

# Acidity Influence of Catalysts on the Process Selectivity for the Hydrogenation of Methyl Oleate

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*The hydrogenation of methyl oleate was conducted on two catalysts based on Ru, Ru-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively Ru-Sn-Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The catalysts were 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 equipment 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<sup>-1</sup> and molar ratio hydrogen/ methyl oleate of 10/1. The main compounds identified were saturated and unsaturated fatty alcohols and saturated hydrocarbons. Ru-Sn catalyst activity was superior to that of Ru-Sn-Ba, probably due to an optimal distribution of the acid strength of this catalyst.*

*Keywords: catalyst, hydrogenation, support acidity, methyl oleate, selectivity*

Fatty alcohols and their derivatives are used in various fields, for example, textile industry, lubricating oils industry, in minerals flotation, insecticides, cosmetics, etc., but their primary use is in the detergent industry, the development of fatty alcohol manufacturing is strictly linked to synthetic detergents [1]. Restrictions environment are the driving force behind the search for new processes, more efficient and less polluting. Thus, the main property of fatty alcohol respectively high bio-degradability degree, recommends it to manufacture detergents [2]. In most countries it was required by law that at least 80% of detergents ingredients must be biodegradable.

Unsaturated fatty alcohols, such as oleyl alcohol ((z)-octodec-9-en-1-ol), provides advantages to those saturated with the same chain length, for example, lower melting point, greater solubility in water and possibility of introducing functional groups [3].

In existing processes, the hydrogenation of fatty acid esters is carried out in the presence of catalysts, at high temperature and high pressure (200-300°C and 200-300 atm). It has been shown that during the hydrogenation of methyl oleate to oleyl alcohol may be obtained by-products [4, 5]. The hydrogenation of esters of unsaturated fatty acids, outside the competition of the carbonyl group hydrogenation and the carbon-carbon double bond hydrogenation can appear two side reactions:

- the transesterification reaction between methyl oleate and formed alcohol, resulting heavy esters (C<sub>36</sub>, oleyl oleate);

- cis-trans isomerization reaction for example of methyl oleate to give the trans ester trans-9-methyl octadecenoate

The hydrogenation of carboxylic acid esters to produce aliphatic alcohols has been studied on different catalysts. Maintaining of carbon-carbon double bond during the hydrogenation reaction of the acid /fatty esters to unsaturated fatty alcohols is of great interest for the industry [6]. Another catalytic hydrogenation reaction is the conversion of vegetable oil to unsaturated compounds, such as oleyl alcohol (liquid at room temperature), which

is an important material for the production of heavy liquid detergents, cosmetics, pharmaceutical products, anti-foaming agents, etc. [7-13].

Ross D. Rieke et. al. studied the commercial production of fatty alcohols derived from natural sources made by the catalytic hydrogenation of fatty acids or fatty methyl esters in a fixed bed reactor. The catalyst used was a copper chromite obtained at different calcination temperatures. Catalytic activity and selectivity were determined on the basis of the reaction products obtained from the process. Both the activity and selectivity are well correlated to the crystallinity of the copper chromite surface; it increases with decreasing of the degree of crystallinity. Based on the diversity of by-products can be optimized catalysts recipe for hydrogenation [14].

Hui Huang et al. studied the deactivation of the Cu/Zn catalyst poisoned with chlorinated derivatives in hydrogenation reaction of fatty acid esters to obtain fatty alcohols [15].

The effect of the catalyst poisoning was studied in the hydrogenation reaction of methyl laureate on the Cu/Zn catalyst in a reactor autoclave type with stirring under the following reaction conditions: 240°C, 750rpm,  $m_{cat}/m_{metil\ laurate}$  0.025/L and 300 min.

In another study, Hui Huang et. al. [16] has studied the catalytic deactivation with water of the Cu/Zn catalyst prepared by co-precipitation using the hydrogenation reaction of methyl of fatty esters to fatty alcohols.

Deactivation of the catalyst was carried out in an autoclave reactor with stirring, by varying the amount of water in methyl laureate and by increasing the pressure to 4MPa. The reactor temperature was increased up to 240°C and the pressure up to 21 MPa. After 5 h of reaction, the reactor was cooled to room temperature, and the gas was released. Liquid samples were analyzed in a GC equipped with flame ionization (FID). 1-octanol was used as a standard compound in the analysis. All compounds were identified with a mass spectrometer GC/MS.

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No.	Component	Concentration, %
1	Methyl Palmitate	2.79
2	Methyl Palmitoleat	2.57
3	Methyl Stearate	2.38
4	Methyl Oleat-1n9	77.48
5	Methyl Oleat-1n7	2.56
6	Methyl Linoleat	12.22

**Table 1**  
THE COMPOSITION OF METHYL  
OLEATE

Normann studied high-pressure hydrogenation of fatty acids and their esters using  $\text{CuCO}_3$  on kieselguhr [17, 18]. At the same time, Adkin et al. [18-20] and Schrauth et al [21- 23] have achieved good results with the same reactions, but using copper chromite catalyst. Adkins used barium as stabilizer of  $\text{CuCr}_2\text{O}_4$  catalyst (type Cu-Cr-O), thus obtaining a higher reaction speed. The free fatty acids can not be hydrogenated [20]. Schmidt [24] reduced ethyl oleate to the corresponding alcohol with  $\text{CuCr}_2\text{O}_4$  on kieselguhr in gas phase at atmospheric pressure, concluding that the catalyst activity is of great importance in this reaction.  $\text{CuCr}_2\text{O}_4$  catalyst activity was studied over time by several researchers. Adkins checked if the catalyst becomes inactive if the content of copper is reduced to zero [25].

Compared to studies of literature that approach the processing of bioresources [26-28], the number of publications that address the hydrogenation of fatty ester is relatively low, priority concerns being directed towards obtaining biofuels [29].

In this paper is studied the influence of two catalysts based on Ru, respectively Ru-Sn/ $\gamma$ - $\text{Al}_2\text{O}_3$  and Ru-Sn-Ba /  $\gamma$ - $\text{Al}_2\text{O}_3$  on the hydrogenation of methyl oleate.

### Experimental part

The raw materials used in experiments were methyl oleate, ruthenium(III) chloride hydrate p.a. (Sigma-Aldrich), tin(II) chloride dehydrate puriss p.a. (Sigma-Aldrich), barium nitrate ACS reagent (Sigma-Aldrich),  $\gamma$ -alumina granulated and electrolytic hydrogen purity from Linde Company. The composition of methyl oleate used in the experiment was determined by GS-MS analysis and are shown in table 1.

The synthesis of catalysts were 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, tin (II) chloride and barium nitrate. The support used in the preparation of the catalyst is  $\gamma$ -alumina. Concentration of catalyst precursor of the impregnation solution is calculated according to the proposed metal content (1% Ru and 2% Sn for Ru - Sn/ $\gamma$ - $\text{Al}_2\text{O}_3$ ; 1% Ru, 2% Sn and 0.5% Ba for Ru - Sn - Ba/ $\gamma$ - $\text{Al}_2\text{O}_3$ ). Conditioning of the catalyst between impregnation 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 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. The acid strength distribution of the active center has been determined by the method of thermal desorption of a weak amine using a DuPont Instruments "Thermal Analyst 2000/

2100" coupled with a module "951 Thermogravimetric Analyzer" [30, 31].

The experimental program was performed in a continuous system and fixed bed catalytic reactor [28]. The process was carried out in isothermal conditions. 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: 100 atm;

-temperature: 275°C;

-volume hourly space velocities of methyl oleate (VHSV):  $0.15\text{h}^{-1}$ ;

-molar ratio hydrogen/ methyl oleate: 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°C corresponds to weak acids centers, in the temperature range 300-450°C corresponds to medium acids centers and in the temperature range 450-600°C corresponds to the strong acids centers (A-thermodesorption from centers with weakly acidic, B-thermodesorption from centers with medium acidity, C-thermodesorption from centers with high acidity). Thermodesorption curve of diethylamine of the  $\gamma$ -alumina support is shown in figure 1.

Table 2 presents data on the distribution of strength acidity of  $\gamma$ -alumina support, calculated based on thermal desorption curve.

Table 2 shows a low content in medium acidic centers (0.1754 meq. / G), a higher concentration of strong acids centers (0.2821 meq. / G) and a weak centers acids

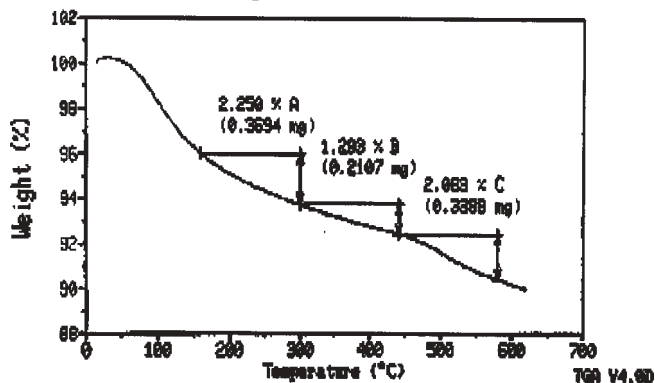


Fig. 1. Diethylamine thermodesorption curve of the  $\gamma$ -alumina support

The type of the acidic centers	Thermodesorption temperature, °C	The acidity strength, meq./G
Weak acids centers	150-300	0.3076
Medium acids centers	300-450	0.1754
Strong acids centers	450-600	0.2821
Totally	150-600	0.7651

**Table 2**  
THE DISTRIBUTION OF ACIDITY STRENGTH OF  $\gamma$ -ALUMINA SUPPORT

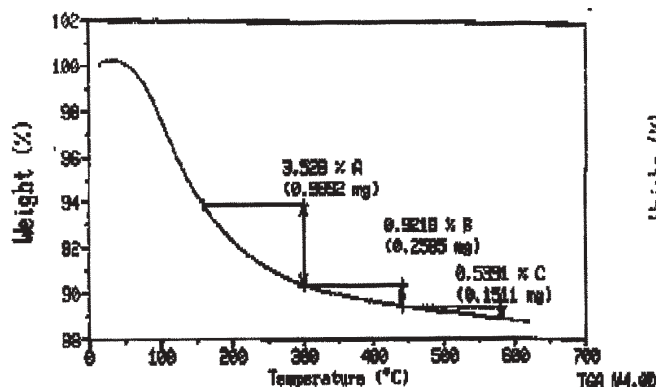


Fig.2. Diethylamine thermodesorption curve for Ru - Sn/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

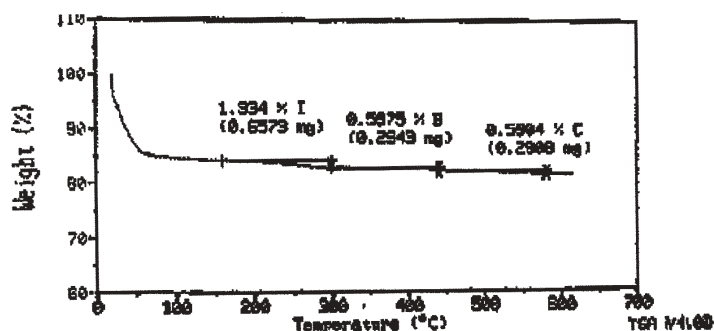


Fig.3. Diethylamine thermodesorption curve for Ru - Sn - Ba/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

The type of the acidic centers	Thermodesorption temperature, °C	The acidity strength, meq./G
Weak acids centers	150-300	0.4824
Medium acids centers	300-450	0.1260
Strong acids centers	450-600	0.0737
Totally	150-600	0.6821

**Table 3**  
THE DISTRIBUTION OF ACIDITY STRENGTH OF Ru - Sn /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

The type of the acidic centers	Thermodesorption temperature, °C	The acidity strength, meq./G
Weak acids centers	150-300	0.1824
Medium acids centers	300-450	0.0817
Strong acids centers	450-600	0.0807
Totally	150-600	0.3448

**Table 4**  
THE DISTRIBUTION OF ACIDITY STRENGTH OF Ru - Sn - Ba/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

concentration greater than of strong and medium acids centers (0.3076 meq. / G). It can be considered that  $\gamma$ -alumina support has a relatively high total acidity.

Thermodesorption curve of diethylamine for the two catalysts is shown in figures 2 and 3 (A-thermodesorption from centers with weakly acidic, B- thermodesorption from centers with medium acidity, C- thermodesorption from centers with high acidity).

Table 3 presents data on the distribution of strength acidity of Ru - Sn/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, calculated based on thermal desorption curve.

From table 3 is observed a low content in strong acidic centers (0.0737 meq./G), a higher concentration of medium acidity centers than of strong acidic centers (0.1260 meq./G) and a weak centers acids concentration

approximately four times higher than concentration of medium acidic centers (0.4824 meq./G). It can be considered that this catalyst has low acidity. Thus, after impregnating with Ru and probably with Sn, concentration of centers with weak acidic grow while concentration of centers with medium acidic and especially with strong acidic decreased.

Table 4 presents data on the distribution of strength acidity of Ru - Sn - Ba/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, calculated based on thermal desorption curve.

From table 4 is observed a low content in strong acidic centers (0.0807 meq./G), a concentration of medium acidity centers closer to strong acidity centers (0.0817 meq./G) and a weak acidity centers concentration approximately two times higher than concentration of

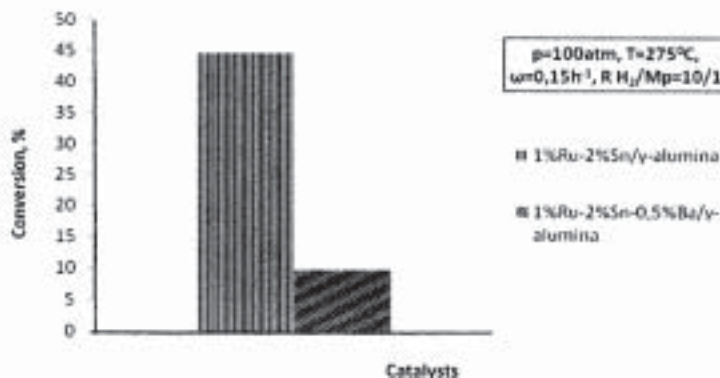


Fig. 4. Conversion of methyl oleate on the catalysts Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

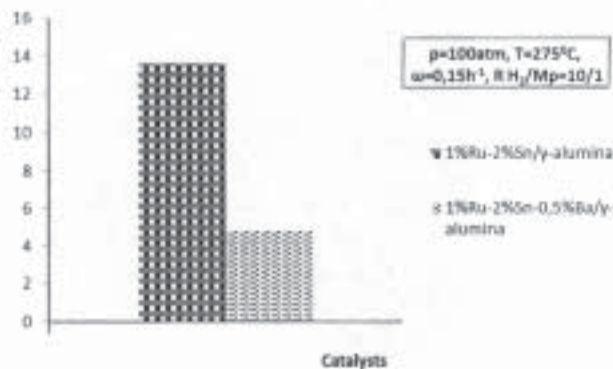


Fig. 5. Yield to saturated fatty alcohols on the catalysts Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

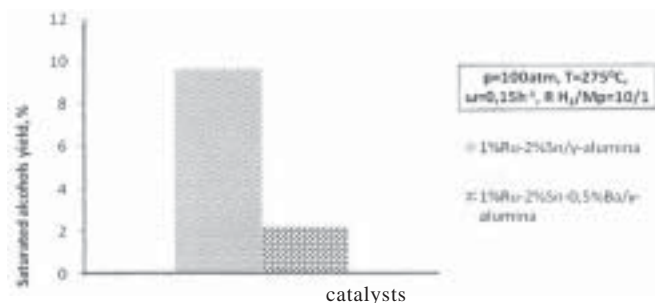


Fig. 6. Yield to unsaturated fatty alcohols on the catalysts Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

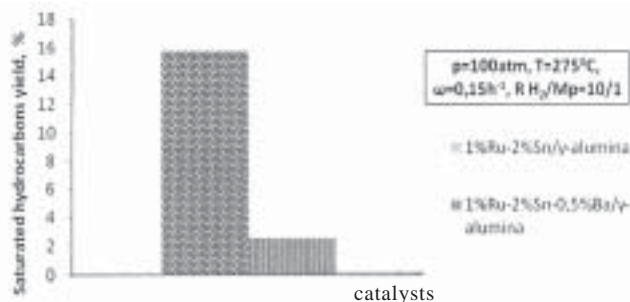


Fig. 7. Yield to saturated hydrocarbons on the catalysts Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

medium acidic centers (0.1824 meq./G). It can be considered that this catalyst has low acidity, the addition of Ba reducing by half the total acidity, both by neutralizing centers of medium acidity but especially by neutralizing of weak acidity centers.

The product composition obtained on the two catalysts in the hydrogenation of methyl oleate is different. Thus, in the case of Ru-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are obtained saturated and unsaturated fatty alcohols, straight unsaturated and saturated hydrocarbons, saturated aldehydes, saturated and unsaturated ethers. On the other hand when the hydrogenation of methyl oleate occurs on the catalyst Ru-Sn-Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were not obtained unsaturated hydrocarbons, saturated and unsaturated ethers, compared to carrying out of the hydrogenation on the catalyst Ru-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Ru-Sn-Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst performance are lower than Ru-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst as shown in Figures 4-7.

In figure 4 is observed a value of methyl oleate conversion on the catalyst Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> over four times than on the catalyst Ru-Sn-Ba/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, for the same parameter values. At the same time it is observed that on the catalyst Ru-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the yield on saturated and unsaturated fatty alcohols, as well as on saturated hydrocarbons, is up to five times higher than on the catalyst Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The selectivity of fatty esters hydrogenation to fatty alcohol is influenced by the distribution of acidity centers. Therefore, in order to improve the selectivity to fatty alcohols, it is probably important the presence of weak acidity centers which will promote the adsorption of those functional groups that favors the formation of fatty alcohols. Also weak acidity centers are likely to be responsible for the production of unsaturated fatty alcohols (e.g. oleic alcohol), while the centers of strong acidity and medium acidity, probably also promotes side reactions (e.g. hydrocracking, isomerization).

## Conclusions

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

The Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has a total acidity greater than the Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, acidity due to a high concentration of weak acids centers.

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

The high concentration of weak acids centers in the case of catalysts Ru-Sn / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than in the case of catalyst Ru-Sn-Ba / $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, is probably responsible for adsorption of those functional groups that favors obtaining of saturated and even unsaturated fatty alcohols and therefore also of high yield in these compounds.

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