Acidity Influence of Ru Catalysts on the Hydrogenation of Naphtalene

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*The hydrogenation of naphtalene was conducted on two catalysts based on Ru, Ru /γ-Al_2O_3 respectively Ru-Sn/*Al-HMS—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 300-360°C, at 60 atm, naphtalene volume hourly space velocities of 1-2h*$^{-1}$ *and molar ratio hydrogen/ naphtalene of 10/1. The main compounds identified were tetralin, alkyl-naphtalene and alkyl-tetralin. The naphthalene conversion on the Ru-Sn /Al-HMS—*γ-Al_2O_3 *catalyst was higher than on the Ru /* γ-Al_2O_3 *catalyst. Higher activity of catalyst Ru-Sn /Al-HMS—*γ-Al_2O_3 *is due to both hydrogenation reactions to tetralin as well as to cracking and alkylation reactions to alkyl-aromatic hydrocarbons.*

Keywords: catalyst, hydrogenation, support acidity, naphtalene, selectivity

Aromatics hydrogenation process occurs in the presence of metal catalysts on various supports with controlled acidity, such as γ-alumina. The active component and support acidity influences the performance of the hydrogenation process. Usually, in the hydrogenation of aromatics, bi-metallic catalysts are used such as Ni-Mo, Ni-W, Co-Mo or catalysts based on noble metals [1].

Factors that affect the composition of the hydrogenation products are the operating conditions, reactant and catalyst type. Thus the effect of temperature on the naphthalene hydrogenation of has been studied on catalysts based Ni, Ni-Mo, and Ru. The conversion of naphthalene and the selectivity to decalin on the catalyst based on NiMo /Al_2O_3 increase with increasing temperature. Maximum conversion and high yields were obtained at a temperature of 320°C [2].

Hassan et al. tested the catalyst NiMo / Al_2O_3 in the naphthalene hydrogenation reaction. The process was carried out in a fixed bed catalytic on cylindrical pellets, nickel oxide serving as a promoter. The catalyst was reduced under a hydrogen atmosphere for 2 h at 300°C [3]. Uniform distribution of pore from the catalytic support results in an effective deposition of the Ru species inside the pores [4].

Although the catalyst based on ruthenium on a TiO_2, SiO_2 or γ-Al_2O_3 support showes selectivity of up to 95%, commercially is not attractive, the price of the metal being much higher than that of catalysts based traditional non-noble metals [5].

It was tested activity of a bimetallic catalyst Ni_2Mo_3 / MCM-41 with of a monometallic catalysts Ni/MCM-41 and Mo/MCM-41, in the reaction of naphthalene hydrogenation. The results showed that Ni_2Mo_3 /MCM-41 under the same reaction conditions present a higher hydrogenation activity than the monometallic catalysts [6].

Monteiro and his colleagues achieved a comparative analysis for catalysts Ni, Ru and NiMo impregnated on alumina support, demonstrating that the speed of naphthalene and hydrogen adsorption on the catalyst surface was considerably higher on Ru/ Al_2O_3 than on Ni / Al_2O_3. These results indicate that the reactants are adsorbed more strongly to the surface of Ru / Al_2O_3 than to the Ni /Al_2O_3. The rate of hydrogen and naphthalene adsorption on the catalyst surface varied in order: Ru> Ni>NiMo. [7]

Ru-based catalyst was prepared by impregnation on different supports: Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, CeO_2, zeolites such as MCM-41 or Zr-MSU. By choosing a support with a high specific surface it was aimed to obtain of an optimal dispersion of ruthenium. Studies have shown that the impregnation of Ru catalyst on activated carbon results in a high conversion of naphthalene [8].

Kourtakis et al. [9] studied the performance of Ru and Pd catalysts deposited on inorganic support by sol-gel method. The metal ions have been incorporated in a matrix of inorganic oxides, such as oxy-hydroxides of Ti, Nb, Ta, Zr, Si, Al, etc. The aluminum chloride hexahydrate was used as the inorganic precursor for obtained of Al_2O_3 powder by sol-gel method. Using $AlCl_3 \cdot 6H_2O$ inorganic precursor and a non-ionic surfactant in the sol-gel synthesis, there was obtained aluminum oxide powder in different polymorphic phases, depending on the calcination temperature.

The selectivity to decalin in the naphthalene hydrogenation depends on temperature. Thus on the temperature range 270-300°C, trans-decalin was the main reaction product, with a selectivity of over 60% [10]. In the temperature range 250-280°C selectivity in trans-decalin increased to 80%, decreasing for higher temperatures, up to 300°C. Tetralin, which is an intermediate product was obtained with a selectivity of 20% at 250°C. Selectivity decreased in this reaction product up to 0.4% at 280°C, demonstrating that almost all of the naphthalene was hydrogenated to form cis- or trans-decalin. By increasing the temperature up to 300°C, it was obtained tetralin with a 14% selectivity. The selectivity for cis-decalin decreased from 20% at 250°C to 9% at 300°C. No intermediates resulting in the partial hydrogenation, such as octahydronaphtalene or hexahydronaphtalene were detected [11].

The literature reveals that using of supports type metal oxides, zeolites and less activated carbon, due to high thermal and chemical stability, but also to the possibilities of obtain high porosity and implicit high specific surface.

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Catalytic active metals most commonly used are the platinum metals Pt and Pd and also Ni. [12]

The catalysts $Pt/A1_2O_3$, $Pd/A1_2O_3$ and Pd/TiO_2 were studied by Montesinos et al., for naphthalene hydrogenation at 280°C. It was observed that in the mild reaction conditions it obtain tetralin which are hydrogenated, more difficult to decalin (cis and trans). The process can be accompanied by unwanted cracking reactions, which lead to compounds with low molecular weight [13].

S. Albonetti and G. Baldi emphasized the nature effect of catalysts on process performance using bimetallic catalysts Pd / Rh and Pd / Pt supported on alumina-silica. The best results were reported for a metal content Pd /Pt of 0.3% compared to the total weight of the catalyst. At a temperature of 340°C was recorded a conversion of naphthalene of 88%, the performance could be attributed to a large specific surface area, to the presence of bimetallic particles, as well as to the acid properties of the catalyst support [14].

Compared to studies of literature that approach the catalysts for processing of bioresources [15,16], the number of publications that address the catalysts for hydrogenation of naphtalene is relatively low, priority concerns being directed towards obtaining biofuels.

In this paper is studied the influence of two catalysts based on Ru, respectively Ru/ γ–Al_2O_3 and Ru-Sn/ Al-HMS —γ-Al_2O_3 on the hydrogenation of naphtalene.

Experimental part

The raw materials used in experiments were naphthalene 99% (Sigma-Aldrich), ruthenium (III) chloride hydrate p.a. (Sigma-Aldrich), tin(II) chloride dehydrate puriss p.a.(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 filling the pores. The precursors of the catalyst are aqueous solutions of ruthenium (III) chloride and tin (II) chloride. The supports used in the preparation of the catalyst are γ-alumina granulated and Al-HMS—γ-Al_2O_3 granulated. Concentration of catalyst precursor of the impregnation solution is calculated according to the proposed metal content (0.8% Ru for Ru / γ-Al_2O_3 and respectively 0.7% Ru and 1.4% Sn for Ru-Sn/Al HMS — γ-Al_2O_3. Conditioning of the catalyst Ru-Sn/Al HMS—γ-Al_2O_3 between impregnations was achieved by drying at 160°C for 4 h and the final conditioning of both catalysts where performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and two-stage reduction by treatment with sodium borohydride in aqueous solution at a temperature of 80°C, followed by activation 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 performed in a continuous system and fixed bed catalytic reactor. The process was carried out in isothermal conditions. The temperature was regulated with an automatic system by using two thermocouples fixed, placed in the reactor jacket. The reaction temperature was measured with a mobile thermocouple placed in a metallic jacket fixed in the axis of the reactor.

Reaction conditions were:

-pressure: 60 atm;

-temperature: 300-360°C;

-volume hourly space velocities of naphtalene (VHSV): 1-2h^{-1};

-molar ratio hydrogen/ naphtalene: 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

Based on thermal desorption curves of diethylamine it was determined the concentration of acidic centers of different acidities. Thus, thermal desorption of diethylamine in temperature range 150-300^{0}C corresponds to weak acids centers, in the temperature range 300-450^{0}C corresponds to medium acids centers and in the temperature range 450-600^{0}C corresponds to the strong acids centers (area A-thermodesorption from centers with weakly acidic, area B- thermodesorption from centers with medium acidity, area C- thermodesorption from centers with high acidity). Thermodesorption curve of diethylamine for the catalyst Ru /γ-Al_2O_3 is shown in figure 1 and for the catalyst Ru-Sn/ Al HMS — γ-Al_2O_3 is shown in figure 2.

Table 1 presents data concerning the distribution of strength acidity for the two catalysts, calculated on the basis of the values from the thermal desorption curves.

For the catalyst Ru /γ-Al_2O_3 is observed a higher content in strong acidic centers (1.105 meq /g), a concentration of medium acids centers at approx. half compared to the content in strong acidic centers (0.588 meq/g) and a lower concentration of weak acids centers (0.160 meq /g). The catalyst Ru-Sn/Al-HMS—γ-Al_2O_3 shows a concentration of

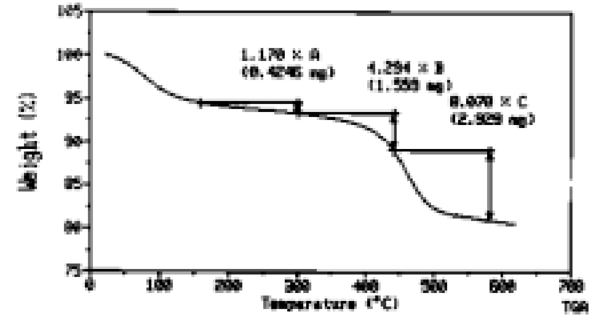


Fig. 1. Diethylamine thermodesorption curve of the catalyst Ru / γ-Al_2O_3

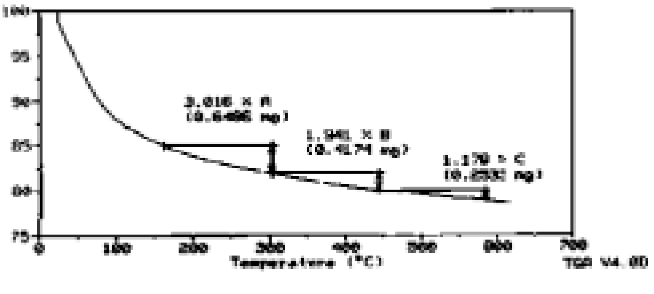
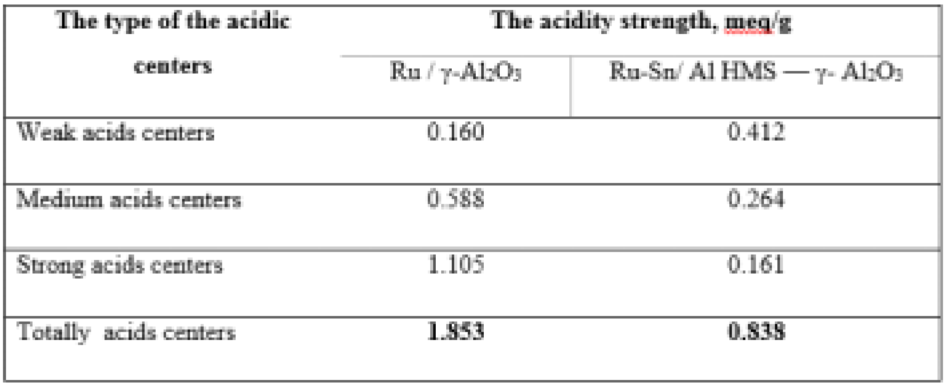


Fig. 2. Diethylamine thermodesorption curve of the catalyst Ru-Sn/ Al HMS — γ-Al_2O_3

Table 1
THE DISTRIBUTION OF ACIDITY STRENGTH FOR THE TWO CATALYSTS



The type of the acidic centers	The acidity strength, meq/g	
	Ru / γ-Al_2O_3	Ru-Sn/ Al HMS — γ- Al_2O_3
Weak acids centers	0.160	0.412
Medium acids centers	0.588	0.264
Strong acids centers	1.105	0.161
Totally acids centers	**1.853**	**0.838**

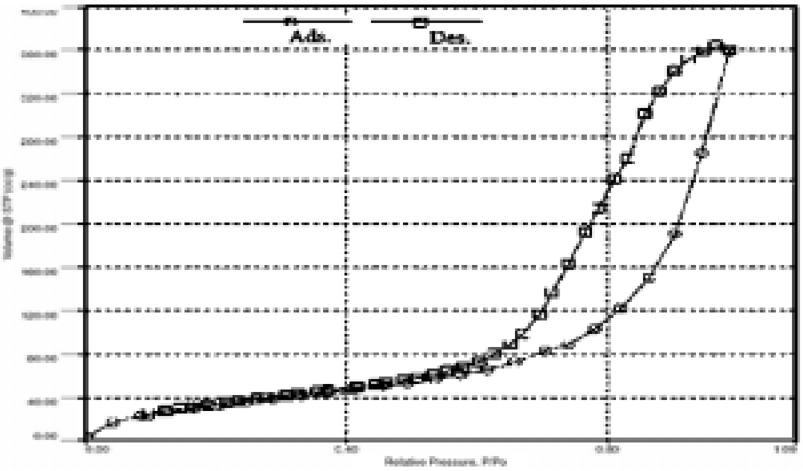


Fig.3. The isotherm of nitrogen adsorption / desorbtion on the catalyst Ru/γ-Al_2O_3

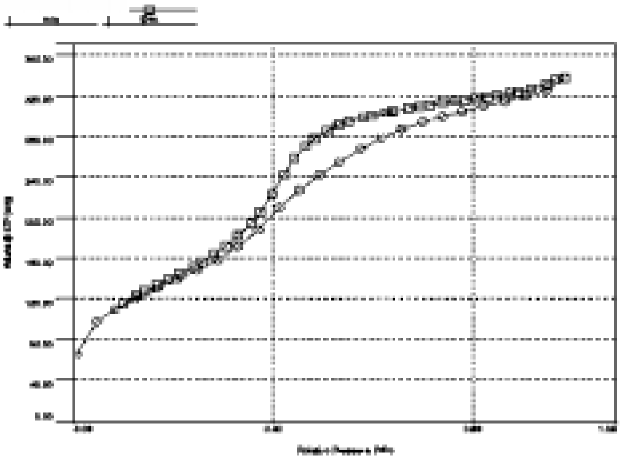
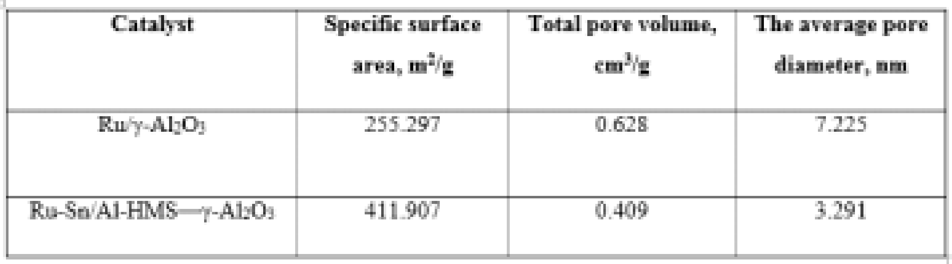


Fig. 4. The isotherm of nitrogen adsorption / desorbtion on the catalyst Ru-Sn/Al HMS—γ-Al_2O_3

Table 2
TEXTURAL DATA OF THE TWO CATALYSTS



Catalyst	Specific surface area, m^2/g	Total pore volume, cm^3/g	The average pore diameter, nm
Ru/γ-Al_2O_3	255.297	0.628	7.225
Ru-Sn/Al-HMS—γ-Al_2O_3	411.907	0.409	3.291

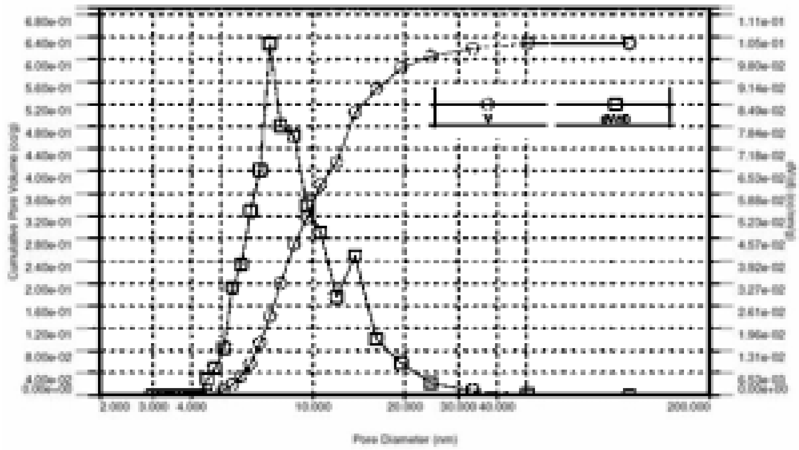


Fig.5. Pore size distributions of the catalyst Ru/γ-Al_2O_3

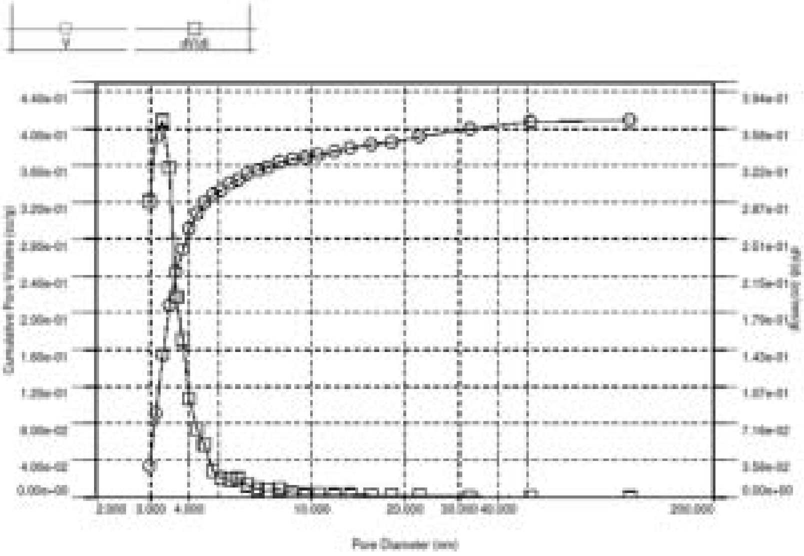


Fig.6. Pore size distributions of the catalyst Ru-Sn/Al-HMS—γ-Al_2O_3

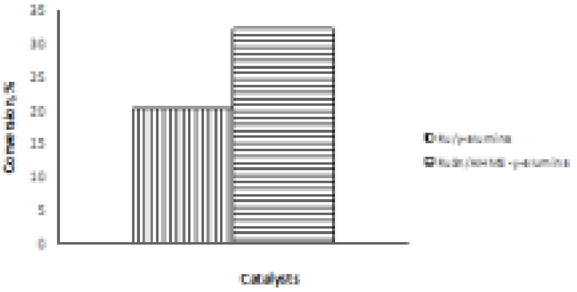


Fig.7. Conversion of naphtalene on Ru /γ-Al_2O_3 and Ru-Sn/Al-HMS—γ-Al_2O_3 catalysts (360^{0}C, 60 atm, 1h^{-1})

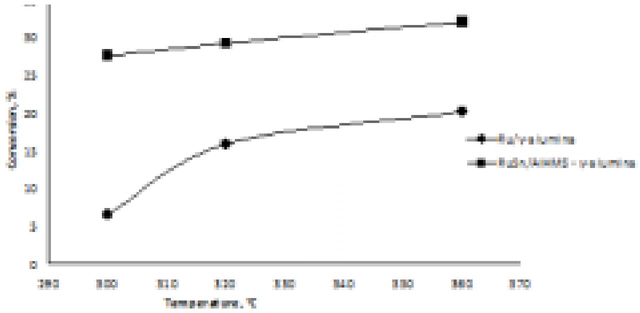


Fig.9. Variation of naphtalene conversion with temperature on Ru /γ-Al_2O_3 and Ru-Sn/Al-HMS—γ-Al_2O_3 catalysts (60atm, 1h^{-1})

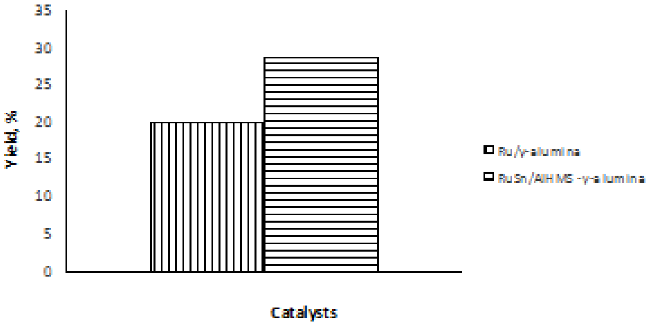


Fig.8. Yield in tetralin on Ru /γ-Al_2O_3 and Ru-Sn/Al-HMS—γ-Al_2O_3 catalysts (360^{0}C, 60atm, 1h^{-1})

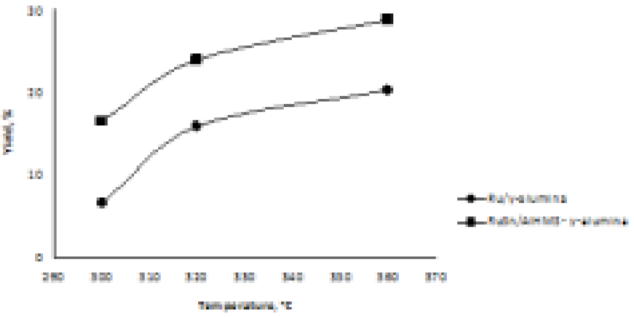


Fig. 10. Variation of yield in tetralene with temperature on Ru /γ-Al_2O_3 and Ru-Sn/Al-HMS—γ-Al_2O_3 catalysts (60atm, 1h^{-1})

acidic centers less than half compared to the centers of Ru /γ-Al_2O_3. The content of weak acids centers is almost three times higher than for the catalyst Ru/γ-Al_2O_3. The concentration of medium acids centers is at approx. half compared to the catalyst Ru /γ-Al_2O_3 and the concentration of strong acids centers is approx. seven times smaller than for the catalyst Ru /γ-Al_2O_3. It can be considered that the both catalysts have a different total acidity and a different distribution of the strength of acidic centers.

Texture data have been obtained by automatic recording and processing of adsorption-desorption isotherms of nitrogen. Isotherms of adsorption-desorption are shown in figures 3 and 4.

Textural characteristics of the catalysts was determined by BJH method of cumulative desorption from pores and are presented in table 2. The surface area of the catalyst Ru-Sn/Al-HMS—γ-Al_2O_3 had a higher value that for catalyst Ru/γ-Al_2O_3. The total pore volume of the catalyst Ru/γ-Al_2O_3 had a higher value that for the catalyst Ru-Sn/Al-HMS—γ-Al_2O_3.

Figures 5 and 6 show that the catalyst Ru/γ-Al_2O_3 possesses a multimodal pore size distribution and the catalyst Ru-Sn/Al-HMS—γ-Al_2O_3 possesses a unimodal pore size distribution with maximum centered around 33Å.

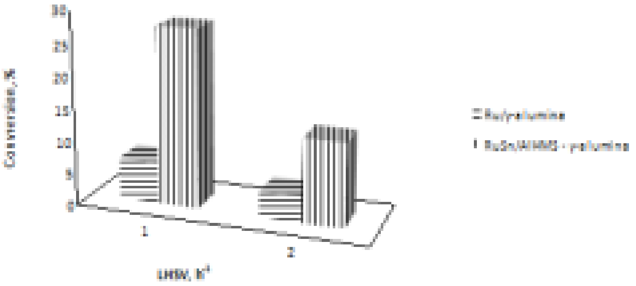


Fig.11. Variation of naphtalene conversion with volume hourly space velocities of naphtalene on Ru /γ-Al_2O_3 and Ru-Sn/Al-HMS—γ-Al_2O_3 catalysts (300^{0}C, 60atm)

The product composition obtained in the hydrogenation of naphtalene on the two catalysts are different. Thus, in the case of Ru /γ-Al_2O_3 are obtained mostly tetralin, concentration of cis-decalin and trans-decalin in the reaction product being very low on the variation range of the parameters studied.

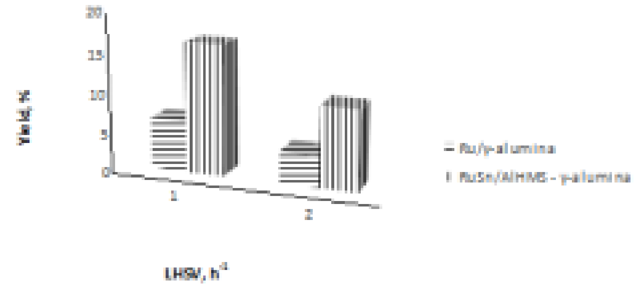


Fig.12. Variation of yield in tetralene with volume hourly space velocities of naphtalene on the Ru /γ-Al_2O_3 and Ru-Sn/Al-HMS—γ-Al_2O_3 catalysts (300^0C, 60atm)

When the hydrogenation of naphtalene occurs on the catalyst Ru-Sn/Al-HMS—γ-Al_2O_3 were obtained both tetralin as well as alkyl-aromatic hydrocarbon like alkyl-naphtalene (1-methyl-naphthalene, 2-ethyl-naphthalene, 2-isopropyl-naphthalene, 2-methyl-1-propyl-naphthalene) and alkyl-tetralin (6-methyl tetralin, 5-methyl tetralin, 5-ethyl tetralin).

The presence of these alkyl-aromatic hydrocarbon is due both to the high concentration in mesopores of silica HMS as well as to the strong acids centers obtained by modifying with Al of silica and by promoting with Sn. This strong acids centers catalyze both cracking and alkylation reactions at the aromatic ring of naphthalene or tetralin on the temperature range studied.

The performance of Ru /γ- Al_2O_3 catalyst are lower than of Ru-Sn/Al-HMS—γ-Al_2O_3 catalyst as shown in figures 7 and 8.

Hydrogenation of naphthalene at 360^0C, 60 atm and at VHSV of naphthalene 1h^{-1}, in the presence of the Ru-Sn /Al HMS-γAl_2O_3 catalyst yielded to higher values of naphthalene conversion than the Ru / γ-Al_2O_3 catalyst (fig. 7). Also the yield in tetralin on the Ru-Sn / Al HMS—γAl_2O_3 catalyst is almost 50% higher than the yield in tetralin on Ru / γ-Al_2O_3 catalyst (fig. 8).

The conversion of naphthalene increases with temperature after a similar slope for both catalysts on temperature range 320-360^0C while the on 300-320^0C range, the slope of conversion variation has a higher value for Ru / γ-Al_2O_3 catalyst (fig. 9). Yield in tetralin increases with temperature after a similar slope for both catalysts. Thus in 300-320^0C range, the variation slopes had higher values, and in 320-360^0C range, the slopes variation had lower values (fig. 10).

A comparative analysis of conversion variantion of naphthalene with volume hourly space velocities for Ru /γ-Al_2O_3 and Ru-Sn /Al HMS - γAl_2O_3 catalysts is shown in figure 11. It observes that increasing of volume hourly space velocities from 1 h^{-1} to 2 h^{-1} favors decreasing of naphthalene conversion. The decrease was more pronounced in the case of Ru-Sn /Al-HMS—γ-Al_2O_3 catalyst. The same behaviour is seen for the yields in tetralin (fig. 12). Thus the yield in tetralin decreases with increasing of volume hourly space velocities by a same slope for the both catalysts.

Higher activity of catalyst Ru- Sn /Al-HMS—γ-Al_2O_3 is due both of hydrogenation as well as cracking and alkylation reactions. Thus, in relatively hard conditions (300°C, 60 atm, LHSV 1 h^{-1}), yield in alkyl-tetralins is almost six times lower than yield in tetralin, while yield in alkyl-naphthalenes is over two times higher than yield in alkyl-tetralins (fig. 13). It can be noted that hydrogenation reactions are the predominant against cracking-alkylation reactions and alkyl-aromatic are obtained preferentially by naphthalene alkylation reaction.

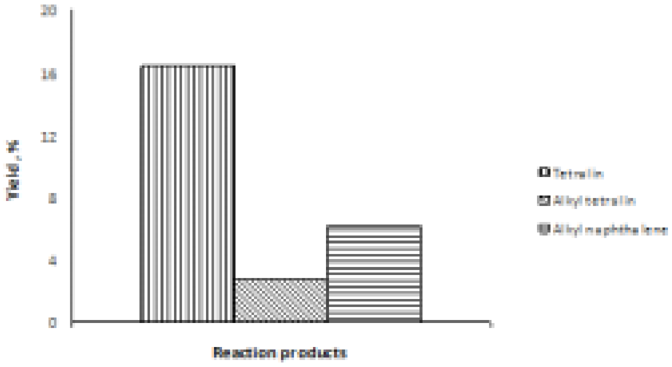


Fig.13. Yield in tetralin and aromatic alkyl-derivatives on Ru-Sn/Al-HMS—γ-Al_2O_3 catalyst(300°C, 60 atm, LHSV 1h^{-1})

Conclusions

Two catalysts with different concentrations of acidic centers were prepared by pore filling method, in order to test in hydrogenation of naphtalene.

The total acidity of catalyst Ru/γ- Al_2O_3 has greater than of catalyst Ru-Sn/ Al HMS—γ- Al_2O_3, acidity due to a high concentration of strong acids centers.

Hydrogenation experiments of naphtalene were performed on the two catalysts in continuous system.

The naphthalene conversion on the Ru-Sn/Al-HMS—γ-Al_2O_3 catalyst was higher than on the Ru /γ- Al_2O_3 catalyst.

Higher activity of catalyst Ru-Sn /Al-HMS—γ-Al_2O_3 is due to both hydrogenation reactions to tetralin as well as to cracking and alkylation reactions to alkyl-aromatic hydrocarbons.

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