

PREPARATION AND CHARACTERIZATION OF Ru-Sn/Al₂O₃ CATALYSTS FOR THE HYDROGENATION OF FATTY ACID METHYL ESTERS

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Ru-Sn/Al₂O₃ catalysts with different Sn loadings were prepared by the coimpregnation method. Several characterization techniques such as TPR, pyridine TPD and catalytic tests for dehydrogenation and hydrogenolysis were used to evaluate and compare such catalysts. TPR results indicate that Sn is deposited both onto the support and as species strongly interacting with Ru. Such non selective deposition modifies the acid and metallic functions of the catalysts. Both total acidity and acid strength distribution are affected: total acidity decreases and new sites of lower acid strength are created. Both dehydrogenating and hydrogenolytic activities are strongly diminished by the addition of Sn. Results of catalytic tests for methyl oleate hydrogenation indicate that methyl stearate is the main product, with only minute amounts of oleyl alcohol produced, and that the addition of Sn diminishes the hydrogenation activity.

Keywords: hydrogenation; methyl esters; Ru-Sn/Al₂O₃.

INTRODUCTION

In recent years, surfactants based on fatty alcohols have won space on the market for detergents due to its excellent deterative properties and their superior biodegradability regarding to conventional oil based detergents.¹ The fatty alcohols are obtained through the catalytic hydrogenation of fatty acids or their corresponding esters. The direct hydrogenation of acids presents the technical difficulty that they are corrosive at high temperature.² Moreover, in some cases can chemically attack the catalysts used. The use of esters involves additional stages of esterification and separation.³

The industry currently focuses on the hydrogenation of methyl esters (FAMES) or esters of fatty alcohol and fatty acid (wax esters, FAWE). Because the oils and fats which are used as raw materials are a mixture of fatty acids of different chain lengths, alcohols of variable carbon number are obtained as products.⁴ The C₁₂-C₁₄ fraction is used to obtain detergents, and as in the case of FAME, there are few uses for the fractions C₈-C₁₀ and C₁₆-C₁₈. In contrast, in the case of fatty acids there are applications for all fractions. This sometimes influences the choice of manufacturing technology. Of the most common manufacturing technologies, such as the hydrogenation of FAME and the hydrogenation of FAWE, the former produces FAMES as byproducts that can not find market, depending upon the length of chain, while the second generates fatty acids that have not this limitation.

Some unwanted byproducts of the process are hydrocarbons (alkanes, alkenes and methane), and aldehydes. With reference to the latter, and depending on the desired quality of the final fatty alcohol (which usually tolerates a maximum of 1-5 ppm of aldehydes), it must have an additional stage of selective hydrogenation to eliminate these compounds. Other steps that normally are used at high production scales, is the distillation of fractions (C₆₋₁₀, C₁₂₋₁₄, C₁₆₋₁₈) or other technical fractionation suitable for separation by carbon atoms number. The hydrogenation of fatty acid methyl esters for the production of long chain fatty alcohols is a process with well established technolo-

gy, which has remained virtually unchanged in the last decades. For this process Cu-based catalysts are commonly used at high pressures (200-300 atm) and temperatures (200-250 °C).⁵⁻⁷

There have been attempts to reduce the pressure and temperature of the process by replacing the catalysts of Cu by others based on noble metals.⁸ These have an increased activity at low temperature but in its pure form (i.e., without modifying the function of metal) have low selectivity. The obtention of fatty alcohols from fatty acid methyl esters requires the selective hydrogenation of carbonyl group and the hydrogenolysis of C-O methoxy group. In addition, there should be no hydrogenation of double bonds or other side reactions such as those leading to the formation of alkanes and aldehydes.

The selective hydrogenation of acids/fatty esters to the respective unsaturated alcohols is currently studied using catalysts of the group VIII. It should be noted that the carbonyl group of fatty acid and esters has lower reactivity than the corresponding one of ketones and aldehydes.⁹ One of the most promising catalysts is based on supported Ru-Sn. The Ru-Sn bimetallic catalysts are very selective for the hydrogenation of ethyl acetate to ethanol,¹⁰ but they are not selective for the hydrogenation of unsaturated fatty acids or their esters to the corresponding unsaturated alcohols.¹¹ On the other hand, chemically modified catalysts of the type Ru-Sn-B,¹² can hydrogenate with good selectivity esters to the corresponding unsaturated fatty alcohols.^{13,14} Mizukami *et al.*¹⁵ studied the performance of Ru-Sn catalysts in the selective hydrogenation of oleic acid to unsaturated alcohols. They found that the activity and selectivity of the catalysts Ru-Sn prepared by the sol-gel method depends greatly on the nature of the medium used in the procedure. Piccirilli *et al.*¹³ observed secondary reactions such as transesterification of oleyl alcohol with methyl oleate, leading to the formation of heavy esters. Costa *et al.*¹⁶ found that metals promote the *cis-trans* isomerization of unsaturated acids, as a side reaction. The effects of support and metal promoters on the selective hydrogenation of carbonyl group, in the case of the group VIII metal catalysts, are currently well understood.¹⁷ However, there are no reports about the effects of catalytic ensembles on activity and selectivity. On the other hand, there is a controversy between different research groups as some have reported the formation of oleyl alcohol

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from oleic acid or methyl oleate^{16,18,19} using Ru-Sn/Al₂O₃ catalysts while others just reported the formation of methyl stearate using the same reagents, operating conditions and catalysts.²⁰

This paper presents a study of the activity of Ru-Sn/Al₂O₃ catalysts in the methyl oleate hydrogenation reaction.

EXPERIMENTAL

Catalysts preparation

All catalysts were prepared using a commercial γ -alumina as support (Cyanamid Ketjen CK-300, pore volume=0.5 cm³/g, specific surface area=180 m²/g, impurities: Na=5 ppm, Fe=150 ppm, S=50 ppm). The alumina pellets were ground to 35-80 mesh and then they were calcined in air at 650 °C for 3 h. The Ru-Sn/ γ -alumina catalysts were prepared by means of coimpregnation with aqueous solution of Ru and Sn salts followed by a calcinations step. In all cases the impregnation volume was adjusted in order to achieve the appropriate final concentration of each metal in the catalysts: 0.1; 0.3; 1.0 or 2.0% Sn and 1% Ru. The salts used were RuCl₃·2H₂O (4 mg Ru mL⁻¹) and SnCl₂·2H₂O (25 mg Sn mL⁻¹). The solution of the Sn precursor was unstable and was prepared just before its use. SnCl₂ was first dissolved in deionized water and heated for 30 min at 70 °C. Then 37% HCl was added until the solution became transparent and was ready to be used. A 0.2 M HCl solution was added to the support (1.5 cm³ g⁻¹) before impregnating the metal salts in order to have chloride as a competing ion and to get an homogeneous metals distribution. The solution containing the catalyst was first left unstirred for 1 h and then it was gently heated at 70 °C in order to evaporate the excess liquid. The catalysts were finally dried at 120 °C overnight, calcined in flowing air (4 h, 450 °C) and reduced in a hydrogen flow (4 h, 500 °C).

Temperature programmed reduction

TPR patterns were recorded in an Ohkura TP2002 apparatus with a thermal conductivity detector. At the beginning of each TPR test the sample was heated in air at 450 °C for 1 h. Then it was heated from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under a reducing gas stream (5.0% H₂ in argon).

Temperature programmed pyridine desorption

The amount and strength of acid sites on the catalysts surface were assessed by means of temperature programmed desorption of pyridine. Catalyst samples (200 mg) were first immersed in a closed vial containing pure pyridine (Merck, 99.9%) for 4 h. Then the catalyst was taken out from the vial and excess pyridine was evaporated at room temperature. The sample was then put in a quartz microreactor and a constant nitrogen flow (40 mL/min) was set up. Weakly adsorbed pyridine was first desorbed in a first stage of stabilization by heating the sample at 110 °C for 2 h. The temperature of the oven was then raised to 600 °C at a heating rate of 10 °C min⁻¹. The reactor outlet was directly connected to a flame ionization detector to continuously measure the amount of desorbed pyridine.

Cyclohexane dehydrogenation

This test reaction was performed in a fixed bed glass reactor in the following experimental conditions: catalyst mass = 100 mg, temperature = 300 °C, pressure = 0.1 MPa, H₂ flowrate = 80 cm³ min⁻¹, cyclohexane flowrate = 1.61 cm³ h⁻¹. Before the reaction was started, the catalysts were treated in H₂ (80 cm³ min⁻¹, 500 °C, 1 h). The reaction products were analyzed in a gas chromatograph connected on-line.

Cyclopentane hydrogenolysis

Before the reaction the catalysts were reduced for 1 h at 500 °C in H₂ (60 cm³ min⁻¹). Then they were cooled in H₂ to the reaction temperature (350 °C). The other conditions were: catalyst mass = 150 mg, pressure = 0.1 MPa, H₂ flow rate = 40 cm³ min⁻¹, cyclopentane flow rate = 0.483 cm³ h⁻¹. The reaction products were analyzed in a gas chromatograph connected on-line.

Methyl oleate hydrogenation

All hydrogenation experiments were performed in a stainless steel, autoclave-type reactor (Parr Instrument Co., 280 cm³ capacity). The reaction conditions were: temperature: 270 °C, hydrogen pressure: 50 atm, stirring rate: 850 rpm, volume of methyl oleate: 20 cm³, volume of inert diluent (*n*-dodecane): 80 cm³, catalyst loading: 1 g. Methyl oleate containing 82% of oleate and 18% of methyl stearate was obtained from technical grade methyl oleate (Indioquímica; methyl myristate: 10%, methyl estearate: 12%, methyl oleate: 69%, unknown minor components: 9%) by high-vacuum distillation. Nitrogen (blanket gas) (99.999% pure) and hydrogen (99.999% pure) were supplied by AGA and further purified by using a deoxo unit (Matheson) and a drying column (Linde 3A zeolites) connected on-line.

The products of reaction were analysed by gas chromatography using an Agilent 6890N GC equipped with an 7683B Series automatic sampler and an Agilent HP-5 (5% phenyl methyl siloxane, 30 m x 0.25 mm ID, 0.32 μ m film thickness) column. Nitrogen gas (4.8 mL/min) was used as carrier. A temperature program was used: initial temperature: 200 °C (5 min), temperature ramp: 15 °C/min, final temperature 250 °C (7 min), post-run (2 min). The flame ionization detector (FID) and injector temperatures were both set at 250 °C. The concentrations of methyl myristate (retention time (RT): 2.5-2.6 min), methyl estearate (RT: 4.4-4.5 min), methyl oleate (RT: 4.2-4.3), and oleyl alcohol (RT: 3.7-3.8 min) were calculated without using either correction factors or an internal standard.

Identification of the reaction products

It was done by GC/MS(EI) using a Shimadzu QP-50000 GC/MS equipped with an electronic impact source at 260 °C, operating with an emission current of 0.7 mA and 70 eV electron energy. The GC column was identical to the previously used for the GC quantitative analysis. The aforementioned temperature program was also settled. Helium gas was used as carrier. The standard oleyl alcohol and the fatty acid methyl esters were characterized by GC-MS(EI) as follows: oleyl alcohol: MS(EI): *m/z* 268 (M⁺, 0.1), 250 (0.9), 97 (15), 96 (36), 95 (30), 83 (27), 82 (57), 81 (43), 70 (13) 69 (42), 68 (38), 67 (54), 57 (31), 56 (24), 55 (100), 54 (40). Methyl myristate: MS(EI): *m/z* 242 (M⁺, 0.7), 87 (48), 75 (19), 74 (100), 69 (11), 59 (11), 57 (18) 55 (31). Methyl oleate: MS(EI): *m/z* 264 (M⁺ - HOMe, 2.9), 110 (10), 98 (16), 97 (21), 96 (22), 95 (13), 87 (23), 84 (24), 83 (27), 82 (15), 81 (22), 74 (44), 70 (12), 69 (46), 68 (19), 67 (33), 59 (21), 57 (26), 56 (22), 55 (100), 54 (25). Methyl estearate: MS(EI): *m/z* 298 (M⁺, 1.1), 87 (51), 75 (21), 74 (100), 69 (13), 59 (10), 57 (21), 55 (34).

RESULTS AND DISCUSSION

Figure 1 shows the TPR profiles of the bimetallic Ru-Sn catalysts and monometallic Ru and Sn catalysts. It can be seen that the monometallic Ru catalyst have two reduction peaks at 120 and 173 °C. According to the literature, the first peak can be attributed to the reduction of chlorinated Ru species,²¹ while the second smaller peak can be assigned to the reduction of ruthenium oxychloride.²² The

monometallic Sn catalyst presents a wide reduction peak that starts at 150 and ends at 550 °C which has two reduction bands in the range of 200-300 and 380-520 °C. This pattern suggests an heterogeneous interaction between Sn oxide and alumina. It has been reported that Sn⁴⁺ is only partially reduced (i.e. to Sn⁺²) when supported on alumina.^{23,24} For bimetallic catalysts the peak attributed to the reduction of chlorinated Ru species is slightly shifted to lower temperatures. This can be due to the fact that Sn modifies the acidity of the support and therefore reduces the Ru-support interaction. It can also be observed an increase in the size of the peak at 173 °C as Sn content increases. This behavior could be explained by the co-reduction of oxides of Ru and Sn. The zone of reduction at about 300 °C should be attributed to the segregation of Sn, away from Ru metal particles.

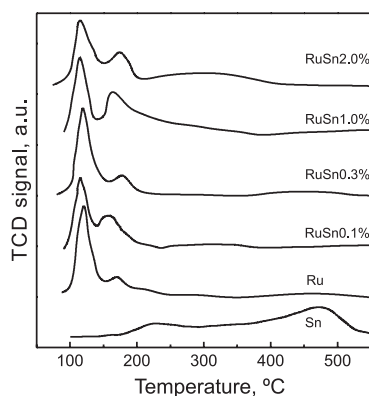


Figure 1. TPR patterns of Ru-Sn catalysts

Pyridine is a standard probe molecule to characterize surface acid sites. Its desorption at low temperatures is related to weak acid sites, while high temperature desorption corresponds to strong ones. Pyridine TPR patterns therefore reveal the distribution of acid sites strength. The area under the TPD profiles is a measure of the total acidity of the catalyst. Figure 2 shows the profiles of pyridine TPD for RuSn and Ru catalysts. It can be seen that the Ru catalyst is the one who possesses the highest acidity (i.e. the area under the curve is the greatest). Most of its acid sites are strong, as most of desorption occurs at high temperatures. The addition of Sn results in a decrease in the amount of strong sites and the formation of lower strength acid sites. This is because oxides of Sn possess basic character and neutralize sites of strong acidity. The formation of centers of low acidity may be related to the addition of chlorine during the impregnation of Sn and the formation of a Ru-Sn “alloy”. The formation of this “alloy” could lead to the elimination of species of chlorinated Ru which had a strong acidity. This explanation is supported by TPR profiles showing a decrease of the reduction peak at 120 °C (attributed to Cl₃Ru) as Sn content increases.

Figure 3 shows the average conversion values obtained during the whole experience (12 measurements) for cyclohexane dehydrogenation and the conversion value for cyclopentane hydrogenolysis obtained at 5 min reaction. It is important to point out that the reaction of cyclopentane is deactivated quickly by the deposition of coke while the reaction of cyclohexane dehydrogenation does not suffer deactivation in the conditions used. It is observed that the incorporation of Sn to the Ru catalyst has a negative effect on both dehydrogenation and hydrogenolysis rates, being this effect more important for the last one. Cyclohexane dehydrogenation is a “non demanding” reaction (i.e. it does not require the existence of a particular assembly of metal atoms). On the other hand, cyclopentane hydrogenolysis is a “demanding” reaction (it needs the presence of some metal atoms “ensembles”). The evolution of the activity upon

Sn addition can now be understood. It is important to note that Ru is active for both reactions while the Sn has no significant activity. The decrease in activity may be not only due to a geometric effect (blocking of the active Ru atoms or scission of ensembles by the Sn atoms). An electronic effect (change in the electronic properties of Ru by the Sn) should also be expected.

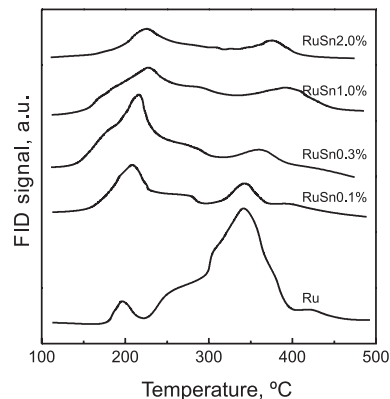


Figure 2. Temperature programmed pyridine desorption patterns of Ru-Sn catalysts

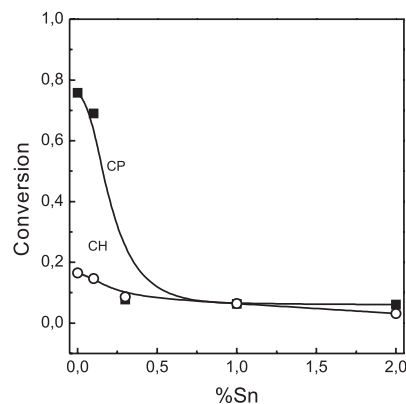


Figure 3. Conversion of cyclohexane (CH) and cyclopentane (CP) as a function of Sn content

Figure 4 shows the values of conversion of methyl oleate as a function of the reaction time for the catalysts studied. Lower conversion values are obtained as the Sn content of the catalyst is increased. Similar results were reported by Desphande *et al.*²⁵ at somewhat different experimental conditions. The blocking of the metal active atoms (Ru) by the Sn (inactive) is the most probable cause of this behavior. It is important to note that the results obtained for cyclohexane dehydrogenation (Figure 3) correlate well with the corresponding ones for the hydrogenation of methyl oleate. The selectivity of the reaction is nearly 100% to methyl stearate for catalysts with ≤ 0.3% Sn, that is, only double bond hydrogenation occurs. For catalysts with 1 and 2% Sn minute amounts of fatty alcohols (stearyl and oleyl alcohols from hydrocracking of carbonyl group) were detected at high reaction times. The incorporation of Sn strongly affects the hydro/dehydrogenating activity of Ru, as it can be seen in Figure 3. A fivefold decrease in activity is observed for cyclohexane dehydrogenation activity at the higher Sn loading. On the other hand, the activity (conversion) for the hydrogenation of methyl oleate is less affected (a 40% decrease in methyl oleate conversion occurs upon the same Sn addition). These findings suggest that the activity of Ru for the hydrogenation of C=C bonds was not sufficiently reduced to improve the selectivity for unsaturated alcohol production. The

hydrogenolytic activity (as measured by the cyclopentane reaction) is highly reduced due to the incorporation of Sn, being its residual value of only 8% of that found for the catalyst without Sn. Such low activity was nevertheless sufficient for the hydrogenolysis of C=O groups of methyl oleate so that some alcohols were formed. As hydrogenation and hydrogenolysis of methyl oleate are steps of a series/parallel mechanism, the unsaturated compounds could have been hydrogenated due to the lower rate of the hydrogenolysis reactions.

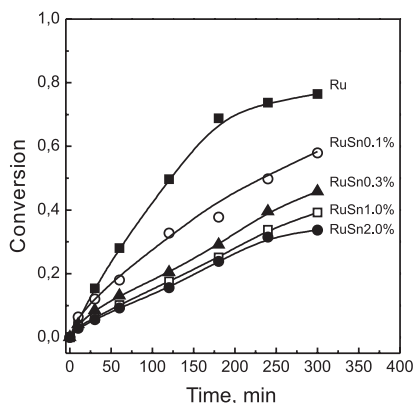


Figura 4. Conversion of methyl oleate on Ru-Sn catalysts as a function of time

CONCLUSIONS

The results of catalyst characterization by TPR show that Sn is deposited both on the metal function in strong interaction with Ru as well as on the support. This non-selective deposition of Sn produces changes on the acid and metal function of catalyst. The total acidity and the distribution of acid sites are modified by Sn addition. Sn lowers the total acidity by eliminating the strongest acid sites and by the creation of weaker ones. The dehydrogenation and hydrogenolysis activity of Ru are strongly diminished by Sn addition. The reaction of hydrogenation of methyl oleate showed that only double bonds are hydrogenated while the carbonyl group does practically not react.

REFERENCES

- Hill, K.; *Pure Appl. Chem.* **2000**, *72*, 1255.
- van de Scheur, F. Th.; U-A Sai, G.; Blied, A.; Staal, L. H.; *J. Am. Oil Chem. Soc.* **1995**, *72*, 1027.
- Kreutzer, U. R.; *J. Am. Oil Chem. Soc.* **1984**, *61*, 343.
- http://www.lurgi.com/website/fileadmin/user_upload/1_PDF/1_Broschures_Flyer/englisch/0235e_Fatty_Alcohol.pdf, accessed December 2008.
- Rieke, R. D.; Thakur, D. S.; Roberts, B. D.; White, G. T.; *J. Am. Oil Chem. Soc.* **1997**, *74*, 341.
- Aring, H.; Burch, K.; Franke, P.; Honetzke, G.; Tietz, W.; Weidemann, R.; *DE. pat.* DD 231,430 **1981**.
- Miya, B.; *US pat.* 4,252,689 **1981**.
- Mendez, M. J.; Santos, O. A. A.; Jordão, E.; *Appl. Catal. A* **2001**, *217*, 254.
- Kluson, P.; Cervený, L.; *Catal. Lett.* **1994**, *23*, 299.
- Sordelli, L.; Psaro, R.; Vlaic, G.; Cepparo, A.; Recchia, S.; Dossi, C.; Fusi, A.; Zaroni, R.; *J. Catal.* **1999**, *182*, 186.
- Ferretti, O. A.; Bourmonville, J. P.; Mabilon, G.; Martino, G.; Candy, J. P.; Basset, J. M.; *J. Mol. Catal.* **1991**, *67*, 283.
- Narasimhan, C. S.; Deshpande, V. M.; Ramnarayan, K.; *Appl. Catal.* **1989**, *48*, L1.
- Piccirilli, A.; Pouilloux, Y.; Pronier, S.; Barrault, J.; *Bull. Soc. Chim. Fr.* **1995**, *132*, 1109.
- Deshpande, V. M.; Ramnarayan, K.; Narasimhan, C. S.; *J. Catal.* **1990**, *121*, 174.
- Cheah, K. Y.; Tang, T. S.; Mizukami, F.; Niwa, S.; Toba, M.; Choo, Y. M.; *J. Am. Oil Chem. Soc.* **1992**, *69*, 410.
- Costa, C. M. M.; Jordão, E.; Mendes, M. J.; Santos, O. A. A.; Bozon-Verduraz, F.; *React. Kinet. Catal. Lett.* **1999**, *66*, 155.
- Pérez-Cadenas, A. F.; Zieverink, M. P.; Kapteijn, F.; Moulijn, J. A.; *Carbon* **2006**, *44*, 173.
- Mendes, M. J.; Santos, O. A. A.; Jordão, E.; Silva, A. M.; *Appl. Catal. A* **2001**, *217*, 253.
- Cheah, K. Y.; Tang, T. S.; Mizukami, F.; Niwa, S.; Toba, M.; Choo, Y. M.; *J. Am. Oil Chem. Soc.* **1992**, *69*, 410.
- Pouilloux, Y.; Autin, F.; Barrault, J.; *Catal. Today* **2000**, *63*, 87.
- Mazzieri, V. A.; Coloma-Pascual, F.; Arcoya, A.; L'Argentière, P. C.; Fígoli, N. S.; *Appl. Surf. Sci.* **2003**, *210*, 222.
- Bossi, A.; Garbassi, F.; Orlandi, A.; Petrini, G.; Zanderighi, L.; *Studies in Surface Science and Catalysis* **1979**, *3*, 405.
- Burch, R.; *J. Catal.* **1981**, *71*, 348.
- Mazzieri, V. A.; Grau, J. M.; Yori, J. C.; Vera, C. R.; Pieck, C. L.; *Appl. Catal. A* **2009**, *354*, 161.
- Deshpande, V. M.; Ramnarayan, K.; Narasimhan, C. S.; *J. Catal.* **1990**, *121*, 174.