TVER TECHNICAL UNIVERSITY

Investigation of the effect of solvents to obtain fatty alcohols

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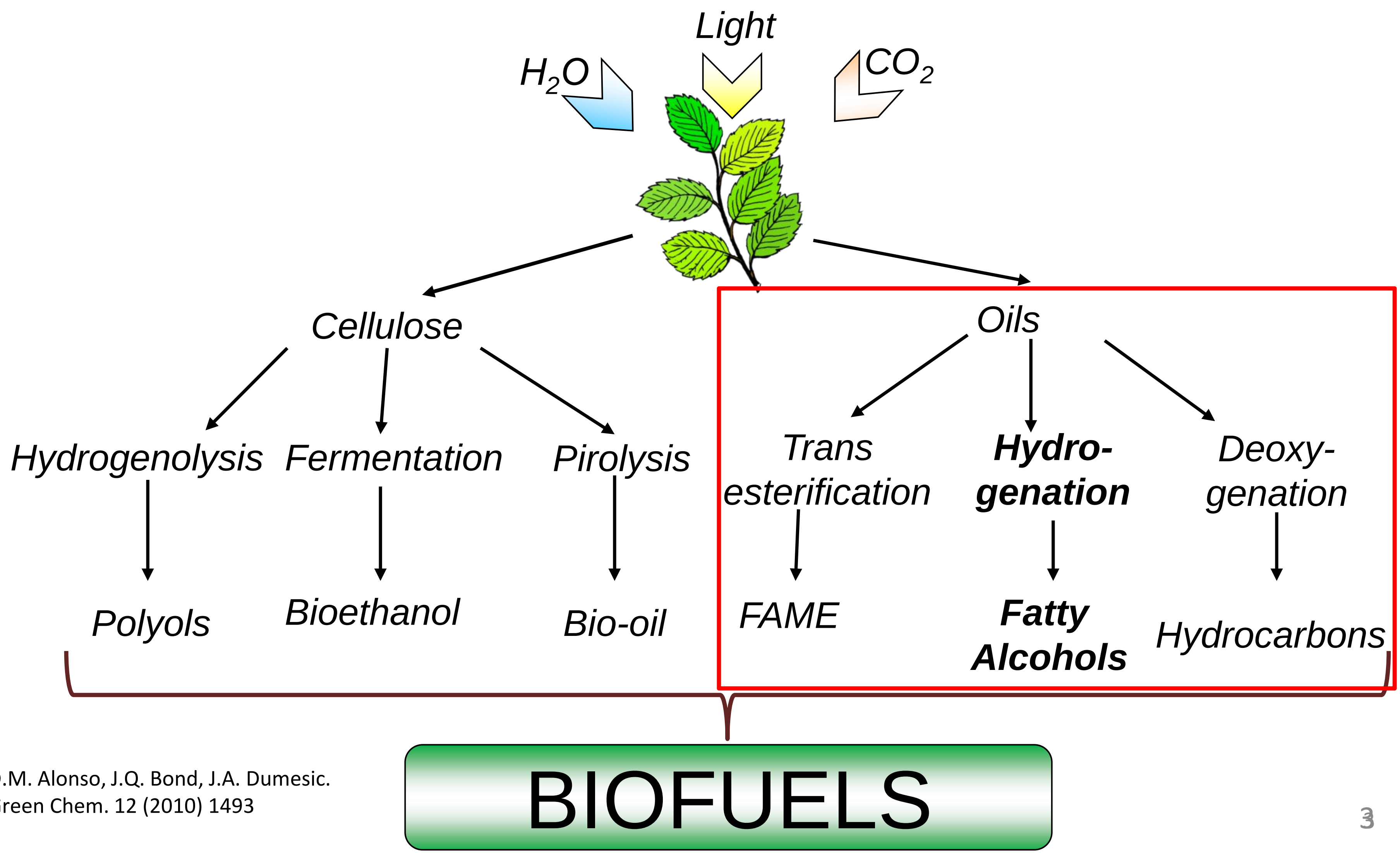
Fatty Alcohols

are widely used as

- ✓ Detergents & Cleaners
- ✓ Cosmetics & Pharmaceuticals
- ✓ Flavour & Fragrances
- ✓ Lubricating Oil Additive
- ✓ Metal Working
- ✓ Textile & Leather Application
- ✓ Polymer Auxiliaries

Another Way to Use Fatty Alcohols



D.M. Alonso, J.Q. Bond, J.A. Dumesic.
Green Chem. 12 (2010) 1493

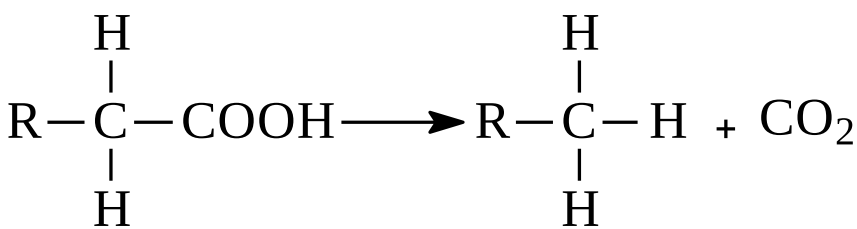
Problems with first generation of biodiesel

- ✓ Non refined oils need pretreatment to remove water and Free Fatty Acids.
- ✓ Prior esterification needed.
- ✓ Free Fatty Acids cause corrosion/soap/emulsions.
- ✓ Presence of water consumes catalysts & creates emulsions.
- ✓ Major problems in the biodiesel - glycerol separation step.
- ✓ Not suitable for production of chemicals (propanediol, acrolein etc.) without major purification.
- ✓ Residual KOH in biodiesel creates excess ash content in the burned fuel/engine deposits/high abrasive wear on the pistons and cylinders.
- ✓ Low oxidative stability due to oxygen content and high iodine number.

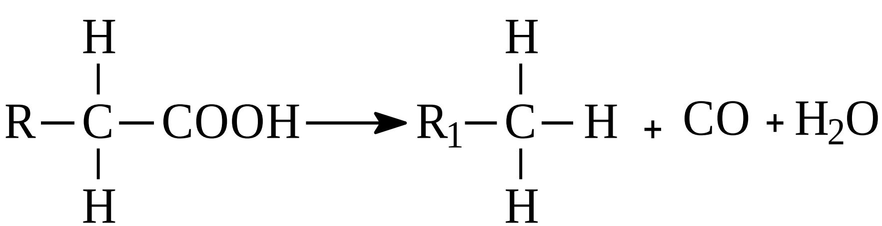
Ways to produce 2nd generation of biodiesel

Without hydrogen

Decarboxylation

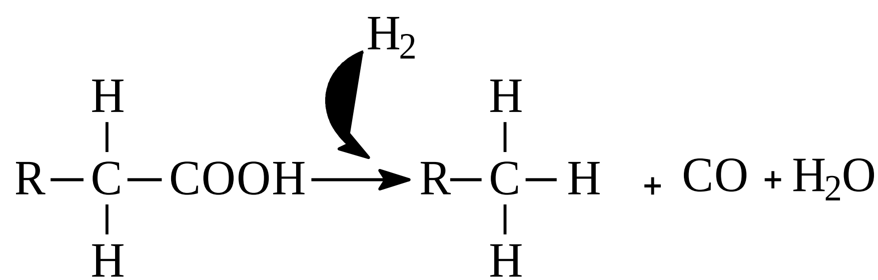


Decarbonylation

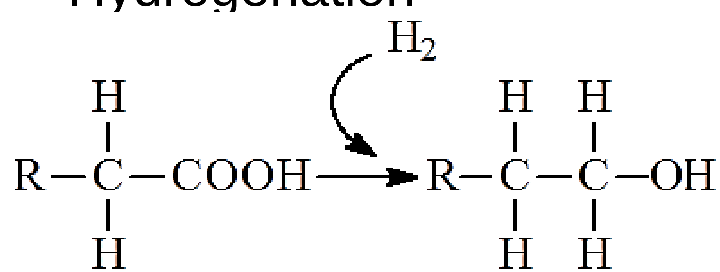


With hydrogen

Hydrodeoxygenation



Hydrogenation



D.M. Alonso, J.Q. Bond, J.A. Dumesic. Green Chem. 12 (2010) 1493
M. Snare, I. Kubickova, P. Maki-Arvela, K. Eranen, D.Yu. Murzin. Ind. Eng. Chem. Res. 16 (2006) 45

EXPERIMENTAL

Parr Series 5000 Multiple Reactor System

GC-2010 chromatograph and GCMS-QP2010S mass spectrometer

Materials

Substrate:

- ✓ stearic acid

Solvents:

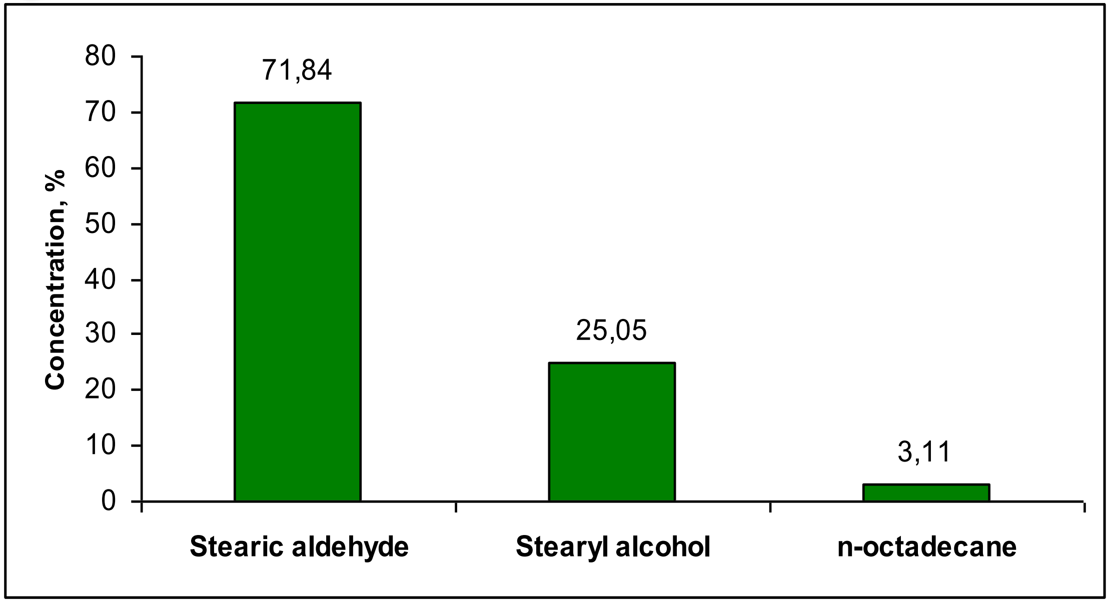
- ✓ hexane,
- ✓ cyclogexane,
- ✓ toluene,
- ✓ dodecane

Catalyst:

- ✓ 1%-Pd/HPS(MN-270)

Temperature – 150 °C,
Hydrogen pressure – 3 MPa,
Catalyst mass – 0.1 g,
Stearic acid concentration – 1 mol/L.

NON-CATALYTIC HYDROGENATION

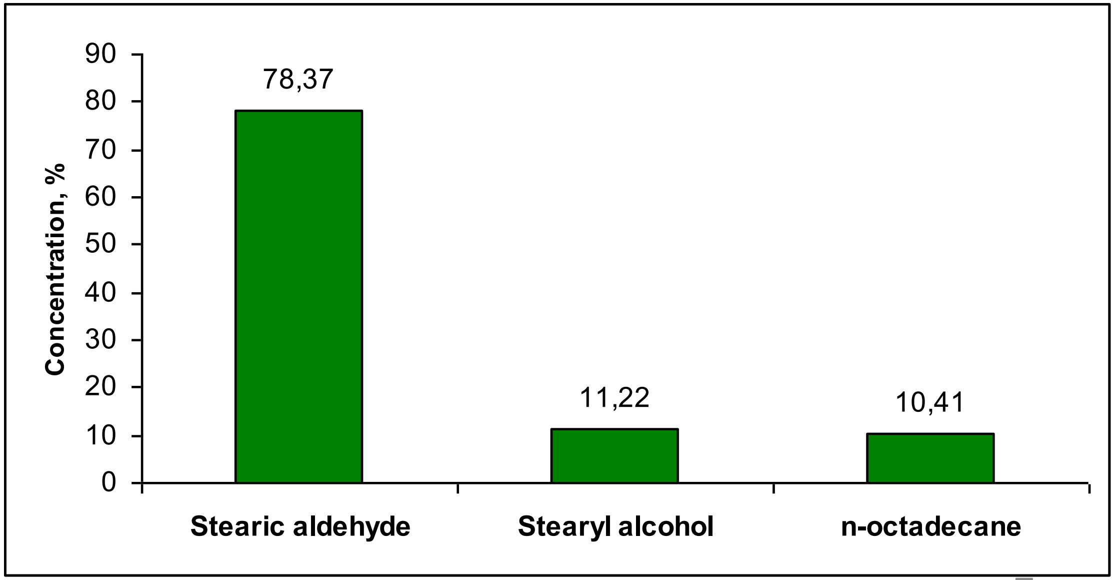


Hexane

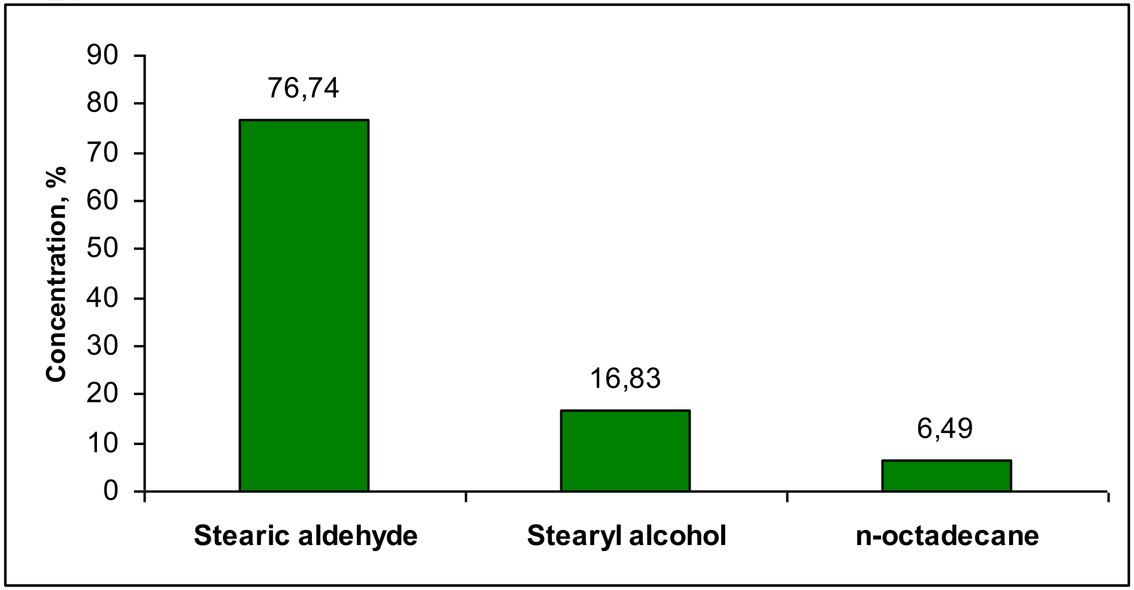
Stearic acid conversion 100%
Selectivity regarding
stearyl alcohol 25,1%

Cyclohexane

Stearic acid conversion 100%
Selectivity regarding
stearyl alcohol 11,2%



NON-CATALYTIC HYDROGENATION

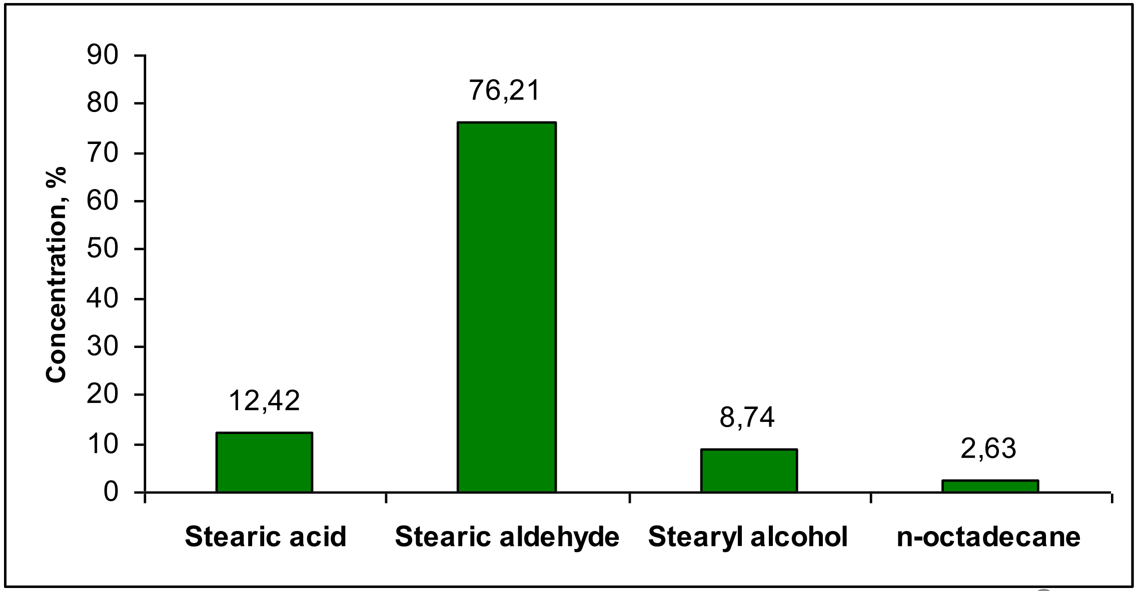


Toluene

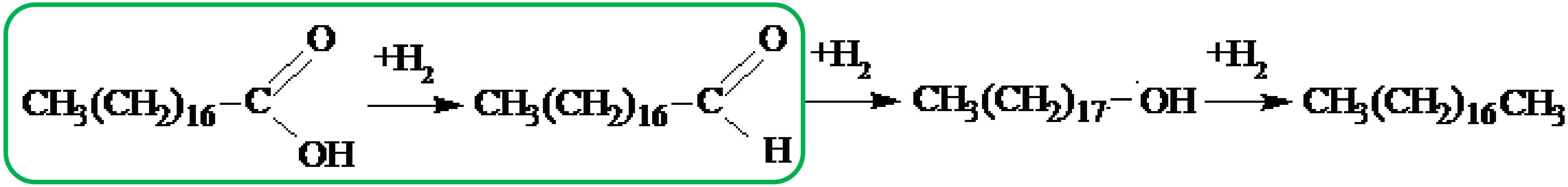
Stearic acid conversion 100%
Selectivity regarding
stearyl alcohol 16,8%

Dodecane

Stearic acid conversion 87,6%
Selectivity regarding
stearyl alcohol 8,7%

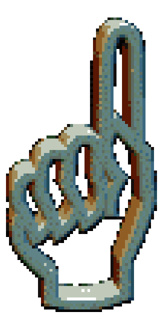


NON-CATALYTIC HYDROGENATION

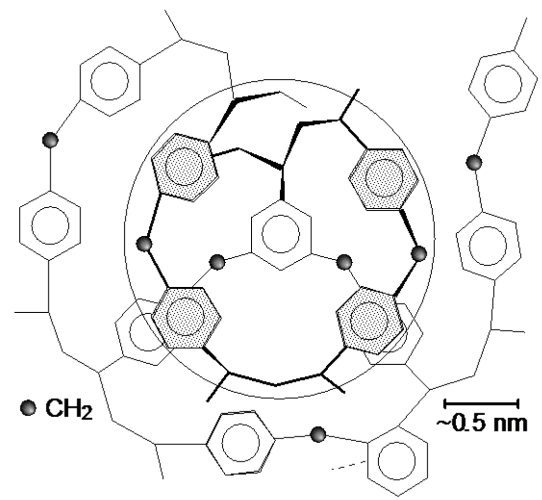


- Since the reaction was carried out without catalyst the main product was found to be stearic aldehyde due to a partial reduction of carboxylic group of stearic acid.
- The lower conversion of substrate was in the case of using n-dodecane that can be caused by its higher viscosity compared to other solvents.
- The use of cyclohexane provides lower selectivity regarding to stearyl alcohol and higher formation of hydrocarbon.
- The use of hexane provides highest selectivity regarding to stearyl alcohol.
- To increase stearyl alcohol yield we decided to use the catalyst which showed a good efficiency in hydrogenation reactions.

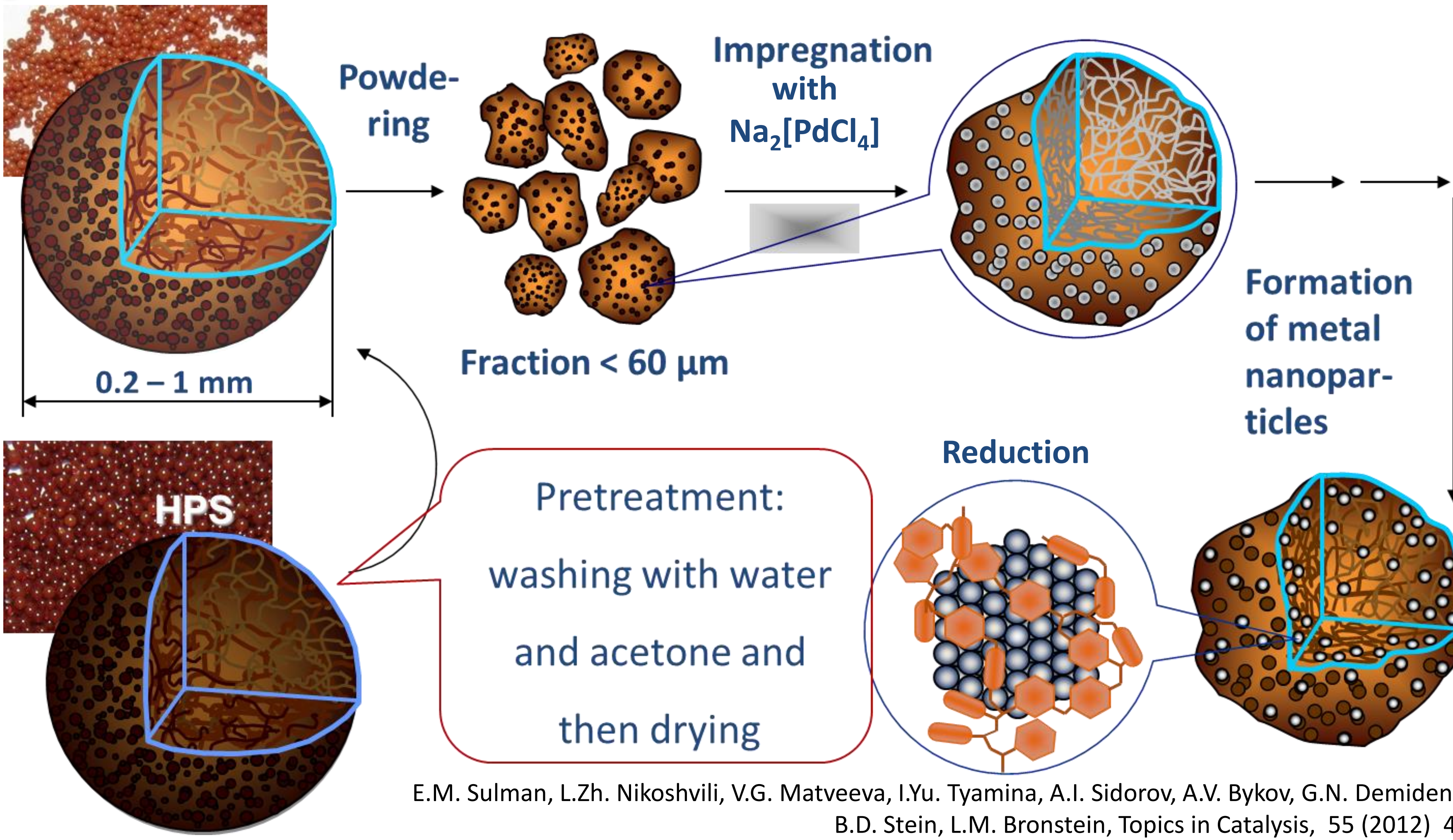
The use of hypercrosslinked polystyrene (HPS) as catalytic support allows:



- Stabilizing active metal phase
- Controlling the size of metal-containing nanoparticles



CATALYST SYNTHESIS



1%-Pd/HPS(MN-270)

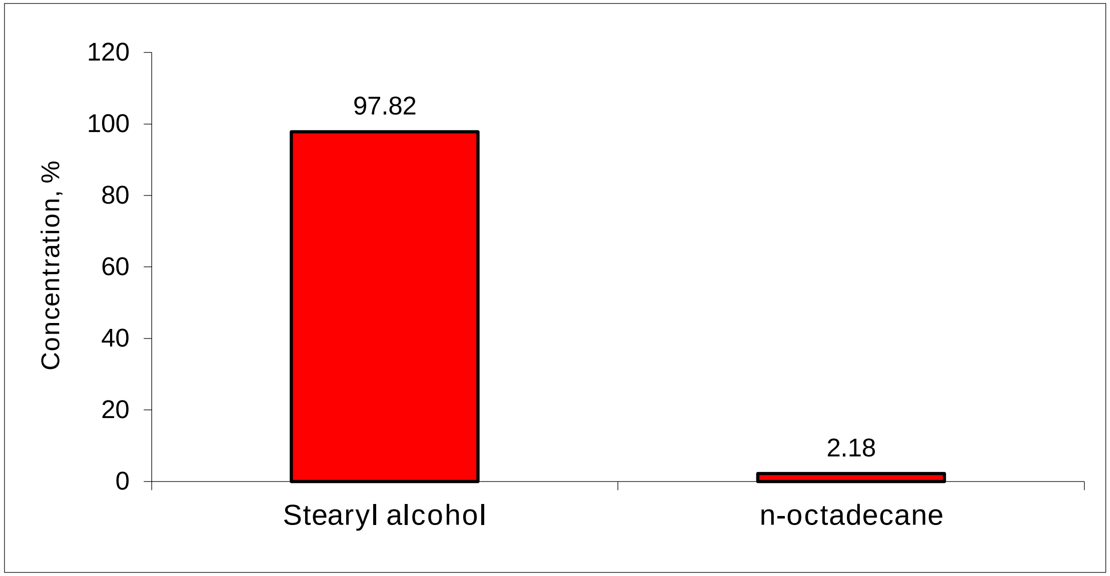
E.M. Sulman, L.Zh. Nikoshvili, V.G. Matveeva, I.Yu. Tyamina, A.I. Sidorov, A.V. Bykov, G.N. Demidenko, B.D. Stein, L.M. Bronstein, Topics in Catalysis, 55 (2012) 492

V.Y. Doluda, I.B. Tsvetkova, A.V. Bykov, V.G. Matveeva, A.I. Sidorov, M.G. Sulman, P.M. Valetsky, B.D. Stein, E.M. Sulman, L.M. Bronstein, Green Processing and Synthesis, 2 (2013) 25

V.N. Sapunov, M.Ye. Grigoryev, E.M. Sulman, M.B. Konyaeva, V.G. Matveeva, J. Phys. Chem. A, 117 (2013) 4073

V.Yu. Doluda, E.M. Sulman, V.G. Matveeva, M.G. Sulman, A.V. Bykov, N.V. Lakina, A.I. Sidorov, P.M. Valetsky, L.M. Bronstein, Topics in Catalysis, 56 (2013) 688

CATALYTIC HYDROGENATION

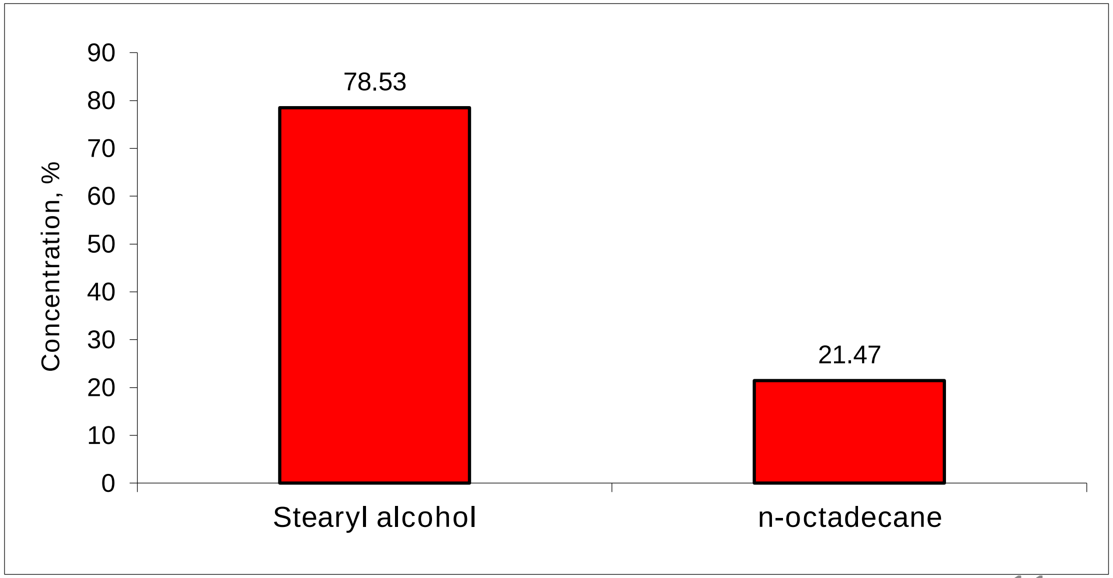


Hexane

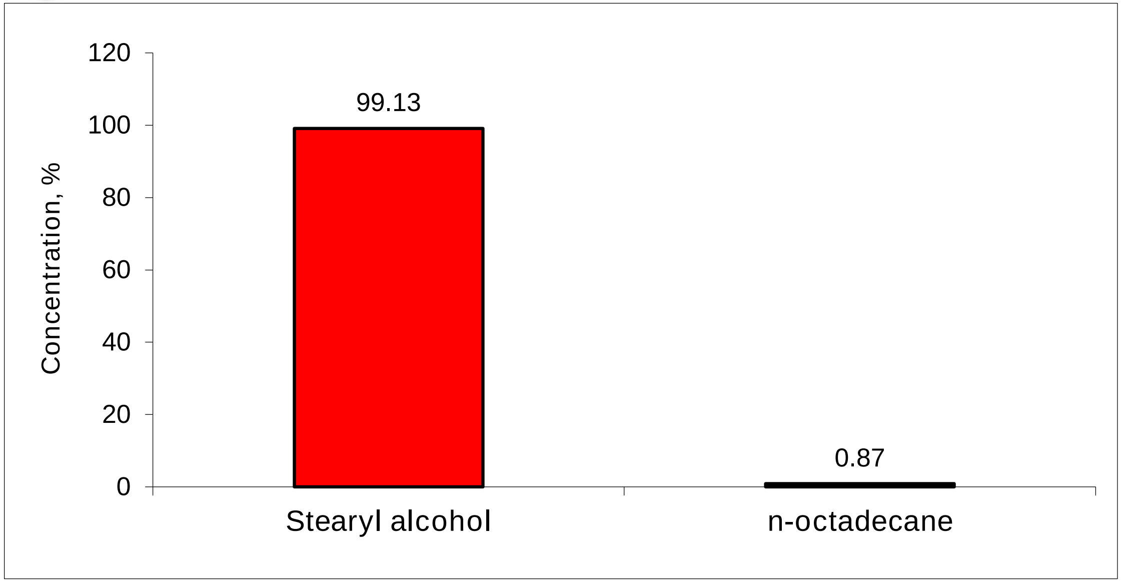
Stearic acid conversion 100%
Selectivity regarding
stearyl alcohol 97,8%

Cyclohexane

Stearic acid conversion 100%
Selectivity regarding
stearyl alcohol 78,5%



CATALYTIC HYDROGENATION

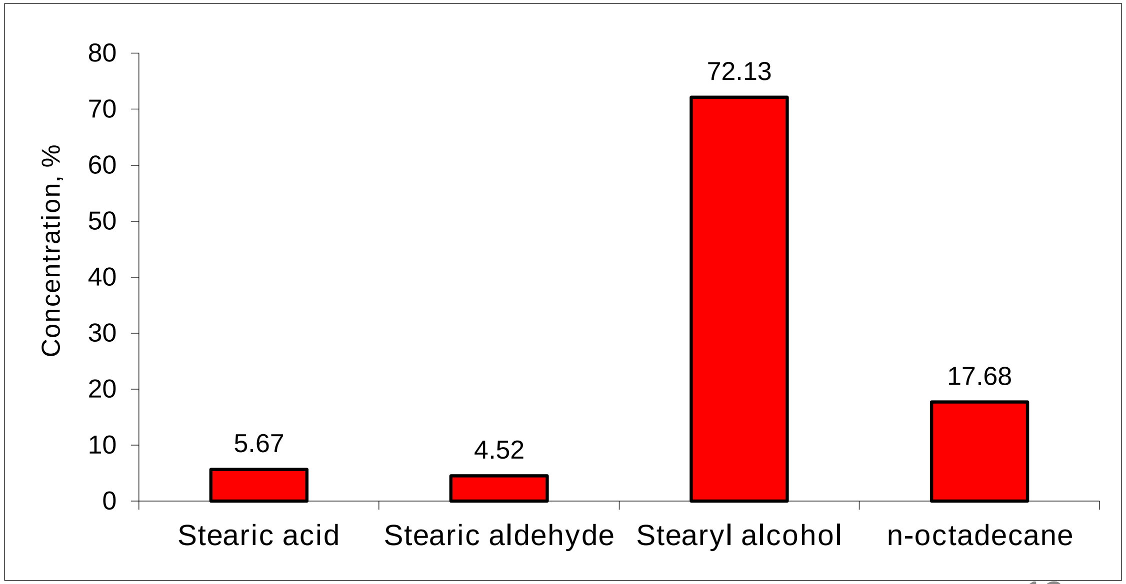


Toluene

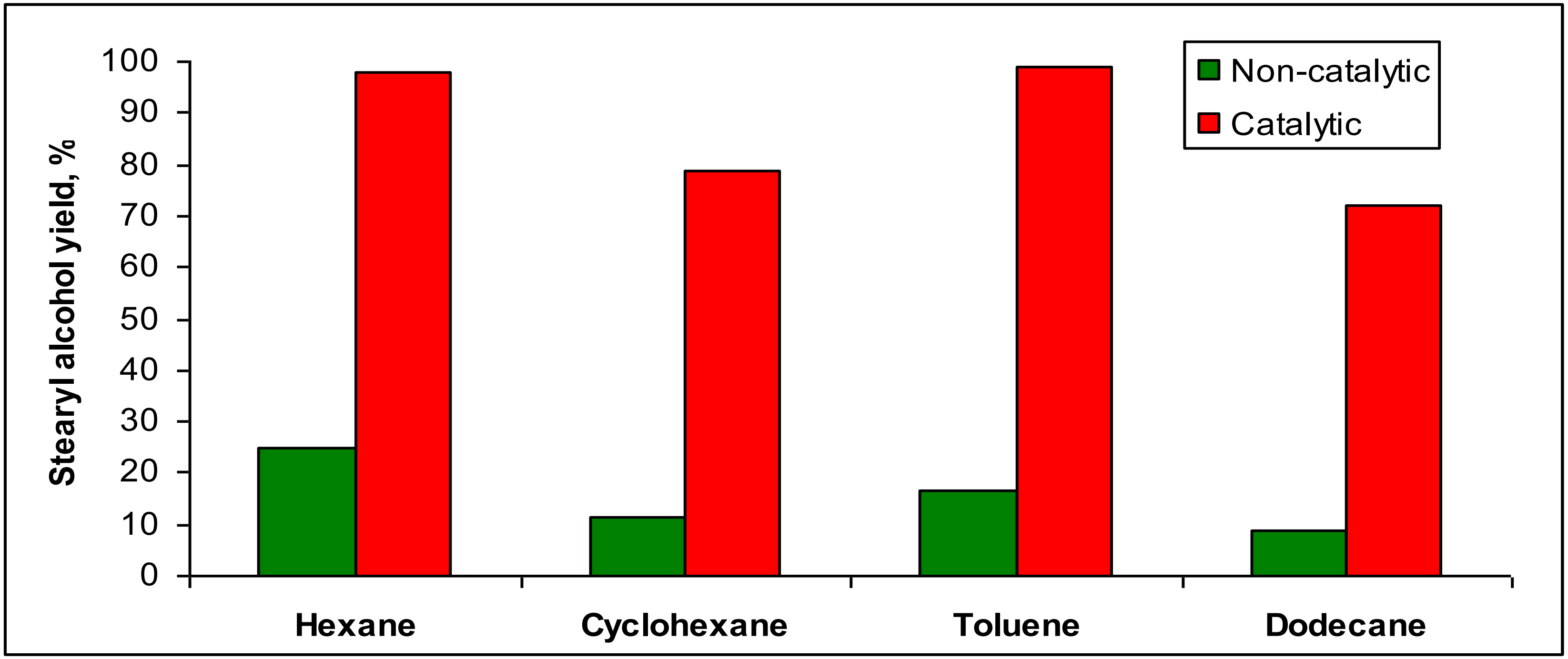
Stearic acid conversion 100%
Selectivity regarding
stearyl alcohol 99,1%

Dodecane

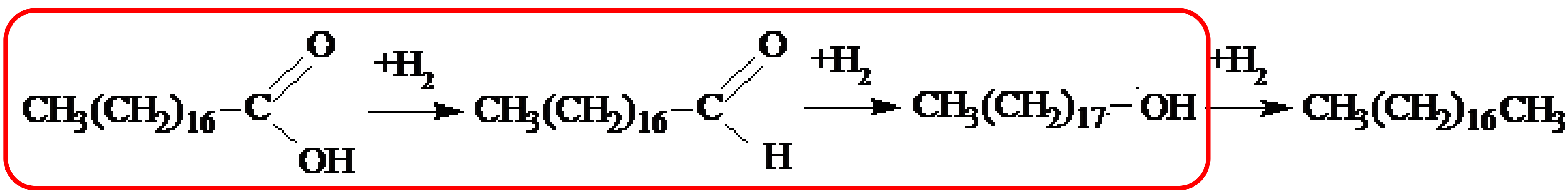
Stearic acid conversion 94%
Selectivity regarding
stearyl alcohol 72,1%



STEARYL ALCOHOL YIELD



The presence of catalyst increases the rate of stearyl alcohol formation and thus its yield more than by 4 times. The use of toluene and hexane as a solvent allows obtaining target product with the yield approximately in 1,2 times higher compared to cyclohexane and dodecane.



CATALYST CHARACTERIZATION

Size of palladium nanoparticles

Transmission electron microscopy

Surface composition, metal state

X-Ray photoelectron spectroscopy

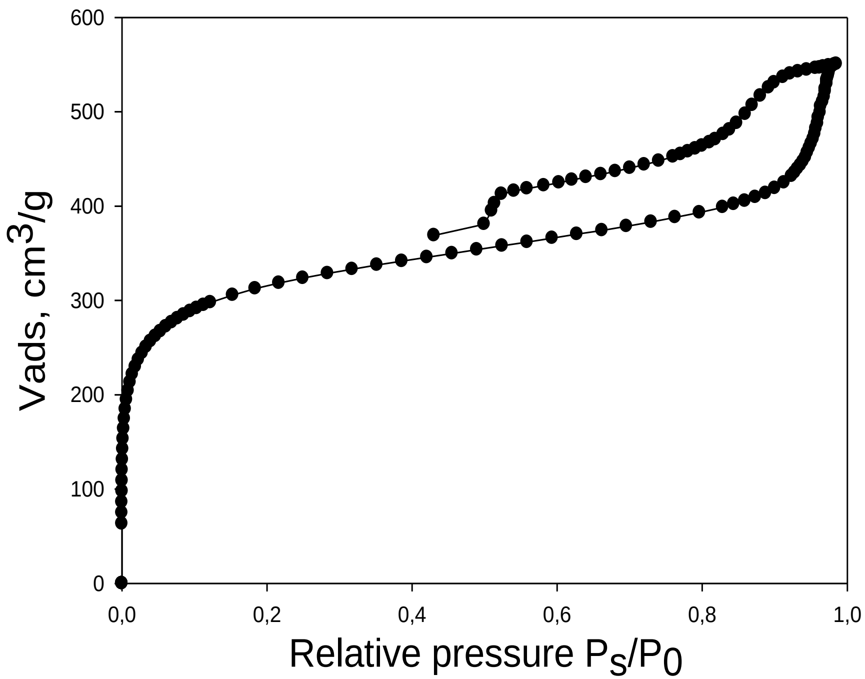
Surface area, pore size

Low-temperature nitrogen physisorption

Polymer thermal stability

Thermo-gravimetric analysis

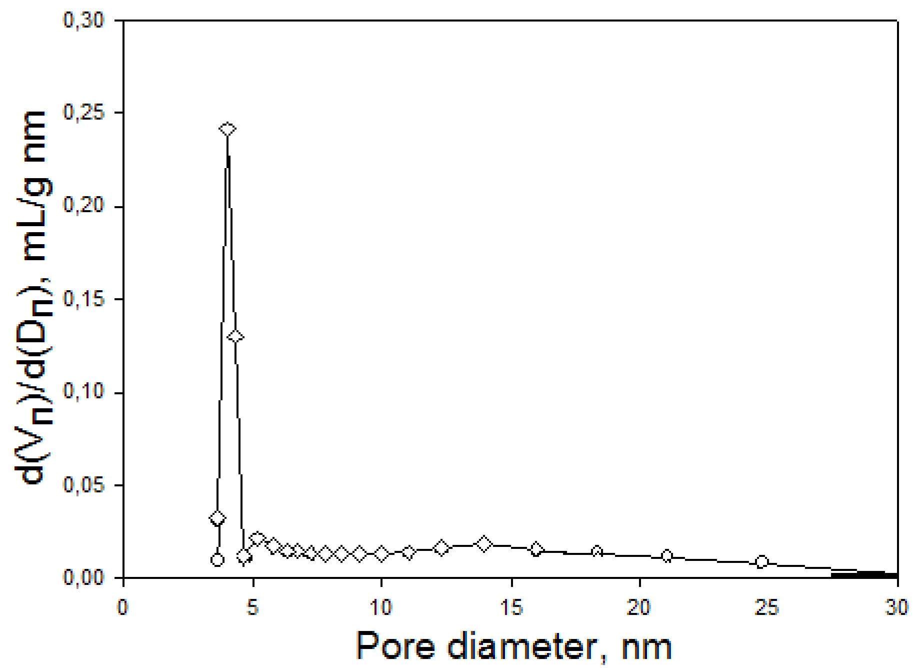
LOW TEMPERATURE NITROGEN PHYSISORPTION



Mesoporous material with narrow slot-like pores

Surface area – 1200 m^2/g

Micropore surface area – 900 m^2/g

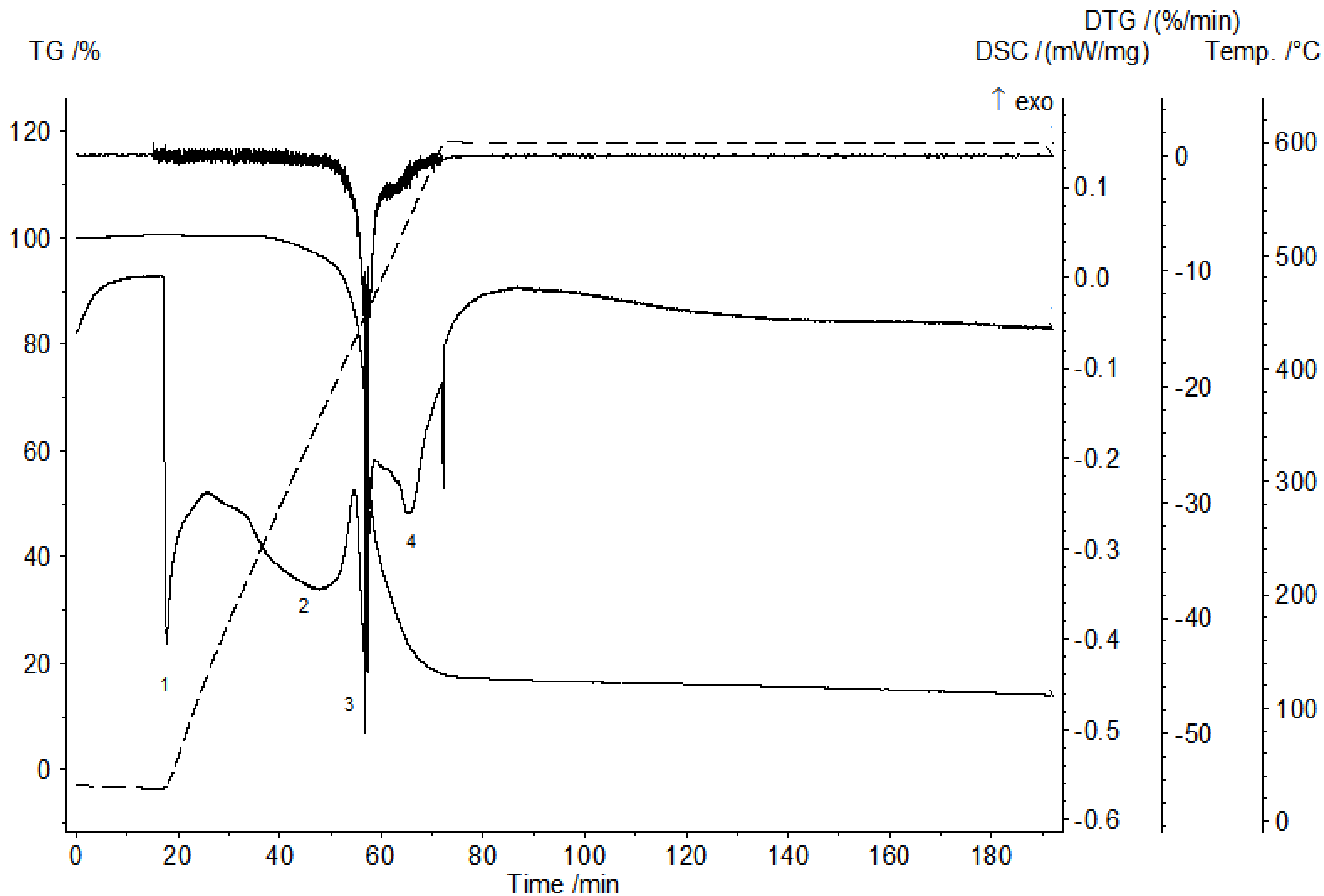


Mean pore diameter – 4,5 nm

The presence of pores with size 10-20 nm

✓ 1%-Pd/HPS(MN-270)

THERMOGRAVIMETRIC ANALYSIS

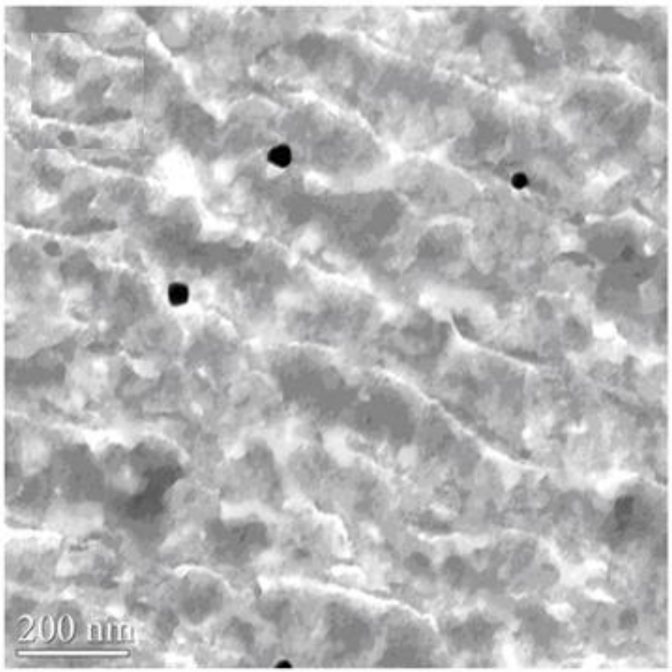


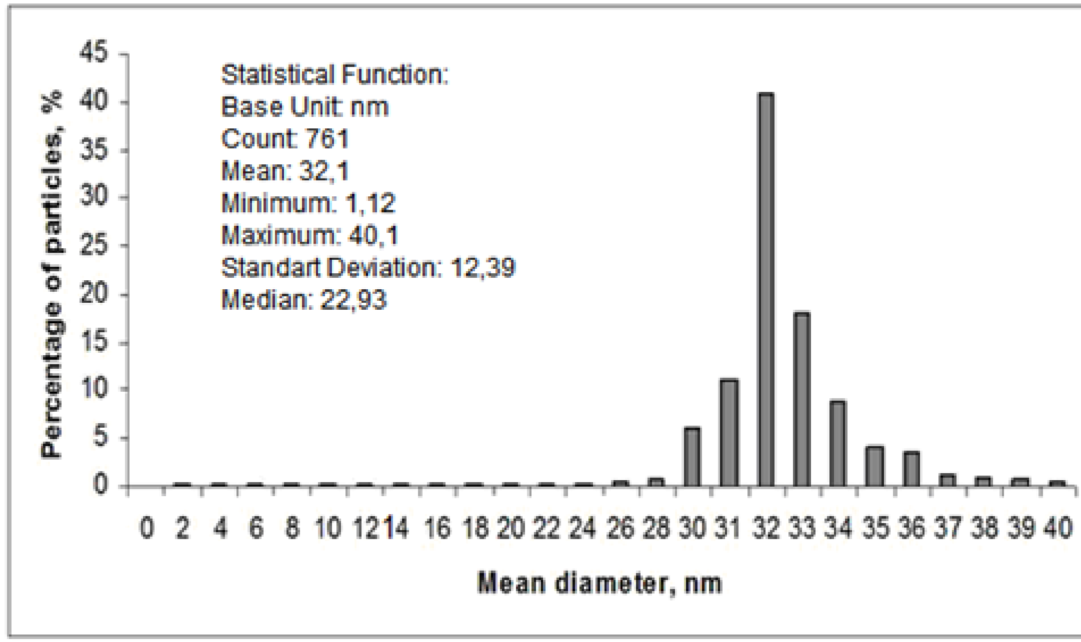
Thermodestruction of polymeric matrix takes place at 450°C.

✓ 1%-Pd/HPS(MN-270)

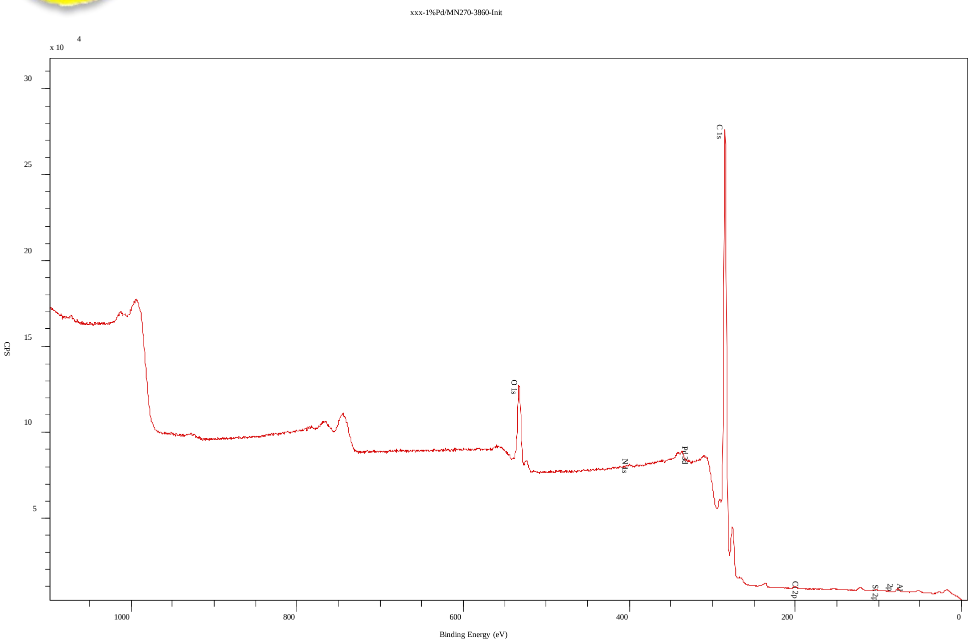
Pd PARTICLE SIZE

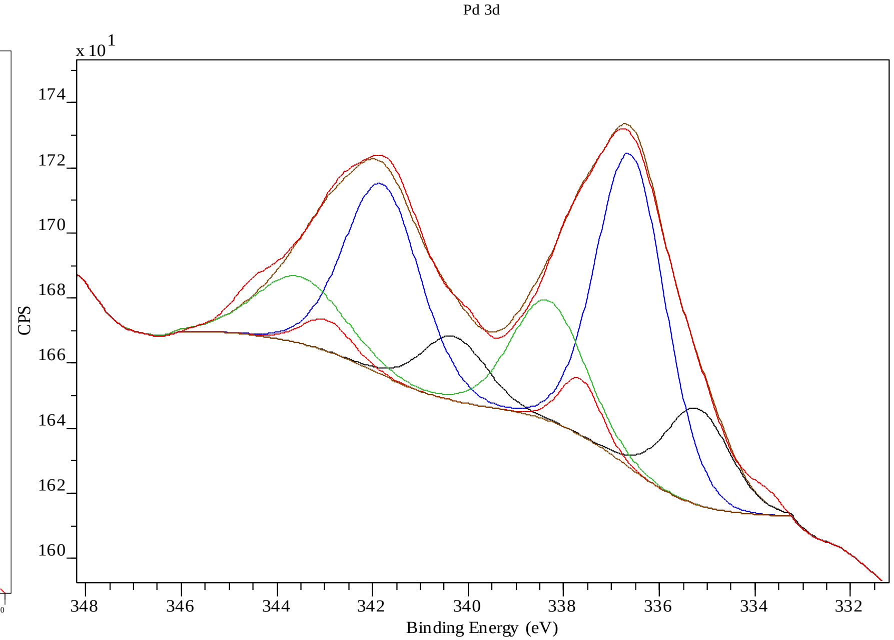
TEM





X-RAY PHOTOELECTRON SPECTROSCOPY



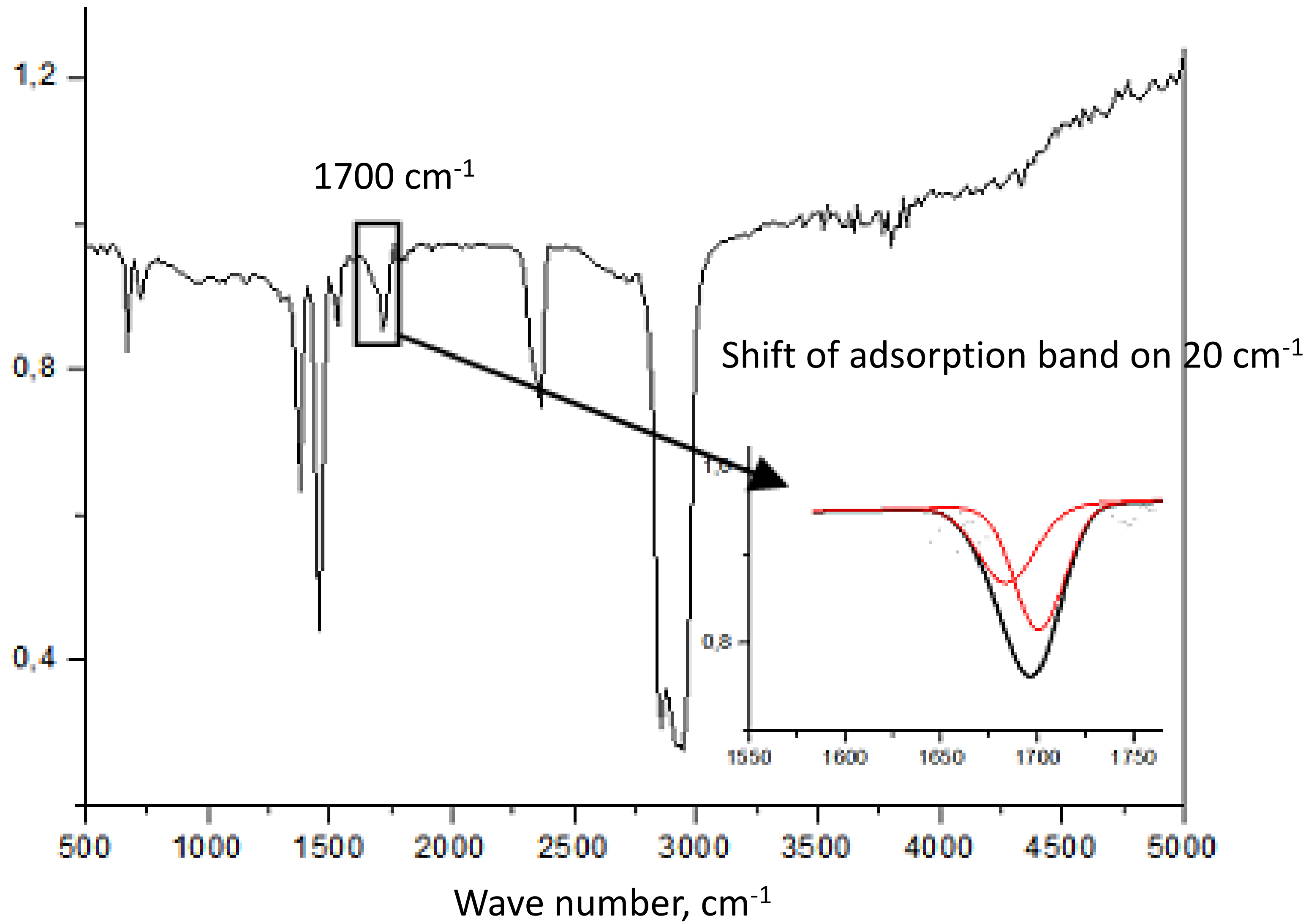


Models of palladium $3d_{5/2}$–sublevel

E_b (Pd $3d_{5/2}$), eV	E_b^* (Pd $3d_{5/2}$), eV	Pd state
336.6 335.5	336.5–336.8 335.1	Pd_n $(4<n<7)$ Pd(0)

T. Wu, W.E. Kaden, W.A. Kunkel, S.L. Anderson. Surface Science. 603 (2009) 2764-2770
S. Penner, at all. J. Phys. Chem. B. 110 (2006) 24577-24584

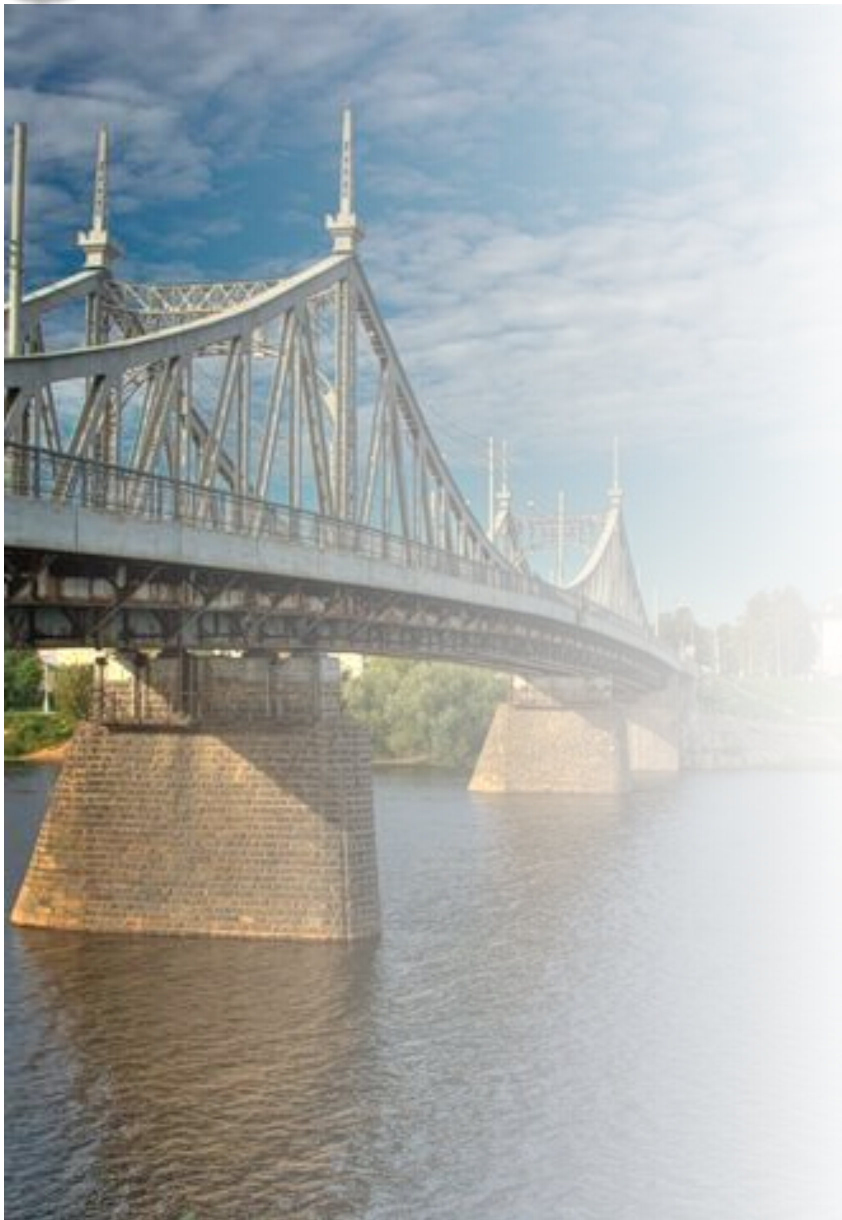
FTIR SPECTROSCOPY



CONCLUSIONS

Basing on the experiments there was found that:

- ✓ Stearic acid hydrogenation reaction in hexane and toluene medium allowed obtaining stearyl alcohol with the yield 98 and 99% relatively at 100% substrate conversion.
- ✓ The presence of catalyst increases the rate of stearyl alcohol formation and thus its yield more than by 4 times.
- ✓ The analysis of the catalyst showed that the active sites are presented by Pd(0) atomic clusters.
- ✓ Hydrogenation reaction processes by the interaction of substrate molecules adsorbed on organometalic center with hydrogen atoms dissociated on metallic active site on the surface of the catalyst and the effect of the solvent consists in the transport of stearic acid molecules to the catalyst active sites.



Acknowledgements

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Thank you very much for your kind attention!