

Component for Gasoline by Hydroconversion of Furfural Derivates in Presence of Methanol

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Hydrotreating of furfural in order to obtain furan derivatives, components for gasoline was studied on two catalysts Ni-Co-Mo γ -Al₂O₃ promoted with Ba and respectively Pt-Pd/ γ -Al₂O₃. Catalysts characterization where performed by determining the acid strength and textural characteristics. For both catalysts the main reaction products identified are tetrahydrofurfuryl alcohol, methyl tetrahydrofurfuryl ether, furfuryl alcohol and furfuryl methyl ether, the most valuable component for gasoline from the resulting mixture being tetrahydrofurfuryl methyl ether. Catalyst Pt-Pd/ γ -Al₂O₃ showed higher activity than catalyst Ni-Co-Mo-Ba γ -Al₂O₃ on the ranges of parameters studied. The yield in ethers was higher than the yield in alcohols for both catalysts for the parameters range studied and the yield in tetrahydrofurfuryl methyl ether was higher in the case of Pd-Pt catalyst than for Ni-Co-Mo-Ba catalyst.

Keywords: furfural, hydrogenation, catalyst, fuel

Fuel production or fuel additives require new catalytic process that converts biomass into valuable products under competitive conditions. Furfural was identified as a direct result derived from biomass, although annual production is only about 300 kTons [1].

The great interest for furfural hydrogenation is due to valuable compounds that are obtained with application in various industries such as plastics industry, pharmaceutical industry, agronomy etc.

Recently, furfural it was considered as one of the options for sustainable production of fuels [2]. In the selective furfural hydrogenation, it have been studied many catalysts on various supports, such as the mono and bi-metallic based on Cu and Ni [1,3,4,6], or noble metal catalysts such as Pd [8], Ru [8], Pt [9].

According to studies from the scientific literature, mono and bimetallic catalysts based on Cu and Ni exhibit a high catalytic activity in the selective furfural hydrogenation to the valuable compounds such as tetrahydrofurfuryl alcohol (THFA) [3,4] furfuryl alcohol (FA) [3-5], cyclopentanone (CPON) [6], compounds with applications in production of pentanediol, ecological solvents, resins and industrial fuel additives [1].

The bimetallic nanocatalysts Cu_xNi_y (x / y 7: 1, 3: 1, 1: 1, 1: 3, 1: 7) / MgAlO present a higher catalytic activity in the furfural hydrogenation process to TFA in comparison with that of the Ni monometallic. It has been demonstrated that bimetallic nanocatalyst of CuNi/MgAlO shows a high selectivity to TFA (95%) (reaction parameters: furfural 5 mmol, ethanol 20 mL, catalyst 0.05 g, 150°C for 3 h, pressure of H₂ 4 MPa). Selectivity in FA increases exponentially with Cu content of the catalyst; in the case of Cu/MgAlO catalyst it was obtaining a selectivity >99% for FA, demonstrating the effect of copper at the selective hydrogenation of C = O bond from furfural [3].

It was studied the activity of the Ni and Cu-Ni catalysts supported on carbon nanotubes (CNT) for selective hydrogenation in the liquid phase of furfural to tetrahydrofurfuryl alcohol. The reaction was performed

under mild conditions (130 °C, pressure H₂ 40 bar, reaction time 10h) observing that the most efficient proved to be the monometallic Ni / CNT (10% wt.) and the bimetallic Cu -Ni / CNT catalyst (molar ratio 1: 1). The TFA yields were 84.3% and 90.03% respectively. Synergetic interaction between Cu and Ni determined obtaining of higher catalytic performance [4].

For the selective hydrogenation of furfural, Changyong et al. prepared four copper catalysts type nanowire (CuNW) and nanodisk (CuND), in the presence of ethylenediamine (EDA). The nanowire CuNW-EDA (surface area of 6.55m² / g) present a much better activity than CuND-EDA nanodisk (surface area of 8.87 m² / g) in the hydrogenation process. Catalyst of CuNW-EDA is the most effective, yielding a selectivity in furfuryl alcohol of 86-96% and less than 4% 2-furan. Comparing the two catalysts CuNW-EDA and CuNP, it was determined that the initial reaction rate for CuNW-EDA was 0.092 mol g⁻¹ / h, much higher than for CuNP (0.012 mol g⁻¹ / h) due to the different number of catalysts active centers. The CuNW-EDA nanowire presented much higher activity than untreated spherical nanocrystal emphasizing a morphology-dependent effect [5].

Cyclopentanone (CPON) an important intermediate for obtaining cyclohexanol, valuable component for gasoline can be obtained by furfural selective hydrogenation in the presence of a Cu-Ni catalyst (molar ratios: 0.25, 0.5, 1.5, 2.5) incorporated into a carbon matrix. The CuNi/C catalyst present a good catalytic performance, furfural conversion being 99.3% and the yield in cyclopentanone 96.9%, in mild reaction conditions (130°C, 5 MPa and 5h reaction time) [6]. Cyclopentanone is obtained by furfural hydrogenation in the liquid phase using nickel-based catalysts and zeolite Y (zeolite with a hierarchical structure). The higher conversion of furfural was 96.4% obtained when it was used 20% wt. Ni / HY-0018 catalyst and a yield in CPON up to 86.5% (at 150 °C, H₂ pressure 4 MPa, reaction time 9 h) [7].

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The Pd and Ru catalysts were synthesized on the black sand supported (CB) and carbon nanotubes (CNT), and studied in the furfural hydrogenation. The 1.5% Pd / CB catalyst presented a high selectivity (99%) in furfuryl alcohol at 50°C and a hydrogen pressure of 0.5 MPa. The 1.5% Pd / CNT catalyst was inactive in mild reaction conditions (50°C, 0.5 MPa), but had a greater tendency to reduce furan ring in more severe conditions (90 °C, 0.5 or 2.0 MPa), when the yield in tetrahydrofurfuryl alcohol was higher. The catalysts based on ruthenium showed a low activity in furfural hydrogenation in liquid phase, indifferently of the support nature and reaction conditions [8].

The furfural hydrogenation in liquid phase and mild conditions was studied on Pt nanoparticles on various supports (SiO₂, ZnO, γ -Al₂O₃, CeO₂ and MgO) [9]. Thus at temperatures of 50°C and atmospheric pressure are obtained high conversions and selectivity to furfuryl alcohol over 99%. The furfural hydrogenation reaction is influenced by the particle size of Pt, so for particle size smaller than 3 nm occurs furfural decarbonylation to furan while between 3-7 nm the hydrogenation arising with getting furfuryl alcohol. A monodisperse size of nanoparticles Pt / MgO, CeO₂ and Al₂O₃ for 4 nm determine optimal activity and selectivity. An another factor which influences the furfural hydrogenation reaction is the used solvent; nonpolar solvents determine low conversions of furfural while alcohol type solvents (n-butanol, methanol) favors increasing efficiency in furfuryl alcohol. Although these supports are different, in terms of their acidity, specific surface area and density, they are recommended for furfural selective hydrogenation to furfuryl alcohol in mild conditions of temperature and pressure [9].

The furfural hydrogenation to furfuryl alcohol was made with catalysts based on various metal such as platinum, palladium, copper and nickel. The use of ethanol as a solvent had a negative effect on the selectivity in furfuryl alcohol, obtaining large amounts of 2-furaldehyde diethyl acetal and difurfuryl ether. By replacing the ethanol with toluene to increase the selectivity of furfuryl alcohol. The metal which increases selectivity to furfuryl alcohol was platinum. Selectivity to furfural alcohol increased by adding a second metal, in the following order tin > molybdenum > manganese > barium > iron > nickel. The hydrogenation took place in the liquid phase, at 100°C and 20 bar hydrogen pressure. On the 0.4% Sn 0.6% Pt / SiO₂ catalyst the furfural conversion was 47% and furfuryl alcohol selectivity of about 100% [10].

The catalysts 1.9% Pd / 1.4% SiO₂ and Pt / SiO₂ is recommended for liquid-phase furfural hydrogenation. There were tested different supports (SiO₂, Al-SBA-15, zeolite beta and TiO₂) and the one who favored obtaining a high selectivity to furfuryl alcohol was SiO₂ [10].

The hydrogenation of furfural in the gas phase (FUR) was achieved with Cu-CeO₂ catalysts. Its stability is due to strong Cu-CeO₂ interaction. The highest conversion (83%) was obtained for catalysts with a higher content of copper, having a higher concentration of metal centers, in these reaction conditions: 190°C, at a molar ratio H₂: FUR 11.5 and WHSV 1.5 h⁻¹. In all cases it was obtained furfuryl alcohol and 2-methylfuran [11].

The objective of this research is the obtaining of a alcohols and ethers mixture, components for gasoline, by furfural hydrotreating. For this purpose we have been tested two catalysts, respectively Ni-Co-Mo-Ba and Pt-Pd.

Experimental part

Chemicals

The raw materials used in experiments were furfural p.a (Sigma-Aldrich), methanol anhydrous (Sigma-Aldrich),

cobalt (II) nitrate hexahydrate puriss p.a. (Sigma-Aldrich), nickel(II) nitrate hexahydrate puriss p.a. (Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich), chloroplatinic acid hexahydrate ACS reagent (Sigma-Aldrich), palladium(II) chloride, ReagentPlus (Sigma-Aldrich), γ -Al₂O₃-SiO₂ granulated, γ -alumina granulated and electrolytic hydrogen purity from Linde Company.

Catalyst preparation

The synthesis of hydrogenation catalysts was achieved by successive impregnation with aqueous solutions of the precursors of catalysts, applying the method of filling the pores for Ni-Co-Mo-Ba / γ -Al₂O₃-SiO₂ and incipient wetness impregnation for Pt-Pd / γ -Al₂O₃. The precursors of the catalysts are aqueous solutions of cobalt nitrate, nickel nitrate and ammonium heptamolybdate tetrahydrate at a suitable concentration according to the proposed metal content (8%Ni, 1% Co and 3%Mo for Ni-Co-Mo-Ba / γ -Al₂O₃ and respectively 1% Pt and 0.5% Pd / γ -Al₂O₃). Conditioning of the catalyst between impregnations was achieved by drying at 160°C for 4 h and the final conditioning was performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and activation in a stream of hydrogen at 450°C for 6 h.

Catalyst characterization

Catalysts characterization where performed by determining the composition, acid strength and textural characteristics. The composition of catalysts used in the experimental program was checked by atomic absorption (Varian AA240FS). The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine using a DuPont Instruments *Thermal Analyst 2000/2100&951TGA* 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 an Autosorb 1 Quantacrome Nova 2200 Analyzer. Texture data have been obtained by the automatic recording and processing of adsorption-desorption isotherms of nitrogen. The specific surface area was calculated using the equation in the linear part of the BET adsorption isotherm. In order to assess the distribution of pores and the pore size was used desorption branch of isotherms with hysteresis, by applying the BJH method.

Hydrogenation of furfural

The experimental program was performed on fixed bed catalytic reactor in a continuous system. The process was carried out in isothermal conditions and the temperature was regulated with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket. A metallic jacket for the mobile thermocouple was also placed in the axis of the reactor in order to measure the reaction temperature.

Reaction conditions were:

- pressure: 60 atm;
- temperature: 150-200°C;
- volume hourly space velocities of furfural (VHSV): 0.5-1 h⁻¹;
- mass ratio furfural/ methanol: 1/1;
- molar ratio hydrogen/ furfural: 10/1.

Characterization of reaction products was performed by GC-MS (Varian -3800). Operational parameters:

GC method: - column VF-5ms 30m X 0.25mm, ID DF=0.25;

- program of oven: temperature gradient 16°C/min up to 175°C;

- carrier gas: He;

- injector temperature: 155p C

MS method:

- collision cell QQQ: Flow Quench Gas (He) 2.2 mL/min; collision gas flow 1.5 mL/min;
- the electron energy: 70 eV;
- the source temperature: 230°C.

Results and discussions

Thermodesorption curve of diethylamine for the catalysts Ni-Co-Mo-Ba / γ -Al₂O₃ and Pt-Pd/ γ -Al₂O₃ are shown in figure 1 and 2 (A: thermodesorption from centers with weakly acidic, B: thermodesorption from centers with medium acidity, C: thermodesorption from centers with high acidity).

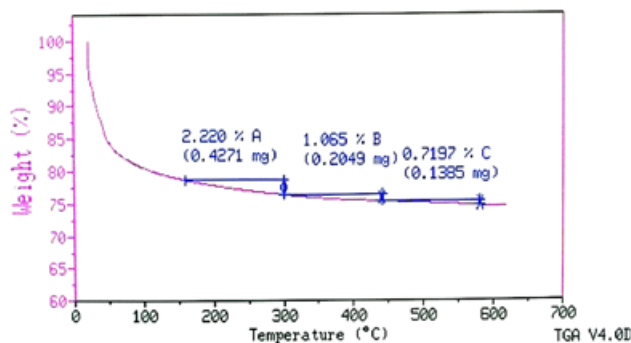


Fig.1. Thermodesorption curve of diethylamine for the catalyst Ni-Co-Mo-Ba / γ -Al₂O₃

Based on diethylamine thermodesorption curves were calculated the distribution of the acid strength for the catalysts which are presented in table 1.

From table 1 is observed that the concentration of acidic centers of the catalyst Ni-Co-Mo-Ba / γ -Al₂O₃ is bigger than of the catalyst Pt-Pd / γ -Al₂O₃. In the case of the catalyst Ni-Co-Mo-Ba / γ -Al₂O₃ acidic centers with medium acidity are found at the lowest concentration. The concentration of

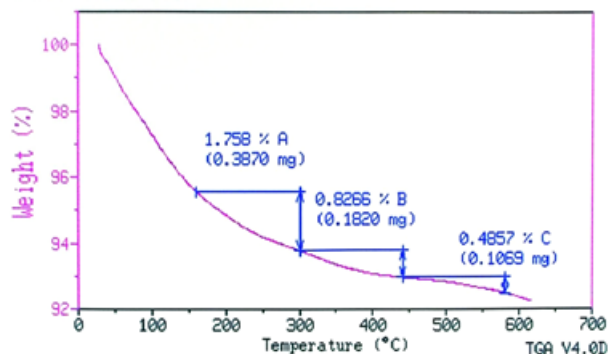


Fig.2. Thermodesorption curve of diethylamine for the catalyst Pt-Pd / γ -Al₂O₃

centers with weak acidity is over three times higher than the concentration of centers with medium acidity and the concentration of centers with high acidity is over twice than the concentration of centers with medium acidity. For the catalyst Pt-Pd / γ -Al₂O₃ the strong acidic centers are found at the lowest concentration. The concentration of centers with low acidity is almost about four times higher than the concentration of centers with high acidity and the concentration of centers with medium acidity is almost twice higher than of the concentration centers with high acidity.

Textural characteristics of the two catalysts was determined by BJH method cumulative desorption pore volume, and are presented in table 2. The specific surface area of the two catalyst has a typical value for γ -alumina-based catalysts.

Figures 3 and 4 shows that the two catalysts possesses a well-defined large pore size with monomodal pore structure and a maximum distribution centered around 51 Å for catalyst Ni-Co-Mo-Ba / γ -Al₂O₃ and around 42 Å for catalyst Pt-Pd / γ -Al₂O₃.

The type of the acidic centers	The acidity strength,	
	Ni-Co-Mo-Ba/ γ -Al ₂ O ₃ meq/g	Pt-Pd/ γ -Al ₂ O ₃ meq/g
Weak acids centers	0.305	0.240
Medium acids centers	0.146	0.113
Strong acids centers	0.098	0.066
Totally acids centers	0.549	0.419

Table 1
THE DISTRIBUTION OF ACIDITY STRENGTH FOR THE TWO CATALYSTS

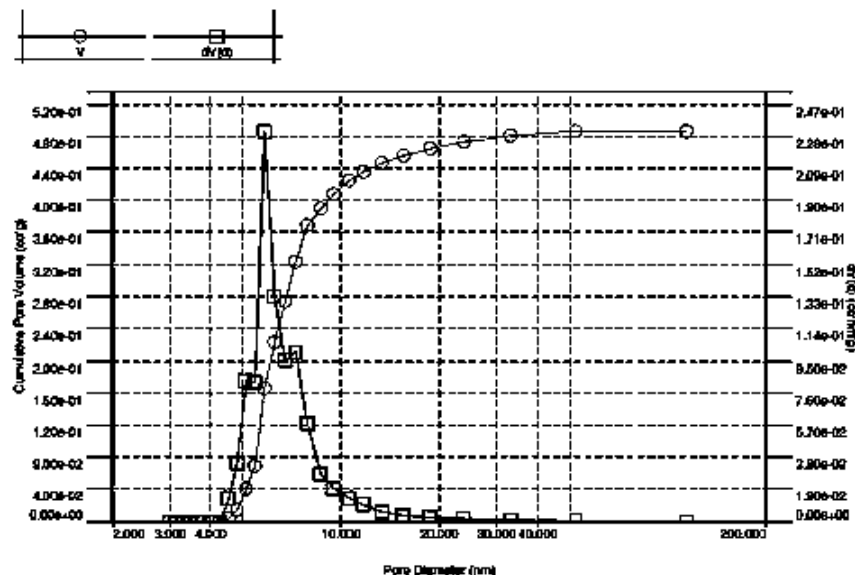


Fig.3. The pore size distribution of the catalyst Ni-Co-Mo-Ba / γ -Al₂O₃ by BJH method desorption

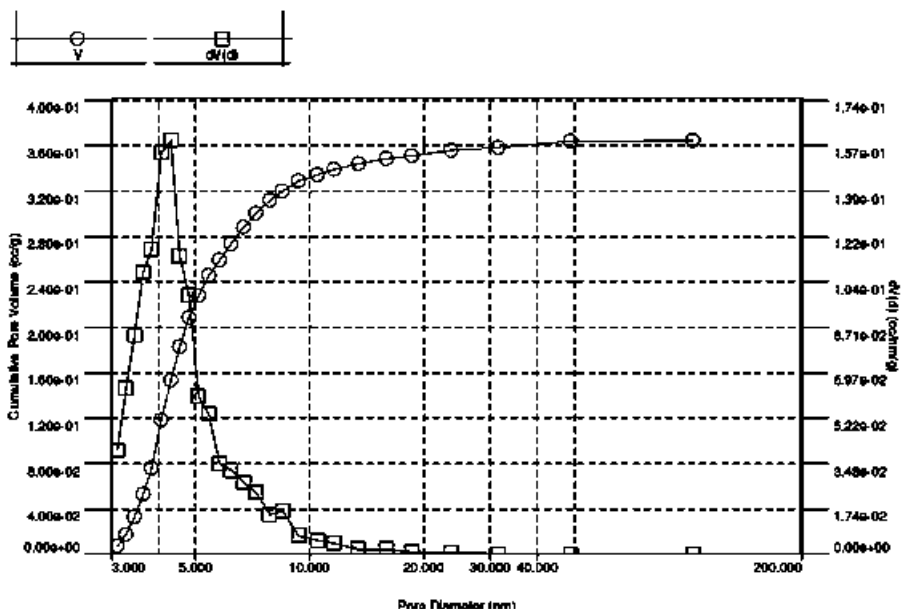


Fig.4. The pore size distribution of the catalyst Pt-Pd/ γ -Al₂O₃ by BJH method desorbtion

Catalyst	Pore Volume, cm ³ /g	Pore Diameter, nm	Specific Surface Area, m ² /g
Ni-Co-Mo-Ba/ γ -Al ₂ O ₃	0.540	5.124	362.588
Pd-Pt/ γ -Al ₂ O ₃	0.273	9.256	89.19

Table 2
TEXTURAL CHARACTERISTICS OF THE CATALYSTS

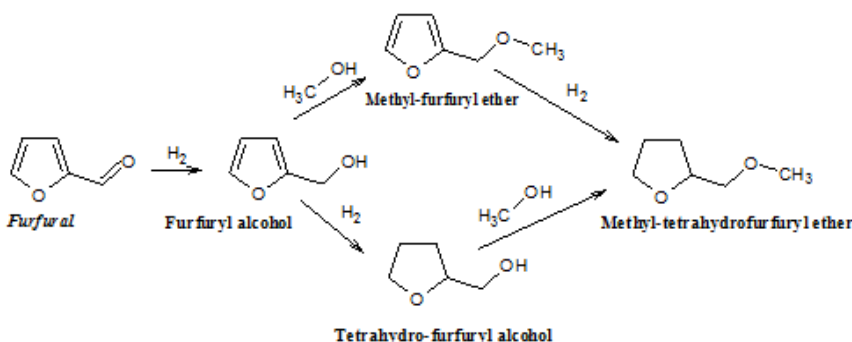


Fig.5. The scheme of reactions for furfural hydrogenation

The scheme of reactions that leads to the mixture of alcohols and ethers is shown in figure 5.

Catalyst Pt-Pd/ γ -Al₂O₃ showed higher activity than catalyst Ni-Co-Mo-Ba/ γ -Al₂O₃ on the ranges of parameters studied. The reaction products identified for the catalyst Ni-Co-Mo-Ba/ γ -Al₂O₃ are tetrahydrofurfuryl alcohol, methyl tetrahydrofurfuryl ether, furfuryl alcohol and furfuryl methyl ether. For the catalyst Pt-Pd were identified the same compounds and additionally tetrahydrofuran. All compounds obtained are oxygenate compounds with anti-detonating property being recommended for addition of gasoline.

The activity of the two catalysts was high on the domain of parameters studied. Thus, the conversion of furfural with temperature varied by a parable with maximum located at approx. 200°C for both catalysts. Pt-Pd catalyst showed higher activity than Ni-Co-Mo-Ba catalyst and the variation slope was different for the two catalysts. The sharp decrease of conversion at temperatures for Ni-Co-Mo-Ba over 200°C catalyst is probably due to pore blocking by condensing byproducts formed on acidic centers present at higher concentrations than on Pd-Pt catalyst.

Across the temperature range studied the yield in ethers was approx. three to four times higher than the yield in alcohols for both catalysts (fig. 7). The yield in the most valuable component for gasoline from the resulting mixture

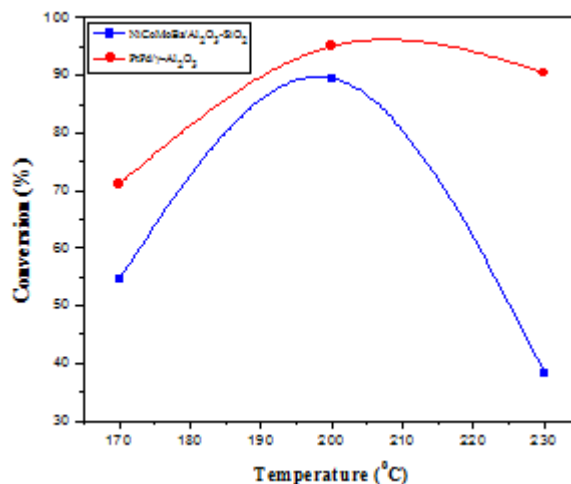


Fig.6. The temperature influence on the furfural conversion at 70 bar and LHSV of 4 h⁻¹

in this process, tetrahydrofurfuryl methyl ether was approx. three times higher in the case of Pd-Pt catalyst than for Ni-Co-Mo-Ba catalyst.

The influence of temperature on yield in oxygenated compounds for the two catalysts is shown in figures 8 and 9. Furfuryl methyl ether yield decreased with increasing temperature for both catalysts, while the yield in tetrahydrofurfuryl methyl ether varied by a maximum located at approx. 200°C for Ni-Co-Mo-Ba catalyst and increased with the temperature for Pt-Pd catalyst. The yield

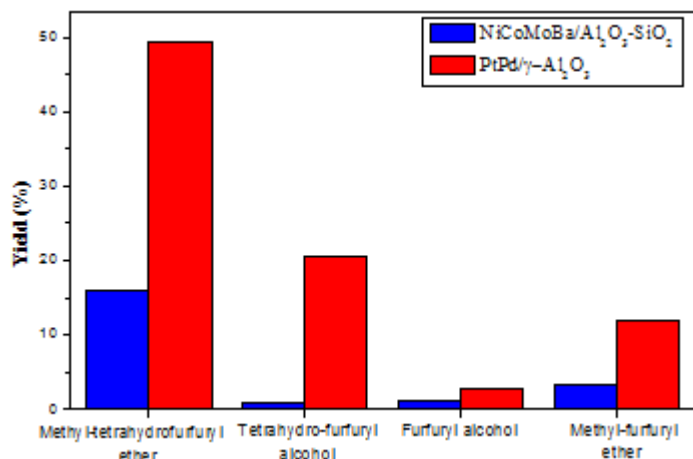


Fig.7. The yield in hydrogenated products at 200 °C 70 bar and LHSV of 4 h⁻¹

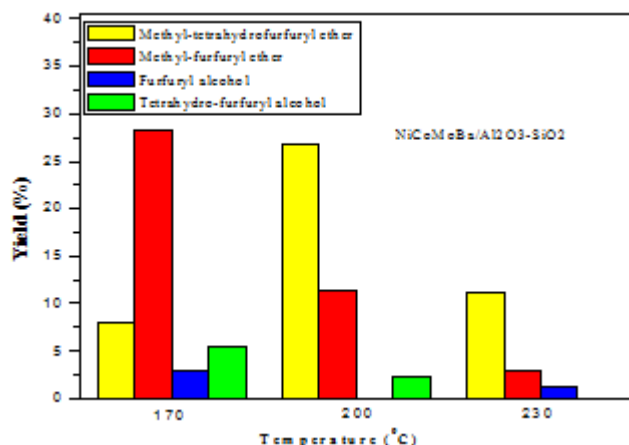


Fig.8. The temperature influence on the yield in hydrogenated products at 70 bar and LHSV of 4 h⁻¹

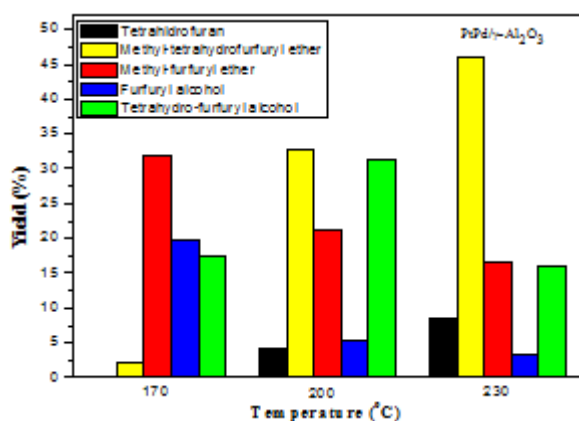


Fig.9. The temperature influence on the yield in hydrogenated products at 70 bar and LHSV of 4 h⁻¹

in the two alcohols increased with temperature increasing for both catalysts with the exception of the value obtained at lower temperatures (170°C) for Ni-Co-B-Mo catalyst. The yield in tetrahydrofuran increased with temperature increasing for Pt-Pd catalyst.

The influence of pressure on yield in oxygenated compounds for the two catalysts is shown in figures 10 and 11. The yield in ethers was higher than in alcohols for the pressure range studied. Furfuryl methyl ether yield increased with increasing temperature for Ni-Co-Mo-Ba catalyst, while the yield in tetrahydrofurfuryl methyl ether decreased with increasing temperature for Pt-Pd catalyst. The yield in tetrahydrofurfuryl alcohol was higher than yield in furfuryl alcohol for both catalysts for the range of pressure studied.

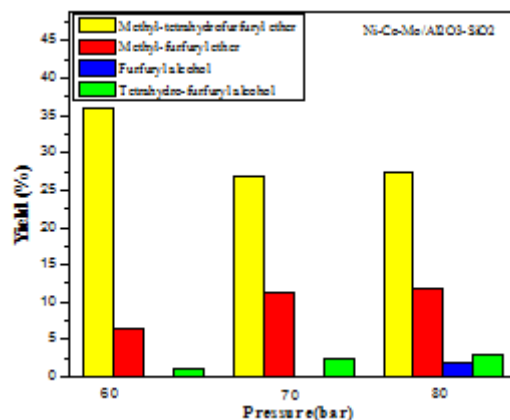


Fig.10. The pressure influence on the yield in hydrogenated products at 200°C and LHSV of 4 h⁻¹

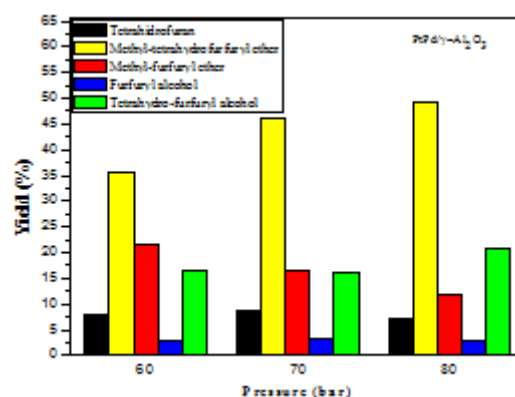


Fig.11. The pressure influence on the yield in hydrogenated products at 200°C and LHSV of 4 h⁻¹

Conclusions

Hydrotreating of furfural in order to obtain furan derivatives, components for gasoline was studied on two catalysts Ni-Co-Mo-Ba / γ -Al₂O₃ and respectively Pt-Pd/ γ -Al₂O₃.

Catalysts characterization were performed by determining the acid strength and textural characteristics.

In order to avoid the condensation reaction of furfural, the acid strength of Ni-Co-Mo catalyst was reduced by promoting with Ba.

For both catalysts the main reaction products identified are tetrahydrofurfuryl alcohol, methyl tetrahydrofurfuryl ether, furfuryl alcohol and furfuryl methyl ether, the most valuable component for gasoline from the resulting mixture being tetrahydrofurfuryl methyl ether.

Catalyst Pt-Pd/ γ -Al₂O₃ showed higher activity than catalyst Ni-Co-Mo-Ba / γ -Al₂O₃ on the ranges of parameters studied.

The sharp decrease of conversion at temperatures for Ni-Co-Mo-Ba over 200°C catalyst is probably due to pore blocking by condensing byproducts formed on acidic centers present at higher concentrations than on Pd-Pt catalyst.

The yield in ethers was higher than the yield in alcohols for both catalysts for the parameters range studied and the yield in tetrahydrofurfuryl methyl ether was higher in the case of Pd-Pt catalyst than for Ni-Co-Mo-Ba catalyst.

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