrate, a solution of nickel nitrate in ethanol and an aqueous solution of nickel citrate. The catalysts showed a similar evolution of conversion depending on the reaction temperature [1]. The best catalytic performance was registered in the case of a nickel-based catalyst prepared by impregnation with an aqueous solution of nickel nitrate [2].

Hydrogenation of aromatic hydrocarbon on bi-metallic catalysts was studied on non-noble metals used such as Ni-Mo, Ni-W, Co-Mo or catalysts based on noble metals [3]. Thus naphthalene hydrogenation was studied on bimetallic catalysts based on Pt and Pd as well as Pt (0.3%) Pd (0.6%) / USY Zeolite, Pt (0.3%) Pd (0.6%) / amorphous SiO_2-Al_2O_3 and Pt (0.3%) Pd (0.6%)/γ-Al_2O_3 at temperature 260-360°C, total pressure 35-80bar, ratio of hydrogen/ hydrocarbon 200-1000 Nm^3 / m^3 and the volume hourly space velocities (VHSV) from 0.75 to 4 h^{-1} [4]. It was observed that highest catalytic activity was registered at 310°C in the presence of Pt catalyst (0.3%) Pd (0.6%) / USY Zeolite. At higher temperatures, catalytic activity decreases.

The efficiency of a catalyst requires the control of its texture by the choice of adequate support, as well as of the most efficient method for the preparation of it. In the hydrogenation of aromatic hydrocarbons, alumina has been found to be an effective support having a high stability and a high concentration of active centers. The acidity of catalyst influence the selectivity of aromatic ring hydrogenation. For example, the hydrogenation of naphthalene on Pt catalyst were was performed on aluminosilicates as catalytic supports such as Si / Zr MCM-41. It revealed that increasing the Si /Zr ratio leads to decrease in the total number of acidic centers [5].

In another study it was found that the texture of supports based alumina are particularly influenced by pore size. The best binder for the support composition has been found to be alumina monohydrate (boehmite) with orthorhombic structure with a specific surface area of 290-300 m^2 / g and pore volume of 0.300 cm^3 / g [6].

Palladium as the metal clusters, was fixed on a substrate type nanotubes, MWNT (multi-walled carbon nanotubes). In the hydrogenation reaction of naphthalene the results showed a better behavior of the catalyst than using the supports zeolite or activated carbon type [7].

Recent studies have demonstrated that the presence of gold particles like promoters for bimetallic catalysts, used in the naphthalene hydrogenation, favored increasing of activity and selectivity to tetralin, decalin and 1,9–octaline as an intermediate product. [8]

Compared to studies of literature that approach the processing of bioresources [9-12], the number of publications that address the hydrogenation of polyaromatics hydrocarbons is relatively low, priority concerns being directed towards obtaining biofuels.

In this paper it was studied the hydrogenation process of naphthalene on a multimetal catalyst of Ni-Co-Mo-Re / γ-Al_2O_3, the metals selection aimed at both improving the hydrogenation activity and correction of catalyst acidity.

Experimental part

The raw materials used in experiments were naphthalene 99% (Sigma-Aldrich), nickel (II) nitrate hexahydrate puriss (Sigma-Aldrich), cobalt (II) nitrate hexahydrate puriss (Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), ammonium

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perrhenate (Sigma-Aldrich), γ-alumina granulated and electrolytic hydrogen purity from Linde Company.

The synthesis of catalysts where achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of pores filling. Concentration of catalyst precursor of the impregnation solution is calculated according to the proposed metal content (0.8%Ni, 2%Co, 11.5% Mo and respectively 0.5% Re). Conditioning of the catalyst Ni-Co-Mo-Re /γ-Al_2O_3 between impregnations was achieved by drying at 160°C for 4 h and the final conditioning of catalyst was performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and reduction in a stream of hydrogen at 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 Analizer. 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 isothermal conditions, on a fixed bed catalytic in a continuous reactor. The temperature was established with an automatic system by two thermocouples placed in the reactor jacket. Reaction conditions were:

- temperature: 280-350°C;

-pressure: 60-80 atm;

-volume hourly space velocities of naphthalene (VHSV): 1.5-6 h^{-1};

-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

Figure 1 shows the thermal desorption curve of diethylamine for Ni-Co-Mo-Re / γ-Al_2O_3 catalysts and table 1 presents the data on the acid strength distribution. It is observed a low content of strongly acid centers (0.105 meq./g) and of medium acids centers (0.150 meq./g). The concentration of weak acids centers was about five times higher than of the strongly acid centers (0.508 meq./g). So this catalyst contains predominantly weak acid centers.

The isotherm of adsorption / desorption for catalyst Ni-Co-Mo-Re / γ-Al_2O_3 is shown in figure 2, and the pore size distribution in figure 3. The isotherm is type IV with a H_3 hysteresis loop, specific for capillary condensation process on mesoporous solid materials with low affinity for molecules adsorbed and a narrow distribution of pore sizes.

In the area of low relative pressure p /po, the nitrogen volume adsorbed by the catalyst is associated with a monolayer adsorption of nitrogen on the surface. At relative pressure close to 1.0 it can be noted an increase in the volume adsorbed and the presence of small hysteresis loops, specific for multilayer condensation of nitrogen in the catalyst pores.

Textural characteristics of the catalyst were determined by the BJH method on the desorption zone and are shown in table 2. The specific surface area of the catalyst Ni-Co-Mo-Re / γ-Al_2O_3 has a specific value for catalysts based on γ- Al_2O_3.

Textural properties of the catalyst Ni-Co-Mo-Re / γ-Al_2O_3 consist in large surface area, pore volume relatively large and in single-mode mesopore size distribution, indicating good accessibility of the catalytic center. Thus figure 3 shows that the catalyst has a distribution with a maximum pore diameter of about 42 Å.

The main reaction products identified in the naphthalene hydrogenation on Ni-Co-Mo-Re /γ-Al_2O_3 catalyst were:

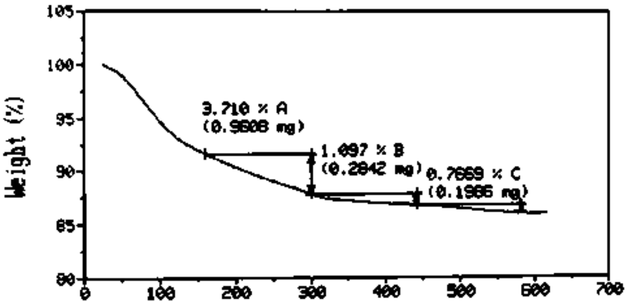


Fig.1. Thermal desorption curve of diethylamine for Ni-Co-Mo-Re / γ-Al_2O_3 catalysts

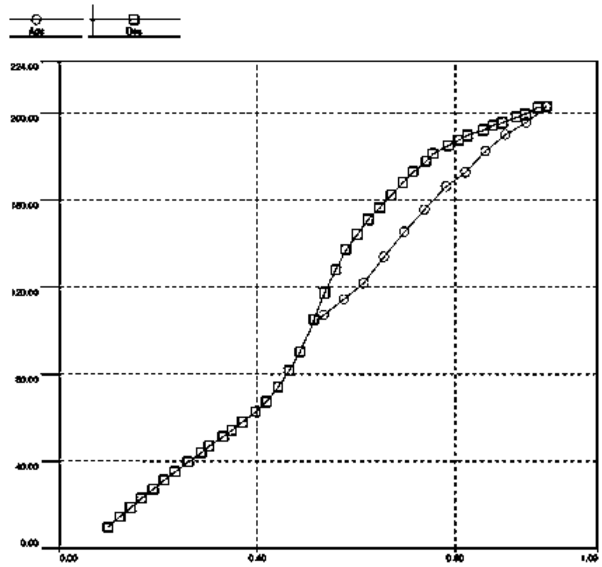
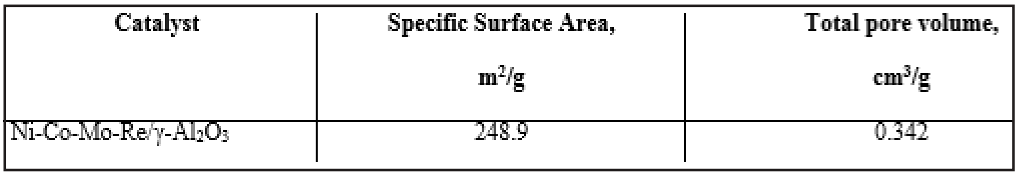


Fig. 2. The adsorption / desorption isotherm for Ni-Co-Mo-Re / γ-Al_2O_3 catalyst

The type of the acidic centers	Temperature range, °C	The acid strength, meq./g sample
Weak acids centers	150-300	0.508
Medium acids centers	300-450	0.150
Strong acids centers	450-600	0.105
TOTAL	150-600	**0.763**

Table 1
THE DISTRIBUTION OF ACIDITY STRENGTH FOR THE CATALYST OF THE Ni-Co-Mo-Re / γ-AL_2O_3

Table 2
TEXTURAL CHARACTERISTICS
OF Ni-Co-Mo-Re / γ-Al_2O_3
CATALYST



Catalyst	Specific Surface Area, m^2/g	Total pore volume, cm^3/g
Ni-Co-Mo-Re/γ-Al_2O_3	248.9	0.342

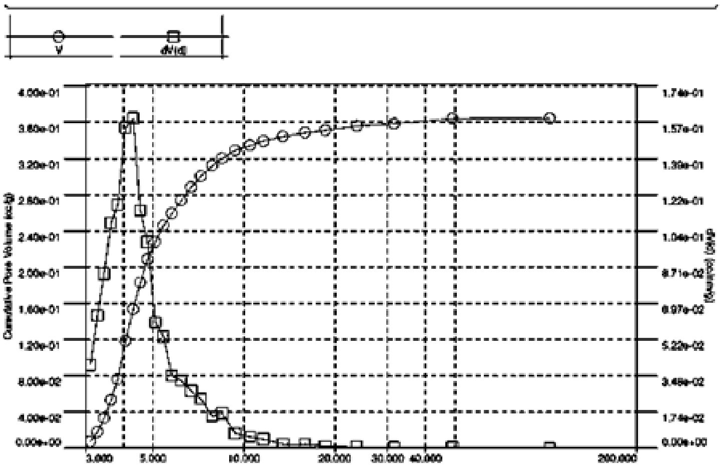


Fig.3. Pore volume distribution based on size, for Ni-Co-Mo-Re / γ-Al_2O_3 catalyst

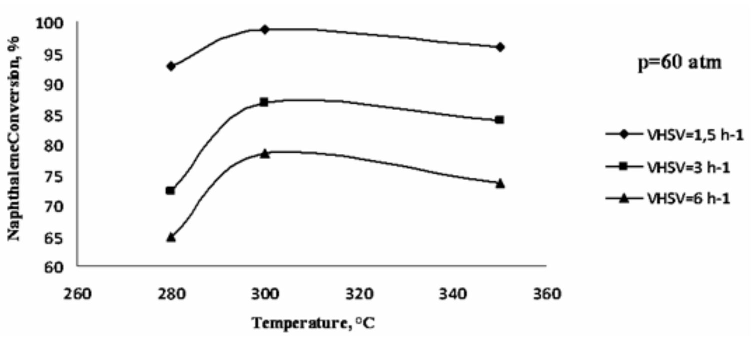


Fig. 4. The temperature influence on the naphthalene conversion

tetralin, cis-decalin and trans-decalin. For volume hourly space velocities studied naphthalene conversion variation with temperature on Ni-Co-Mo-Re /γ-Al_2O_3 catalyst arises after a curve with maximum (fig. 4). The temperature range in which is carried out the catalytic hydrogenation of naphthalene is one of the factors determining on the nature and proportion of the reaction products results. Thus naphthalene conversion, on the temperature range studied, was higher (98%) for volume hourly space velocities of 1.5 h^{-1} compared with those obtained for the higher volume hourly space velocities. In the temperature range 300-350°C, there is a relatively small variation in slope for the three curves.

Hydrogenation of naphthalene on the Ni-Co-Mo-Re / γ-Al_2O_3 catalyst carried out with the formation mainly of tetralin. The influence of temperature on the yield in tetralin on this catalyst is shown in figure 5. It is noted that for the three values of the volume hourly space velocities studied, the yield of tetralin varies with temperature according to a parabola with a maximum at 300°C.

The yield in trans-decalin, in the range of 280-350°C, varies according to a parabola with a minimum located at 300°C (fig. 6). The highest value of the yield in trans-decalin is noted for temperature 350°C and 1.5 h^{-1}VHSV, parameters to which the yield in trans-decalin is about 20%.

The yield in cis-decalin highlights an increase with temperature on the range studied. Thus, for all values of

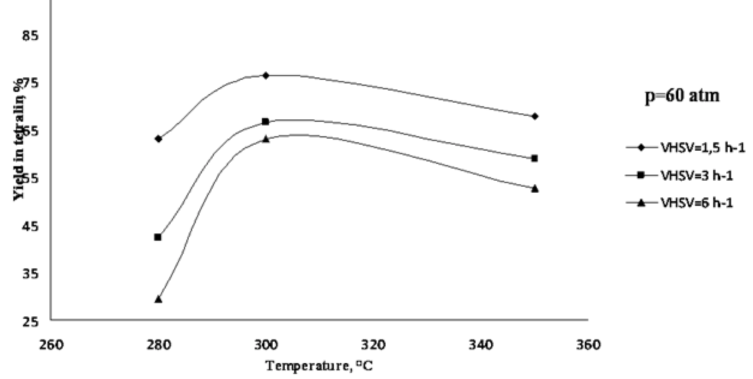


Fig.5. The temperature influence on yield in tetralin

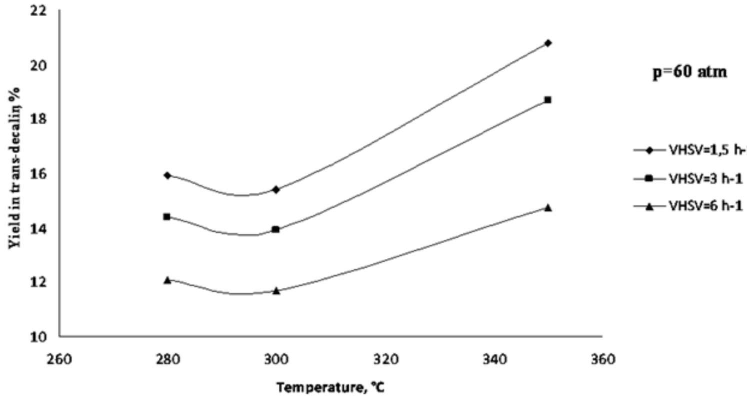


Fig.6. The temperature influence on yield in trans-tetralin

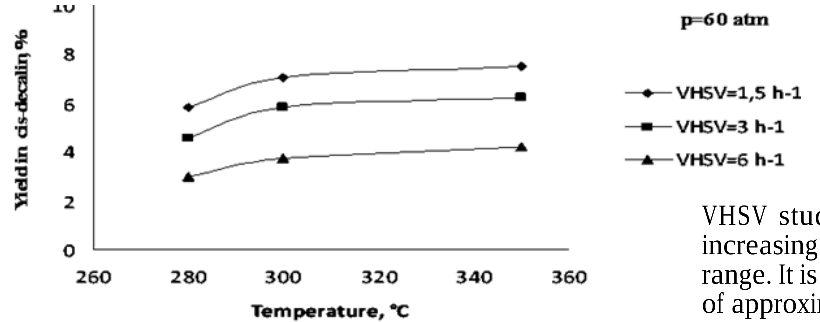


Fig.7. The influence of temperature on the yield in cis-decalin

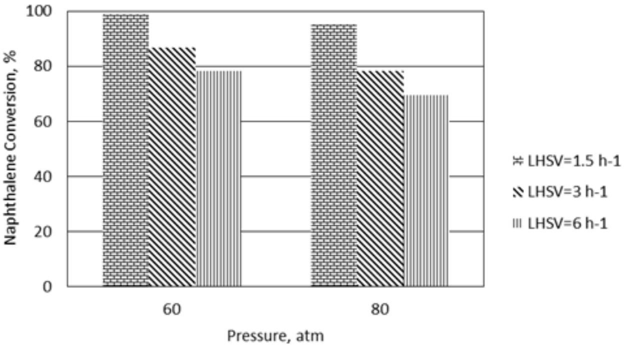


Fig.8. Influence of pressure on the naphthalene conversion at 300°C

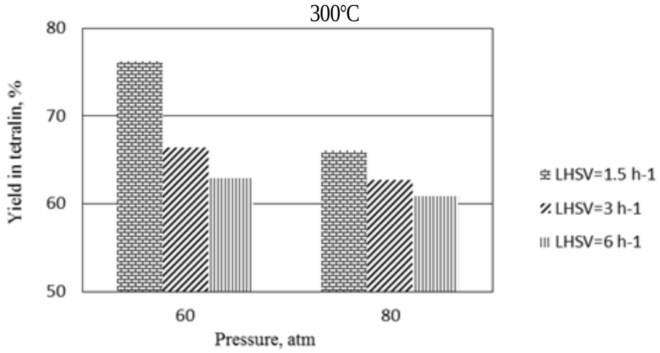


Fig. 9. Influence of pressure on the yield in tetralin at 300°C

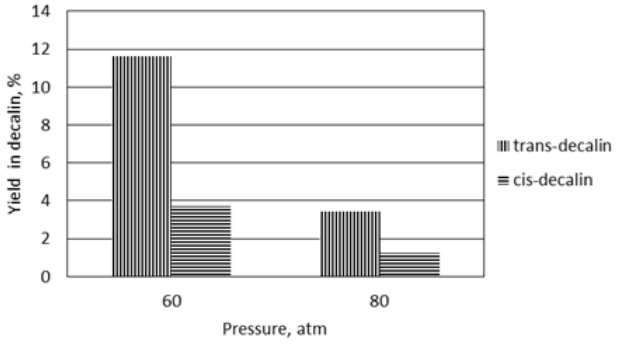


Fig.10. Influence of pressure on the yield in trans and cis-decalin at 300°C and VHSV of 6 h^{-1}

VHSV studied, in 280-300°C temperature range, the increasing occurs by a higher slope than in the 300-350°C range. It is noted that the yield in trans-decalin has values of approximately three times higher than the yield in cis-decalin. The lower value of yield in cis-decalin beside in trans-decalin is due to greater thermodynamic stability of trans-decalin. The temperature range studied favors the isomerization reaction of cis-decalin in trans-decalin (fig. 7).

The variation of naphthalene conversion with pressure is shown in figure 8. It has been observed a very high value of naphthalene conversion, of about 98%, for small contact time of the reactants (VHSV of 1.5h^{-1}). At higher values of VHSV hydrogenation reaction of naphthalene is disadvantaged, naphthalene conversion decreasing significantly. The naphthalene conversion decrease with increasing pressure throughout the parameters studied.

The reducing of naphthalene conversion with the increase of pressure on 60-80 atm pressure range is probably due to external diffusional braking that occurred following the transition of process from gas-solid system in gas-liquid-solid system with increasing of pressure.

Figures 9 and 10 shows the variation of yield in tetralin and decalin with pressure, at 300°C and volume hourly space velocities between 1.5 and 6 h^{-1}. It is noted that the increase of pressure causes the decrease of yield in tetralin, decrease more obvious at low values of volume hourly space velocities. Also, doubling of the volume hourly space velocities does not significantly influence the yield in tetralin, especially at higher values of pressure. For example, for the volume hourly space velocities of 3 h^{-1} the yield in tetralin decrease from 66.44% at 60 atm to 62.96% at 80 atm. Perhaps, increases of the volume hourly space velocities and hence of the linear speed favored reduction of the thickness of the limit layer and hence of the external diffusional braking.

The yield in trans-decalin and *cis*-decalin, at 300°C and volume hourly space velocities of 6h^{-1}, decreases with increasing of pressure, from 11.65% at 60 atm to 3.45% at 80 atm in case of trans decalin, and from 3.74% at 60 atm, to 1.27% at 80 atm, in the case of the cis isomer (fig. 10). The decrease of the yield in decalin by increasing the pressure from 60 atm to 80 atm is probably due to the occurrence of braking diffusional generated by the forming of liquid phase at 80 atm and is most evident for the trans isomer.

Volume hourly space velocities influence on the naphthalene conversion is illustrated in figure 11. Maximum

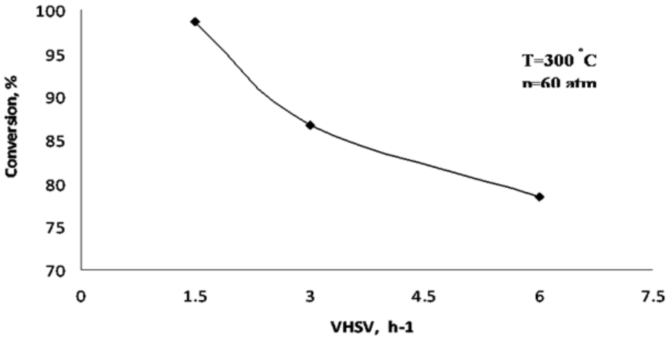


Fig.11. The VHSV influence on the naphthalene conversion

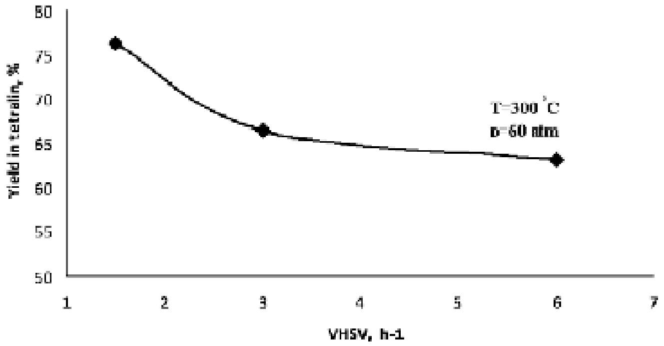


Fig. 12. The VHSV influence on the yield in tetralin

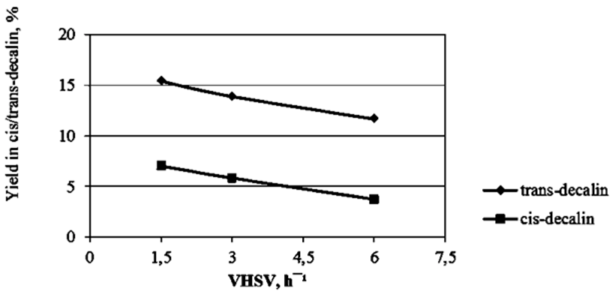


Fig.13. The VHSV influence on the naphthalene yield at 300°C and 60 atm

conversion of naphthalene (98.69%) was obtained when the naphthalene hydrogenation takes place at 300°C and 60 atm for a low VHSV (1.5 h^{-1}). At higher volume hourly space velocities, the naphthalene conversion is reduced with a relatively constant slope variation.

Figure 12 presents the variation of yield in tetralin with naphthalene volume hourly space velocities. It is notice that the value of yield in tetralin is not significantly influenced by contact time. Thus, the yield in tetralin decreases with volume hourly space velocities with a relatively small variation of slope from about 75% at 1.5 h^{-1} to about 65% at 3h^{-1} and is maintained almost constant for values of the volume hourly space velocities between 3 and 6 h^{-1}.

Figure 13 presents the values of yields in cis and trans-decalin with naphthalene volume hourly space velocities. Increasing of volume hourly space velocities lead to decrease of yield in cis and trans-decalin. The yield in cis-decalin presents much lower values than of trans-decalin.

Conclusions

The catalyst Ni-Co-Mo-Re/γ-Al_2O_3 was prepared by pore filling method, in order to test in hydrogenation of naphtalene.

The catalyst shows a low content in strongly acid centers and medium acid centers and a concentration of weak acids centers of about five times higher than of the strongly acid centers.

Hydrogenation experiments of naphtalene were performed in continuous system.

The main reaction products identified in the naphthalene hydrogenation on Ni-Co-Mo-Re / γ-Al_2O_3 catalyst were tetralin, cis-decalin and trans-decalin, reaction arising mainly with forming of tetralin.

The yield in tetralin varies with temperature according to a parabola with a maximum at 300 °C, while the yield in trans-decalin varies according to a parabola with a minimum situated at the same temperature.

The reduction of the naphthalene conversion and of the yield in tetralin, trans-decalin and cis-decalin with the increase of pressure on the 60-80 atm pressure range is probably due to the occurrence of braking diffusional generated by the forming of liquid phase

References

1. SIETSMA, J., FRIEDRICH, H., Journal of Catalysis, 2008, 260, p. 227;
2. LINDFORS, L. P., SALMI, T., Catalyst. Ind. Eng. Chem. Res. 1993, 32, p. 34;
3. MONTEIRO, A.C.A., Hydrotreating: HDA Studies on NiMo-Ni- and Ru/Al_2O_3 Catalysts for the HYD of Naphthalene, PhD Thesis, The University of Birmingham, UK, 2005;
4. KAN, T., SUN, X., Energy Fuels, 2012, 26 (6), p. 3604;
5. WANG, H., ZHANG, W., Catalysis Letters, 2005, 100, p.71;
6. VILLARROEL, M., MENDEZ, A., AGUILA, G., ESCALONA, N., BAEZA, P., GIL-LLAMBÍAS, F., Catalysis Today, 2010, 156, p.65;
7. ANDREW, D., BOWERS, G., SONG, C., Shape selective hydrogenation of naphthalene over zeolite supported Pt and Pd catalysts, Materials Science and Engineering Fuel Science, Academic Projects Building Pennsylvania State University, 2009;
8. VENEZIA, A.M., LA PAROLA, V., Applied Catalysis A: General, 2004, 264, p.43;
9. DUSESCU, C., BOLOCAN, I.,Rev. Chim. (Bucharest), **63**, no.3, 2012, p.305
10. DUSESCU,C., BOLOCAN, I., Rev. Chim. (Bucharest), **63**, no.7, 2012, p.732
11. CRISTEA, S., BOLOCAN, I., BOMBOS, D., BOMBOS, M., VASILIEVICI, G., JUGANARU, T., CHIVU, R., PANAITESCU, C., Rev. Chim.(Bucharest), **66**, no. 8, 2015, p.1177
12.DUTESCU, D. ROTCA,P., D. BOMBOS, T. JUGANARU, D. POPOVICI, R. DRAGOMIR, Rev. Chim. (Bucharest), **63**, no. 2, 2012, p.229

Manuscript received: 13.04.2016