

Pt-Containing Catalysts for Primary Biomass Products Conversion into Hydrocarbons

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Development of alternative approaches to fuel components and basic organic synthesis precursors producing based on biomass treatment products is important objective for ecology and chemistry. In the present work a number of original Pt-Sn containing catalysts were used for ethanol and rapeseed oil conversion. The peculiarities of used catalysts are usage of heterometallic precursors that possesses metal-metal bonds. Such kind of catalysts precursors allow obtaining more active and selective catalysts then ones based on a mixture of monometallic Pt and Sn precursors.

Catalyst with molar ratio of Pt:Sn equal to 1:5 was the most prospective for ethanol conversion into alkanes and olefins C₃-C₈. Shown that over Pt-Sn containing catalysts rapeseed oil converts into alkanes or olefins C₃-C₁₈. The highest selectivity close to 100 % during rapeseed oil conversion into hydrocarbons C₃-C₁₈ was found to be over Pd-Sn/Al₂O₃ catalyst with Pt:Sn molar ratio equal to 1:5.

Structural peculiarities of catalysts were characterized with X-ray diffraction and XAS technique. Relations between Pt clusters structure and its catalytic properties were determined.

1. Introduction

Nowadays a significant interest has been concentrated on effective approaches related to renewable biomass conversion into fuels. Ethanol produced via the fermentation of biomass (Hasheminejad et al., 2011) can be incorporated into gasoline either directly or after chemical/catalytic conversion into more effective additives. It can be used as a fuel for vehicles (John et al., 2011). However, there are some obstacles to the wide application of alcohol-based biofuel. Using the pure bioethanol is not possible without changing the overall engine design and, accordingly, without changing the entire production line. The fuel efficiencies for hybrid cars using the E85 mixture (85 % bioethanol, 15 % gasoline) are only 75 % those of standard cars. Converting of bioethanol into the common gasoline components (C₃+ hydrocarbons) is the most promising way of its application in the transport industry.

Development of motor fuel production processes on the basis of promising types of plant oils is being a subject of intensive research nowadays (Demirbas, 2008). Well-known the process of oils conversion towards aromatics over zeolite containing catalysts modified with Pd and Zn (Chistyakov et. al., 2013), Ni-Mo or Ni-W (Mikulec et. al., 2009) and Co (Kovács et.al., 2010). But due to aromatics containing reduction in modern gasoline fuels this route loses its perspective.

The investigations focus on the production of first generation biodiesel, which is methyl or ethyl esters of the fatty acids present in vegetable oils. The transesterification process most effectively proceeds in the presence

of homogeneous catalysts and, as such, is less economical because of the very costly steps of catalyst recovery from the product mixture and its utilization. Another significant disadvantage of this technology is the problem of utilization of significant amounts of the byproduct glycerol containing esterifying agents (methanol, ethanol) as impurities. The problem of isolation of glycerol free of the impurities of the esterifying alcohols can be solved with the use of a three stage process, according to which oils are saponified at the first stage to yield watered glycerol and salts of the corresponding fatty acids, after which the acids are converted into the H-form and subjected to hydrogenation (Mäki-Arvela et al., 2011).

In our previous works was found that ethanol (Tsodikov et al., 2014) and rapeseed oil (Chistyakov et al., 2013) could be converted into a number of fuel hydrocarbons over industrial Pt/Al₂O₃ catalyst. Aim of the current work is ethanol and rapeseed oil high selective conversion into fuel components and monomers over Pt-Sn/Al₂O₃ catalysts with different molar ratio of active components. The peculiarities of used catalysts are usage of heterometallic precursors that possesses metal-metal bonds. Such kind of catalysts precursors allow obtaining more active and selective catalysts than ones based on a mixture of monometallic Pt and Sn precursors.

2. Materials and methods

For catalytic experiments original Pt-Sn containing catalysts were used supported on γ -Al₂O₃ modified with heterometallic precursors represented in Table 1. The peculiarity of heterometallic precursors is the presence of metal-metal bonds as shown in Figure 1 for (PPh₄)₃(Pt(SnCl₃)₅) precursor.

Table 1: List of studied catalysts

Designation	Pt, wt. %	Sn, wt. %	Precursor
1Pt-1Sn	0.4		(PPh ₄) ₃ Pt(SnCl ₃)
1Pt-3Sn	0.4	0.75	(PPh ₄) ₃ (Pt(SnCl ₃) ₃)
1Pt-5Sn	0.4	1.2	(PPh ₄) ₃ (Pt(SnCl ₃) ₅)
1Pt-5Sn separate	0.4	1.2	K ₂ PtCl ₄ + SnCl ₂
Sn	-	1.2	SnCl ₂

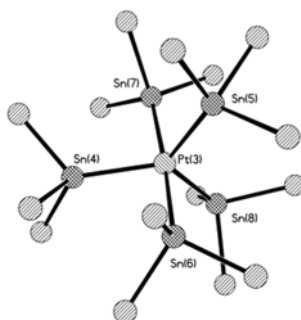


Figure 1: (PPh₄)₃(Pt(SnCl₃)₅) precursor structure

Both gaseous and liquid organic products in aqueous and organic phases were identified by GC-MS. Catalyst testing was performed in a PID Eng & Tech microcatalytic fixed-bed flow reactor unit, equipped with relevant instrumentation and control devices, under pressure 50 atm of H₂, temperature 400-480 °C, and substrates space velocity in the range of 1.2 h⁻¹. As a substrate rapeseed oil was used without preliminary purification. Fatty acids composition of used rapeseed oil was determined by methanol interesterification followed by GS-MS analysis. The results are represented in Table 2.

Table 2: Fatty acids composition of used rapeseed oil

elementary unit	number of C atoms	containing, wt. %
methyl stearate	16	4,79
methyl oleate	18	93,313
methyl gondoate	20	1,795
methyl erucate	22	0,102
Σ		100

The local structure and charge state of platinum were studied by XAFS spectroscopy. The XANES and EXAFS X-ray absorption spectra for two catalyst samples (initial and after experiment 1Pt-5Sn/Al₂O₃ catalyst) and standard materials (platinum foil and the oxide and chloride derivatives of Pt²⁺ and Pt⁴⁺) were measured at the Structural Materials Science station of the Kurchatov Center for Synchrotron Radiation and Nanotechnology. The spectra were measured in the transmission mode using two ionization chambers filled with argon. A monoblock monochromator with a Si(111) cut was used for the monochromatization of a synchrotron radiation beam. To prepare a sample, catalyst powder was pressed into a pellet 1.5 mm thick in an atmosphere of H₂ or Ar; the pellet was covered with a thin polymer film and transferred to the spectrometer under anaerobic conditions. For each particular sample, three to four independent measurements were performed to check the reproducibility of the results.

3. Results and discussion

Over Pt-Sn/Al₂O₃ catalysts under 400 °C, VHSV 1,2 h⁻¹ ethanol converts into alkanes and olefins C₃-C₈ fraction (Figure 2). As shown earlier (Tsodikov et.al., 2014) ethanol converts into alkanes C₃-C₁₀ fraction over Pt/Al₂O₃ catalyst under 330 °C. Over 1Pt-1Sn/Al₂O₃ catalyst ethanol mainly converts into methane and carbon oxides. Total yield of hydrocarbons C₃-C₈ did not exceed 16 wt.%. Over 1Pt-3Sn/Al₂O₃ catalyst aim fraction yield increased up to 23 wt.%. Among ethanol conversion products dominates oxygenates. Oxygenates fraction mainly consisted of diethyl ether, ethyl acetate, butyl acetate and ethyl butyl ether. Over 1Pt-5Sn/Al₂O₃ catalyst the maximum yield of hydrocarbons C₃-C₈ was obtained equal 50 wt.% calculated on passed carbon. Also aromatics were obtained with yield of 6 wt.%. The composition of obtained products is presented on Figure 3. Among hydrocarbon products olefins dominate with even number of carbon atoms in its carbon skeleton. C₁ products yield did not exceed 2.5 wt.%. It should be noted that monometallic catalyst Sn/Al₂O₃ is not active in ethanol conversion into hydrocarbons. Consequently Sn content in Pt containing catalyst led to significant changes in ethanol conversion into hydrocarbon fuel components and olefins.

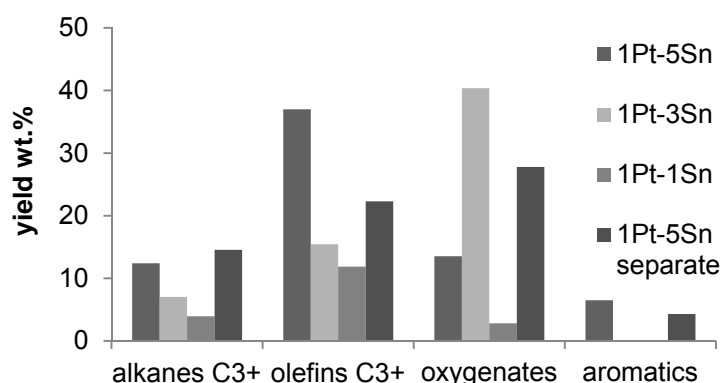


Figure 2: Ethanol conversion products over Pt-Sn-containing catalysts

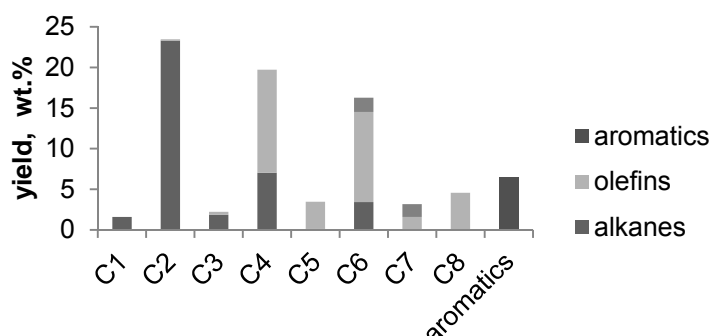


Figure 3: Composition of hydrocarbons obtained during ethanol conversion over 1Pt-5Sn/Al₂O₃ catalyst

Over Sn/Al₂O₃ catalyst under 400 °C, VHSV 1,2 h⁻¹ rapeseed oil converts into alkanes and olefins C₃-C₁₇ fraction and aromatics. As shown in Figure 4 among aliphatic products hydrocarbons C₄-C₈ dominates that

testify about intensive cracking of C-C bond of fatty acids fragments. Also considerable amount of aromatics was obtained. Its yield was 14 wt.%.

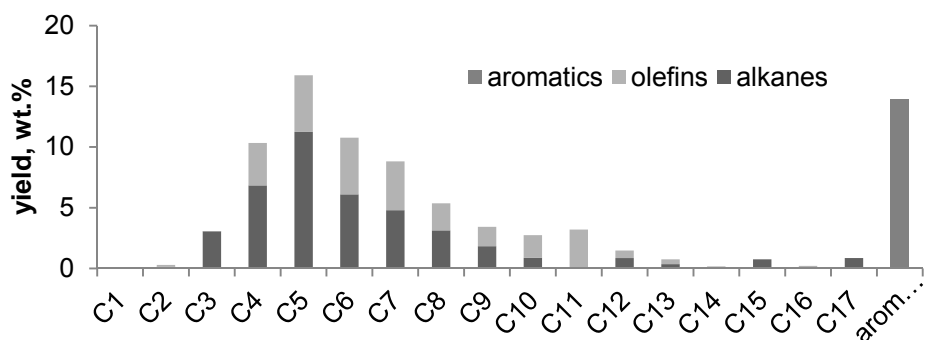


Figure 4: Composition of hydrocarbons obtained during rapeseed oil conversion over Sn/Al₂O₃ catalyst

Comparison of products composition of rapeseed oil conversion over Pt-Sn/Al₂O₃ catalysts showed that Sn content increasing led to intensification of C-O bonds hydrogenation and reduction of cracking and decarboxylation processes. Over 1Pt-1Sn/Al₂O₃ catalyst significant yield of alkane C17 was observed equal 30 wt.% (Figure 5). This result testifies about considerable intensive decarboxylation process. Over 1Pt-3Sn/Al₂O₃ decarboxylation process significantly decreasing. Alkane C17 yield was only 5 wt.%. However, cracking process becomes faster. Hydrocarbons C1-C4 yield reaches 25 wt.% (Figure 6). Also in the conversion products olefins were found that testifies the reduction of Pt hydrogenative function.

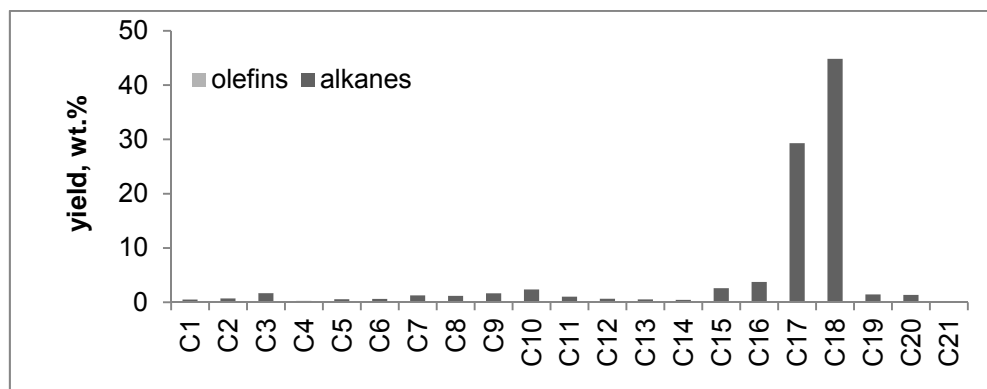


Figure 5: Composition of hydrocarbons obtained during rapeseed oil conversion over 1Pt-1Sn/Al₂O₃ catalyst

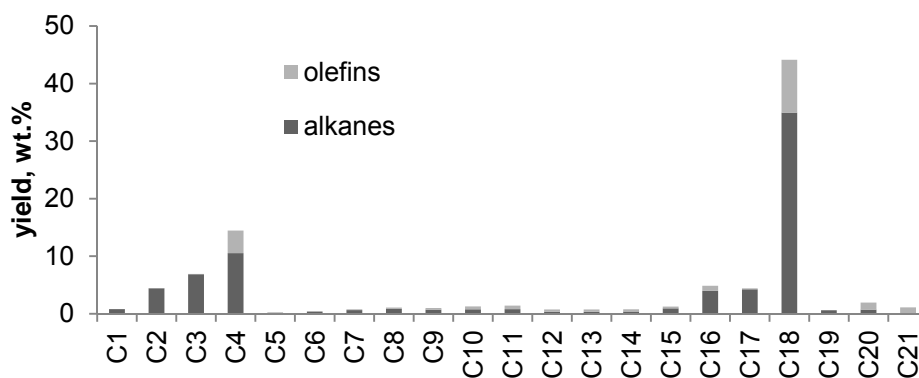


Figure 6: Composition of hydrocarbons obtained during rapeseed oil conversion over 1Pt-3Sn/Al₂O₃ catalyst

Over $1\text{Pt-5Sn/Al}_2\text{O}_3$ the highest yield of C_3+ hydrocarbons was reached equal 99,5 wt.% from which 84 wt.% was C_{18} fraction and 4.5 wt.% $\text{C}_3\text{-C}_4$ fraction (Figure 7). Among C_{18} fraction was found 23 wt.% of olefins of which 7-10 wt.% were linear alpha olefins. Obtained products may be used as $\text{C}_3\text{-C}_4$ fuel components extraction followed by disengagement of linear alpha olefins and the rest alkanes may be incorporated into high quality diesel fuel by hydroisomerization process. Should be noted that over $1\text{Pt-5Sn/Al}_2\text{O}_3$ catalyst take place mainly reduction acyclic fragments of initial rapeseed oil into alkanes or olefins. Products of cracking and decarboxylation processes did not exceed 8 wt.%. Moreover, total yield of C_1 products (methane, carbon oxides) observed lower then 0,1 wt.%.

Consequently, in the present work we found optimal catalyst composition over that all of passed carbon mass of initial oil could be converted into alkanes and olefins with dominant C_{18} and $\text{C}_3\text{-C}_4$ fractions. So selective process may be only when oxygen of initial oil converts in water.

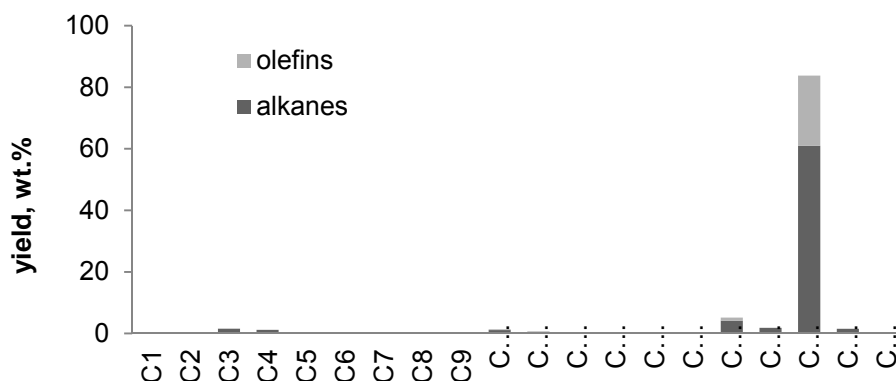


Figure 7: Composition of hydrocarbons obtained during rapeseed oil conversion over $1\text{Pt-5Sn/Al}_2\text{O}_3$ catalyst

Obtained XAS data (Figures 8, 9) showed that fine dispersion of Pt in initial and after experiment $1\text{Pt-5Sn/Al}_2\text{O}_3$ catalyst. In-depth quantitative analysis became more complicated due to absence of order in Pt envelope. In initial catalyst Pt has a wide range of near atoms (O, Cl, Pt) with considerable differences in interatomic distances and coordination numbers. After catalytic experiments Pt reduction into Pt^0 was observed but fine dispersion keep stable.

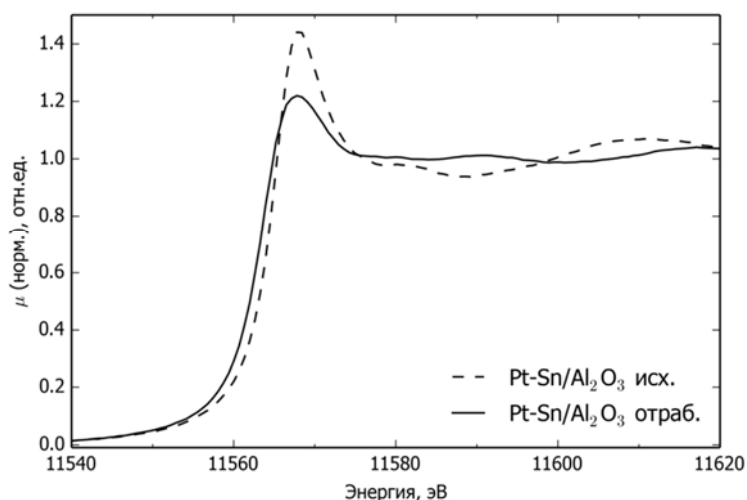


Figure 8: XANES spectra for $1\text{Pt-5Sn/Al}_2\text{O}_3$ catalyst

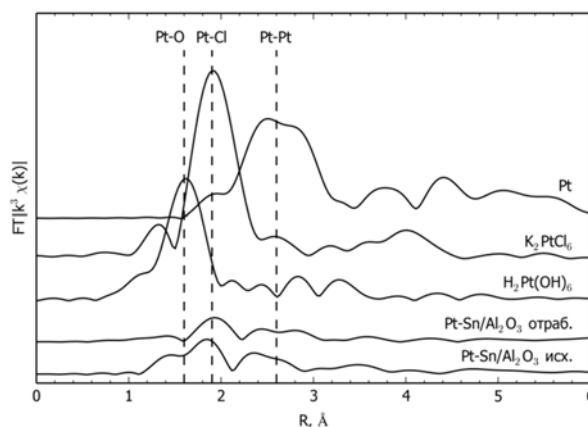


Figure 9: EXAFS spectra for 1Pt-5Sn/Al₂O₃ catalyst and a number of standards

4. Conclusions

Modification of Pt/Al₂O₃ catalyst with Sn lead to hydrogenating and cracking activity decreasing. That results in methane and carbon oxides formation suppression. Over Pt-Sn containing catalysts during ethanol or rapeseed oil conversion the C-O hydrogenating selectivity significantly increases. For effective ethanol conversion into hydrocarbons C₃-C₈ desired temperature rises up to 400 °C in comparison with 330 °C over Pt containing catalysts. The most prospect catalyst for ethanol and rapeseed oil conversion was found to be 1Pt-5Sn/Al₂O₃. During ethanol conversion aim fraction yield of alkanes and olefins C₃-C₈ was 50 wt.%. Also aromatic hydrocarbons were obtained with 6 wt.% yield. During rapeseed oil conversion under 400 °C a aliphatic hydrocarbons C₃-C₁₈ were obtained with total yield about 99% calculated on passed carbon. Noted that only two fractions of C₃ and C₁₈ hydrocarbons selectively formed. Obtained results allow minimizing loss of initial carbon weight due to cancelation of carboxyl fragment of fatty acids and glycerol conversion into methane and carbon oxides. Olefins C₁₈ were found in products composition. Its yield was 23 wt.% of which 7-10 wt.% were linear alpha olefins. This result made rapeseed oil conversion over 1Pt-5Sn/Al₂O₃ catalyst prospective for fuel components and monomers production.

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