

The Influence of a Mesoporous Silica on Ru-Sn Catalyst Activity in the Hydrogenation of Methyl Oleate

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The hydrogenation of methyl oleate on a Ru-Sn catalyst deposited on Al-HMS was studied in comparison to that conducted on the same catalyst deposited on a conventional support, i.e. γ -Al₂O₃. The catalyst was prepared by sequential impregnation. 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 laboratory echipament using a fixed bed catalytic reactor at a temperature of 275°C, pressure of 100 atm with a methyl oleate volume flow rate (VHSV) of 0.15h⁻¹ and molar ratio hydrogen/methyl oleate of 10/1. The main compounds identified were saturated and unsaturated fatty alcohols and saturated hydrocarbons. Ru-Sn/ Al-HMS + γ -Al₂O₃ shows a higher conversion to liquid products than the Ru-Sn-Ba / γ -Al₂O₃ probably due to a favorable distribution of the acid strength.

Keywords: catalyst, hydrogenation, acidity, methyl oleate, mesoporous silica

The high bio-degradability of fatty alcohol recommends it to manufacture surfactants like detergents. In most countries it was required by law that at least 80% of detergents ingredients must be biodegradable. The cheapest way to manufacture fatty alcohols is to hydrogenate fatty acid esters. Typically, the process of hydrogenation of fatty acid esters is carried out in heterogeneous catalysis, a process used in most catalytic processes [1-3]. Catalysts commonly used in industrial processes for the hydrogenation of fatty acid esters are based on chromium [4-6]. Current concerns are directed to replacing chromium-based catalysts, metal with high toxicity, with others on less toxic metals [7,8]. In a recent article [9], catalytic hydrogenation of stearic acid on NiMo / zeolite β -Al₂O₃ catalysts is shown. NiMo catalysts were prepared by impregnating a β - γ -Al₂O₃ zeolite support with Ni and Mo salts, followed by reduction with hydrogen at temperatures between 400-600°C. The performance of the hydrogenation process on this catalyst has been studied compared to those obtained on the NiMo (Cox) oxide catalyst and one deposited on a composite support. The NiMo / zeolite β -Al₂O₃ catalyst that was reduced to 450°C resulted in the highest conversion value (about 100%) and a selectivity in C18 (58%) of hydrocarbons much higher than that obtained on the support composite and Cox. XRD and H₂-TPR analyzes indicated that reduction treatment contributed to improved dispersion of active metallic centers, resulting in high hydrodeoxygenation activity.

Other catalysts studied [10] in this process were those based on platinum. They were promoted with tungsten oxide at various concentrations (Pt-WOx/Al₂O₃), by the wet impregnation method and reduced in hydrogen atmosphere. X-ray diffraction and photoelectronic spectroscopy showed that Pt is completely reduced to metallic state while tungsten is in oxidation state +6 and +5. CO-chemisorption and electron beam microscopy analyzes revealed that Pt crystallites sizes increased in presence of WOx (from 1.2 to 1.4 nm and 2.5 to 3 nm, respectively). Addition of tungsten has also resulted in increased concentration of strong acid centers. This

significantly improved the catalytic activity of Pt/Al₂O₃ in the process of deoxygenation of fatty acids and methyl esters. Tungsten modified the mechanism of reaction from decarbonylation / decarboxylation to hydrodeoxygenation. Catalyst with 4 wt.% Pt and 8 wt.% W has high catalytic performance.

In another paper [11] the activity of the Cu and Zn / Al₂O₃ composite catalyst was studied. Catalysts were prepared by a controlled co-precipitation process by adjusting the initial concentration of the alkaline precipitant. The correlation between structure and catalytic activity was studied and the LDH-derived catalyst (double layered hydroxides) showed the highest activity in the hydrogenation of fatty esters, as well as a high selectivity for fatty alcohol. Concentrations of the active species in the hydrogenation process have also been studied. High catalytic performance was attributed to the relatively high metal dispersion (low crystal size) and to the high degree of copper species reduction. The structure and activity of the CuO / ZnO / Al₂O₃ catalyst could be controlled and optimized by altering the initial precipitation agent concentration in the co-precipitation process. For values higher than 2.0 M of the initial concentration (CZA-2.0), the precipitated precursor has a unique structure of LDHs (double layered hydroxides) and the composite is derived from its calcination to give CuO particles smaller than 12 nm, which were strongly dispersed in amorphous ZnO and in the Al₂O₃ phase. The CuO catalyst was slightly reduced in situ during the hydrogenation of ethyl stearate at 230°C, obtaining stearic alcohol in optimal conditions. Regarding the structure-activity relationship, it was observed that the single LDH phase was formed in the precipitated precursor. The double layered hydroxides were partially thermally decomposed into copper oxide and then dispersed into amorphous zinc oxide particles. There has been evidence of a stronger electron interaction between the CuO, ZnO and Al₂O₃ components, an interaction that has led to the mild reduction of the composite in situ during the reaction. The yield in stearic alcohol was high (> 98%) on the CZA-

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2.0 catalyst. It has been confirmed that the active species for the hydrogenation of ethyl stearate are Cu^+/Cu^0 .

A series of chromium-free copper hydrogenation catalysts prepared for this purpose [12] were studied to hydrogenate the fatty acid methyl esters of the corresponding alcohol. In particular, the stability of the catalyst in the formation of metallic soap and the mechanical stability of the catalyst particles in the presence of fatty acids have been pursued. The results obtained with this catalyst were compared with those obtained on the commercial copper chromite catalyst. The stability of the Cr-free catalyst can be improved by avoiding high pressures or applying ex-situ reduction techniques so that the reducing water is removed from the catalyst pores before starting the hydrogenation process.

The production of fatty alcohols by selective hydrogenation of fatty acids was studied on a 4% ReOx/TiO_2 catalyst [13]. The stearic acid was hydrogenated to octadecanol at temperatures and pressures between 180°C-200°C and 2-4 MPa with a selectivity of 93%. A high yield of octadecanol has been obtained due to the strong acid-adsorption of the acid as compared to the alcohol, which inhibits the subsequent conversion of the alcohol to the alkanes. Small amounts (<7%) of alkanes (mainly octadecane) were formed during conversion. It has been demonstrated that a decrease in temperature and an increase in pressure has led to a higher selectivity in the main reaction product. However, it has been observed that this catalyst could also be used for the production of alkanes. The reaction intermediates were octadecanal and stearyl stearate.

Although many studies address the processing of bioresources by catalytic processes, [14-17], the number of publications that address the hydrogenation of fatty ester is relatively low, priority concerns being directed towards obtaining biofuels.

In this paper is studied the influence of two catalysts based on Ru which is distinguished by its textural and acidic features, respectively $\text{Ru-Sn}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ru-Sn}/\text{Al-HMS} + \gamma\text{-Al}_2\text{O}_3$, on the hydrogenation of methyl oleate.

Experiment part

The raw materials used in experiments were methyl oleate, ruthenium chloride p.a., stannous chloride p.a. from Sigma-Aldrich, HMS type mesoporous silica modified with alumina during crystallization, and electrolytic hydrogen purity from Linde Company. The composition of methyl oleate used in the experiment, determined by GS-MS analysis, are shown in table 1[7].

Table 1
THE COMPOSITION OF METHYL OLEATE USED IN THE EXPERIMENT

No. crt.	Component	Concentration, wt. %
1.	Methyl palmitate	2.79
2.	Methyl palmitoleat	2.57
3.	Methyl stearate	2.38
4.	Methyl oleate	77.48
5.	Methyl cis-7-octadecenoate	2.56
6.	Methyl linoleat	12.22

The mesoporous silica was incorporated during the granulation of the alumina catalytic support at a concentration of 40%. The catalytic supports were granulated by extrusion, dried at 160°C for 4 h and calcined at 450°C for 5 h. The two catalysts which have the same concentration of Ru and Sn, 0.7% Ru -1.4% Sn / $\gamma\text{-Al}_2\text{O}_3$ and 0.7% Ru -1.4%Sn /Al-HMS + $\gamma\text{-Al}_2\text{O}_3$, were prepared by wet impregnation. After impregnation, the catalysts were dried in the oven for 6 hours at 120°C, then calcined in the oven for 8 hours at 450°C.

The textural characteristics of the catalysts were determined on an Autosorb 1 Quantacrome. The textural data of the catalysts were obtained by automatic recording and processing of adsorption /desorption nitrogen isotherms. The specific surface area was calculated using the BET equation in the linear part of the adsorption isotherm. For evaluation of pore distribution and pore size, the isotherms desorption branch with hysteresis was applied using the BJH method.

The total concentration of acidic centers as well as the distribution of the acidic strength of the catalysts were determined by thermal desorption of diethylamine in the temperature range of 20-700°C. Thermal Analysis (ATG) was performed on a DuPont Instruments *Thermal Analyst 2000/2100* coupled with a *912 Differential Scanning Calorimeter* module and a 951 Thermogravimetric Analyzer module.

Characterization of the catalysts in terms of morphology and structure were achieved with the Scanning electronic microscopy method. Images were obtained at the TESCAN Mira electronic microscope.

The experimental program was performed in a fixed bed catalytic reactor and continuous system in isothermal conditions. The temperature was controlled with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket. Reaction conditions were:

- pressure: 60 atm;
- temperature: 260°C;
- volume hourly space velocities of methyl oleate (VHSV): 0.12h^{-1} ;
- molar ratio hydrogen/ methyl oleate: 10/1.

Results and discussions

The acid characteristics of the $\text{Ru-Sn} / \gamma\text{-Al}_2\text{O}_3$ catalyst were presented in a previous paper [7]. Figure 1 shows the thermal desorption curve of diethyl amine for the $\text{Ru-Sn} / \text{Al-HMS} + \gamma\text{-Al}_2\text{O}_3$ catalyst. The total weight loss of the chemically adsorbed diethyl amine on the acidic centers of the $\text{Ru-Sn}/\text{Al-HMS} + \gamma\text{-Al}_2\text{O}_3$ catalyst was 6.135% (determined by thermodesorption of diethylamine in the temperature range 150°C-600°C). Loss of diethylamine chemical adsorbed on weak acidic centers (in the temperature range 150-300°C) was 3.016%. Loss of diethylamine chemical adsorbed on medium strength acids was 1.941% (the temperature range 300°C-450°C) and the loss of diethyl amine chemical adsorbed on strong acid centers was 1.178% (the temperature range 450°C-600°C).

The distribution of the acidic strength of the $\text{Ru-Sn}/\text{Al-HMS} + \gamma\text{-Al}_2\text{O}_3$ catalyst was determined by processing the data obtained from the thermogravimetric desorption curve of the diethylamine based on the following premises:

- dynamic profile the weight loss of the catalyst sample from room temperature to 600°C corresponds to the physical and chemical desorption of diethyl amine;
- chemical desorption begins at 150°C;
- the presence of weak acidic centers (A), medium strength (B) and strong acids (C) is differentiated by the

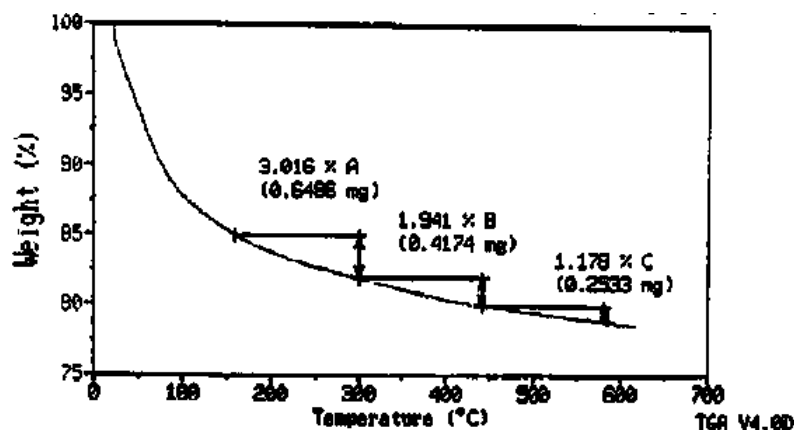


Fig. 1. Thermal desorption curve of diethylamine for Ru-Sn/Al-HMS + γ -Al₂O₃ catalyst

temperature range where it takes place thermal desorption of diethyl amine;

- these temperature ranges are:

-A: 150°C -300 °C

-B: 300°C -450 °C

-C: 450°C -600 °C;

Table 2 presents the data on the distribution of the acid strength of Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst obtained by processing the diethyl amine losses presented in the thermogravimetric analysis curve.

Table 2 shows a low content in strong acids centers (0.1611 meq./g), a higher concentration of medium strength (0.2645 meq./g) and a weak acid centers concentration of more than two times higher than of strongly acidic centers (0.4124 meq./g). On the basis of the data obtained, it can be considered that this catalyst has a relatively high acidity, the sum of the strong acid centers and of the medium strength centers being higher than the concentration of weak acid centers.

Table 2
DISTRIBUTION THE ACID STRENGTH OF
Ru-Sn/Al-HMS + γ -Al₂O₃ CATALYST

Type of acidic centers	Temperature range, °C	Acid strength, meq/g
Weak acids	150-300	0.4124
Medium strength	300-450	0.2645
Strong acids	450-600	0.1611
TOTAL	150-600	0.8380

The adsorption / desorption isotherms of the two catalysts are shown in figures 2 and 3, their textural characteristics are shown in table 3, and the size distribution of pore volume of the two catalysts are shown in figures 4 and 5.

According to the IUPAC classification [18, 19], the isotherm of the Ru-Sn / γ -Al₂O₃ catalyst is type IV with the hysteresis loop H2. This hysteresis loop is specific to pores networks or pores interconnected. In such systems, the distribution of pore size and shape is not well defined. In the case of the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst, the isotherm is a type H2 with hysteresis loop. The hysteresis loop type H2 is specific to interconnected pores.

The specific surface area of the Ru-Sn catalyst deposited on γ - Al₂O₃ is 322.416 m² / g, and the total pore volume is 0.438 cm³ / g. According to the IUPAC classification, this catalyst falls within the mesoporous material category, the

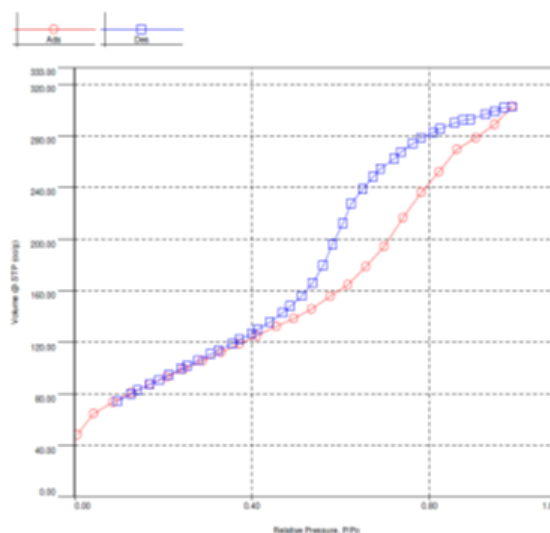


Fig. 2. Adsorption / desorption isotherm for Ru-Sn/ γ -Al₂O₃ catalyst

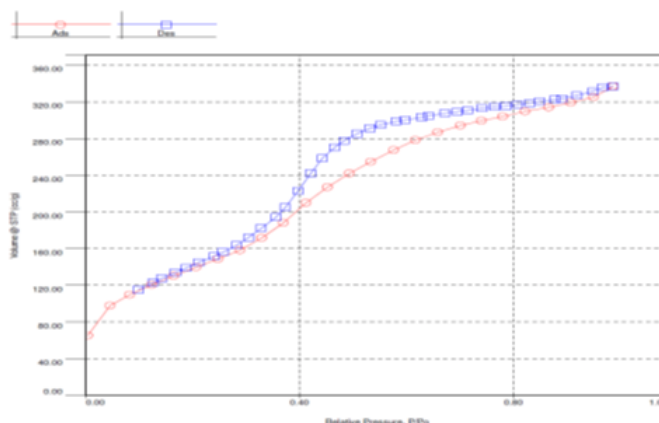


Fig. 3. Adsorption / desorption isotherm for Ru-Sn/Al-HMS + γ -Al₂O₃ catalyst

average pore diameter being 4.832 nm. The textural properties of the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst consist of a relatively large surface area and high pore volume. Thus, this catalyst has a mean pore diameter of 3.291 nm, which falls within the category of mesoporous materials, and the specific surface area is 411.907 m² / g.

The SEM image recorded for characterization of the Ru-Sn / γ -Al₂O₃ catalyst, shown in figure 6, illustrates a large dispersion of species deposited on the catalyst support.

The SEM image recorded for characterization of the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst is shown in figure 7. The method allowed to highlight the dispersion of the metallic phase deposited on the support. From the figure there is a large dispersion of species deposited on the catalyst support.

Catalyst	Specific surface area, m ² /g	Total pore volume, cm ³ /g	Average pore diameter, nm
Ru-Sn/ γ -Al ₂ O ₃	322.416	0.438	4.832
Ru-Sn/Al-HMS + γ -Al ₂ O ₃	411.907	0.409	3.291

Table 3
TEXTURAL CHARACTERISTICS OF THE TWO CATALYSTS

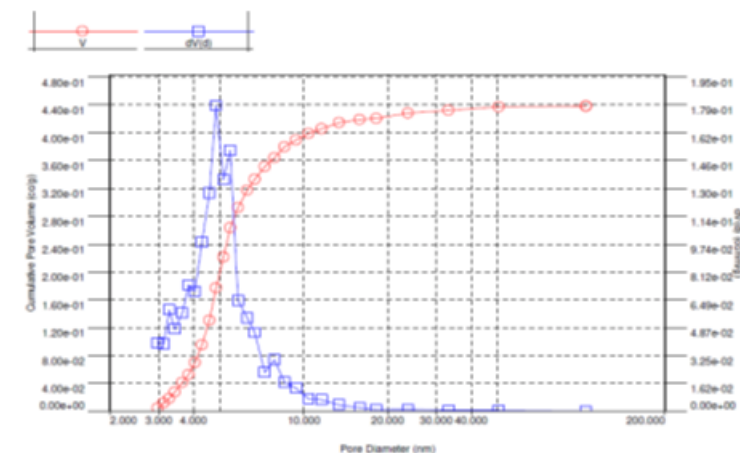


Fig. 4. Pore volume distribution function of size, for the Ru-Sn/ γ -Al₂O₃ catalyst

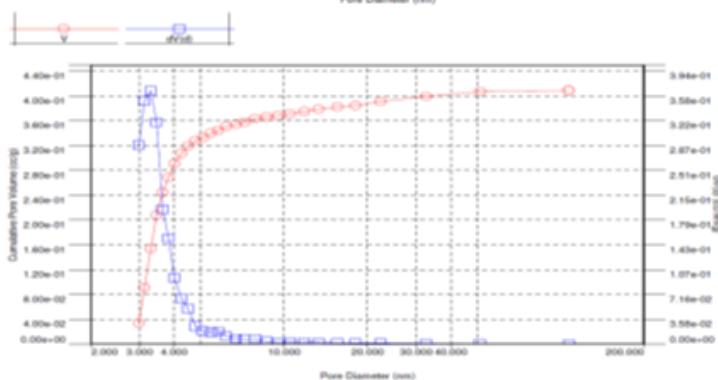


Fig. 5. Pore volume distribution function of size, for the Ru-Sn/Al-HMS + γ -Al₂O₃ catalyst

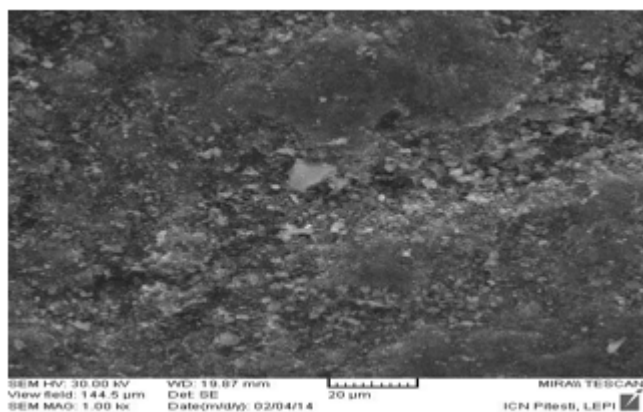


Fig. 6. The SEM image of the Ru-Sn/ γ -Al₂O₃ catalyst

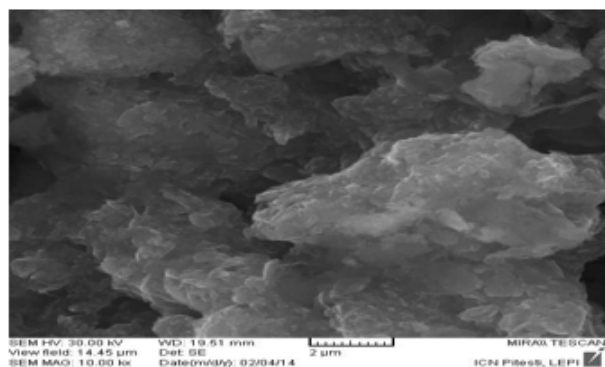


Fig. 7. The SEM image of the Ru-Sn/Al-HMS + γ -Al₂O₃ catalyst

If after the hydrogenation process of the methyl oleate on the catalyst 1% Ru-2% Sn / γ -Al₂O₃ at 60 atm, 260°C, at the volumetric velocity 0.12 h⁻¹ and the molar ratio of hydrogen / methyl oleate molar ratio of 10/1, a wide range of reaction products such as unsaturated and saturated fatty alcohols, unsaturated aldehydes, alkanes and alkenes [7] were obtained, the hydrogenation reaction of methyl oleate under the same reaction conditions on the 0.7% Ru-1.4% Sn / Al-HMS + γ - Al₂O₃ results only in hydrocarbon formation.

Figure 8 shows the conversion of methyl oleate on the Ru-Sn / γ -Al₂O₃ catalyst and on the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst at 60 atm, 260°C, hourly space velocities of methyl oleate 0.12 h⁻¹, hydrogen / methyl oleate molar ratio equal to 10/1. It can be seen that the conversion of methyl oleate into liquid products on the two catalysts is close. Thus, the conversion of methyl oleate on the Ru-Sn / γ -Al₂O₃ catalyst was 30.02% and on the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst was 31.5 %. The Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst, although it has a specific surface area of almost 30% greater than the Ru-Sn / γ -Al₂O₃ catalyst, exhibits a catalytic activity close to that.

Figure 9 shows the yields in liquid saturated hydrocarbons on the Ru-Sn / γ -Al₂O₃ catalyst and on the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst at 60 atm, 260 °C, the hourly space velocities of methyl oleate 0.12 h⁻¹ and the hydrogen / methyl oleate molar ratio equal to 10/1. A value of more than five times more saturated saturated hydrocarbon on the Ru-Sn / Al-HMS + γ -Al₂O₃ catalyst than the Ru-Sn / γ -Al₂O₃ catalyst is observed. The yield of liquid saturated hydrocarbons on the Ru-Sn / Al-HMS + γ -Al₂O₃

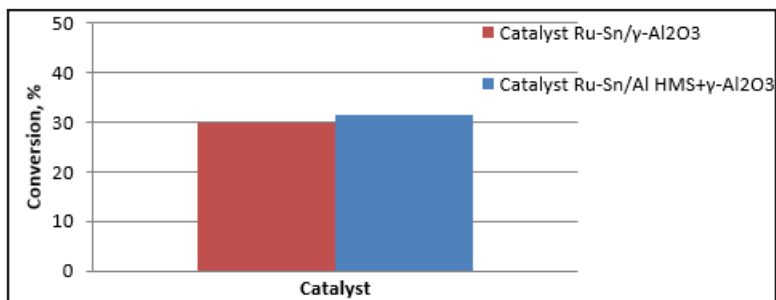


Fig. 8. Conversion of methyl oleate to liquid products on the two catalysts at 60 atm, 260°C, VHSV of 0.12 h⁻¹

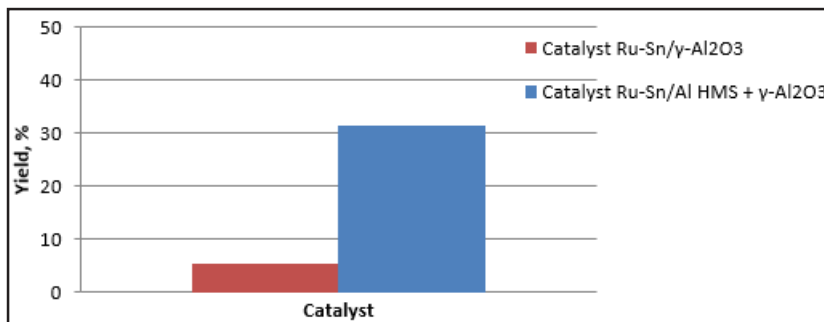


Fig. 9. Yields in liquid saturated hydrocarbons on the two catalysts at 60 atm, 260°C, VHSV of 0.12 h⁻¹

catalyst is 31.5%, while the Ru-Sn / γ-Al₂O₃ catalyst is only 5.53%.

The distribution of the strength of the acidic centers of the Ru-Sn / Al-HMS + γ-Al₂O₃ catalyst is probably disadvantageous to the selective hydrogenation to fatty alcohols and therefore favorably to the hydrogenolysis to hydrocarbons. This behavior is probably due to the high concentration of strong and medium acidic centers responsible for hydrogenolysis reactions with hydrocarbon formation.

Conclusions

The addition of Al-HMS mesoporous silica significantly alters the textural and acidic characteristics of the Ru-Sn / γ-Al₂O₃ catalyst. Thus, the Ru-Sn/Al-HMS + γ-Al₂O₃ catalyst has a specific surface area, a volume of pores and an acidic strength greater than the Ru-Sn / γ-Al₂O₃ catalyst. Both catalysts have average pore diameters in the mesoporous range. Also, the distribution of acid center strength changes especially by increasing the concentration of medium-strength acid centers and high acidity centers. These changes in the characteristics of the catalyst are manifested by changing its activity. Thus, under the same operating conditions, the Ru-Sn / Al-HMS + γ-Al₂O₃ catalyst shows a higher conversion to liquid products than the Ru-Sn / γ-Al₂O₃ catalyst and the yield in liquid saturated hydrocarbons on the Ru-Sn / Al-HMS + γ-Al₂O₃ is much higher than on the Ru-Sn / γ-Al₂O₃ catalyst.

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