CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216
DOI: 10.3303/CET1543142

Pt-Containing Catalysts for Primary Biomass Products Conversion into Hydrocarbons

Andrey V. Chistyakov[*a,b], Mark V. Tsodikov[a,b], Polina A. Zharova[a,b], Alexander E. Gekhman[b,c], Sergey S. Shapovalov[c], Alexandr A. Pasinskiy[c], Michele Corbetta[d], Flavio Manenti[d]

[a] Topchuev Institute of Petrochemical Synthesis, Leninskiy prospect, 29, Moscow, 119991, Russian Federation
[b] Moscow Institute of Physics and Technology, 9 Institutskiy per., Dolgoprudny, Moscow Region, 141700, Russian Federation
[c] Kurnakov Institute of general and inorganic chemistry RAS, Leninskiy prospect, 31, Moscow, 119991, Russian Federation
[d] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci, 32, 20133 Milano, Italy
chistyakov@ips.ac.ru

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 C_3-C_8. Shown that over Pt-Sn containing catalysts rapeseed oil converts into alkanes or olefins C_3-C_{18}. The highest selectivity close to 100 % during rapeseed oil conversion into hydrocarbons C_3-C_{18} was found to be over Pd-Sn/Al_2O_3 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

Please cite this article as: Chistyakov A., Tsodikov M., Zharova P., Gekhman A.E., Shapovalov S.S., Pasinskiyc A.E., Corbetta M., Manenti F., 2015, Pt-containing catalysts for primary biomass products conversion into hydrocarbons, Chemical Engineering Transactions, 43, 847-852 DOI: 10.3303/CET1543142

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/Al_2O_3 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 then 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-Al_2O_3 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 $(PPh_4)_3(Pt(SnCl_3)_5)$ precursor.

Table 1: List of studied catalysts

Designation	Pt, wt.%	Sn, wt.%	Precursor
1Pt-1Sn	0.4		$(PPh4)_3Pt(SnCl_3)$
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_2PtCl_4 + $SnCl_2$
Sn	-	1.2	$SnCl_2$

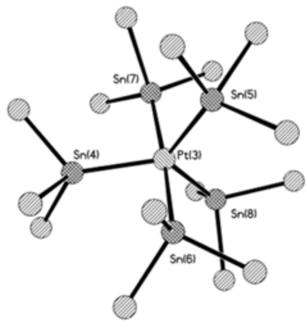

Figure 1: $(PPh_4)_3(Pt(SnCl_3)_5)$ precursor structure

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 H_2, 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/Al_2O_3 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 H_2 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/Al_2O_3 catalysts under 400 °C, VHSV 1,2 h^{-1} ethanol converts into alkanes and olefins C_3-C_8 fraction (Figure 2). As shown earlier (Tsodikov et.al., 2014) ethanol converts into alkanes C_3-C_{10} fraction over Pt/Al_2O_3 ctatlyst under 330 °C. Over 1Pt-1Sn/Al_2O_3 catalyst ethanol mainly converts into methane and carbon oxides. Total yield of hydrocarbons C3-C8 did not exceed 16 wt.%. Over1Pt-3Sn/Al_2O_3 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/Al_2O_3 catalyst the maximum yield of hydrocarbons C_3-C_8 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. C_1 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.

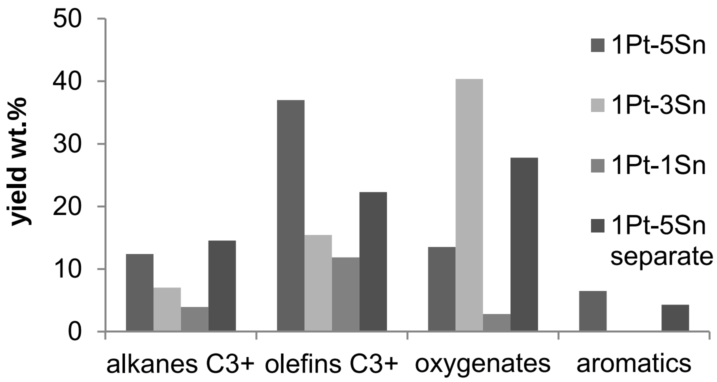

Figure 2: Ethanol conversion products over Pt-Sn-containing catalysts

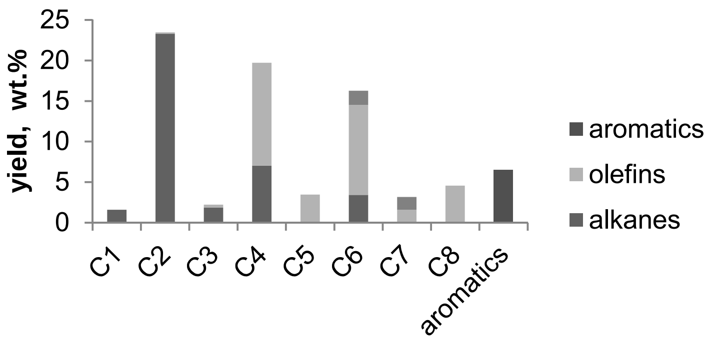

Figure 3: Composition of hydrocarbons obtained during ethanol conversion over 1Pt-5Sn/Al_2O_3 catalyst

Over Sn/Al_2O_3 catalyst under 400 °C, VHSV 1,2 h^{-1} rapeseed oil converts into alkanes and olefins C_3-C_{17} 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.%.

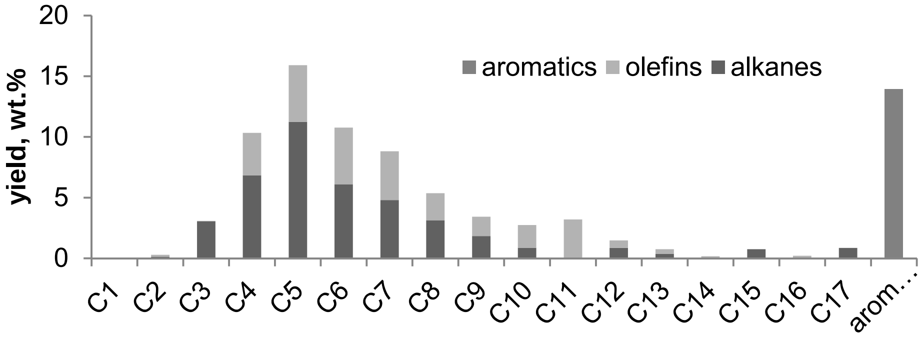

Figure 4: Composition of hydrocarbons obtained during rapeseed oil conversion over Sn/Al_2O_3 catalyst

Comparison of products composition of rapeseed oil conversion over Pt-Sn/Al_2O_3 catalysts showed that Sn content increasing led to intensification of C-O bonds hydrogenation and reduction of cracking and decarboxylation processes. Over 1Pt-1Sn/Al_2O_3 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 wasonly 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.

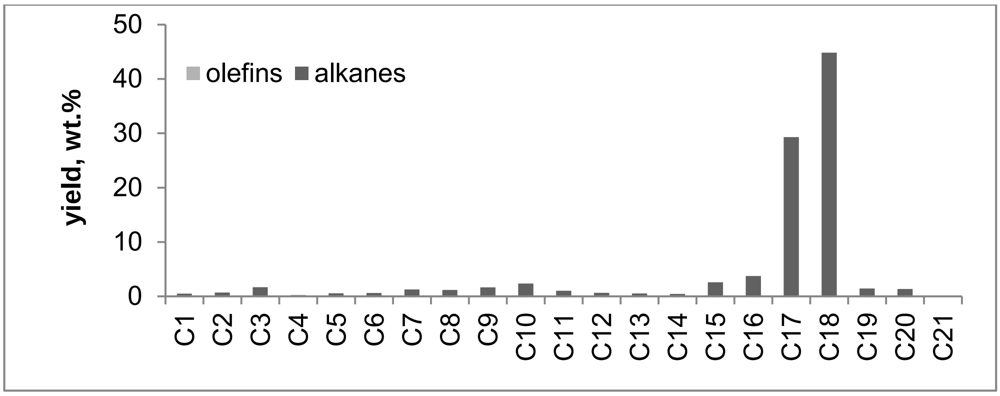

Figure 5: Composition of hydrocarbons obtained during rapeseed oil conversion over 1Pt-1Sn/Al_2O_3 catalyst

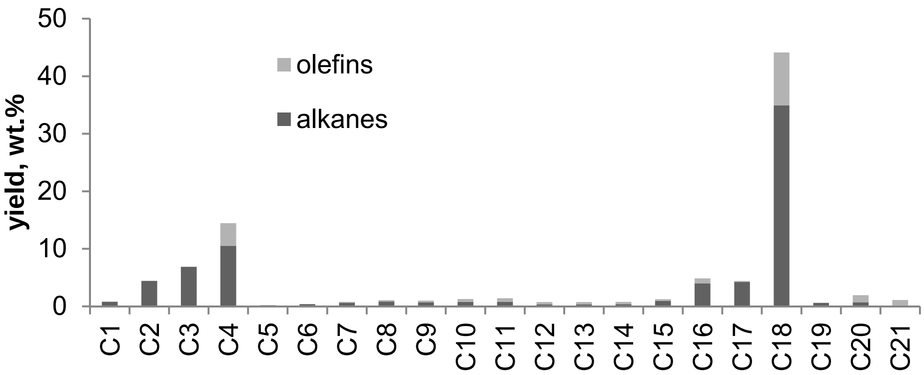

Figure 6: Composition of hydrocarbons obtained during rapeseed oil conversion over 1Pt-3Sn/Al_2O_3 catalyst

Over 1Pt-5Sn/Al_2O_3 the highest yield of C_{3+} hydrocarbons was reached equal 99,5 wt.% from which 84 wt.% was C18 fraction and 4.5 wt.% C3-C4 fraction (Figure 7). Among C18 fraction was found 23 wt.% of olefins of which 7-10 wt.% were linear alpha olefins. Obtained products may be used as C3-C4 fuel components extraction followed by disengagement of linear alpha olefins and the rest alkanes may be incorporated into high quality diesel fuel by hydroizomerization process. Should be noted that over 1Pt-5Sn/Al_2O_3 catalyst take place mainly reduction acyllic fragments of initial rapeseed oil into alkanes or olefins. Products of cracking and decarboxylation processes did not exceed 8 wt.%. Moreover, total yield of C1 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 C18 and C3-C4 fractions. So selective process may be only when oxygen of initial oil converts in water.

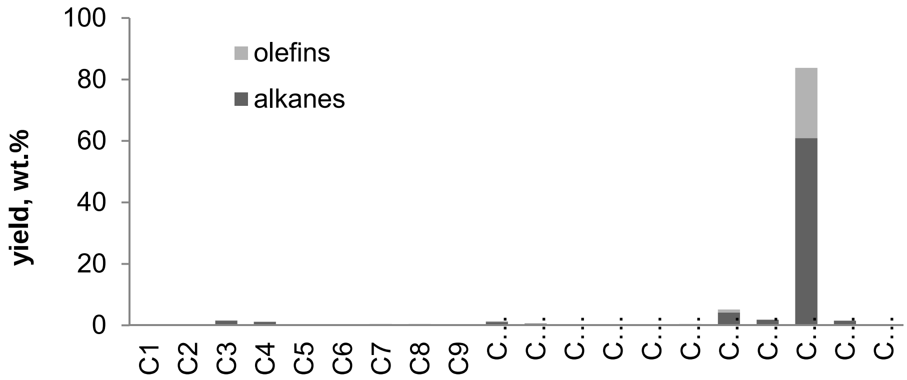

Figure 7: Composition of hydrocarbons obtained during rapeseed oil conversion over 1Pt-5Sn/Al_2O_3 catalyst

Obtained XAS data(Figures 8, 9) showed that fine dispersion of Pt in initial and after experiment 1Pt-5Sn/Al2O3 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.

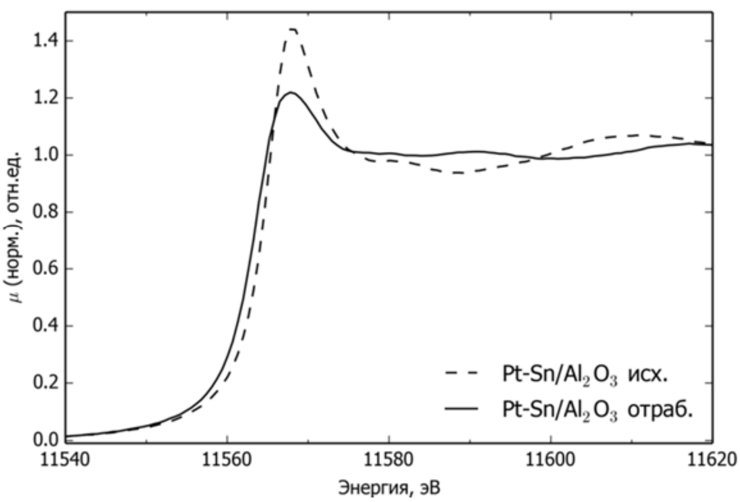

Figure 8: XANES spectra for 1Pt-5Sn/Al2O3 catalyst

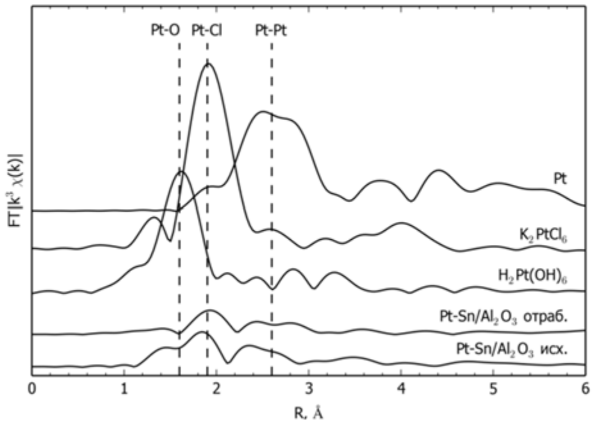

Figure 9: EXAFS spectra for 1Pt-5Sn/Al2O3 catalyst and a number of standards

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 C_3-C_8 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 conversionwas found to be 1Pt-5Sn/Al_2O_3. 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 C_3-C_{18} were obtained with total yield about 99% calculated on passed carbon. Noted that only two fractions of C_3 and C_{18} 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 C_{18} 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/Al_2O_3 catalyst prospective for fuel components and monomers production.

Acknowledgements

The current research made with financial support of The Ministry of education and science of the Russian Federation via Federal target program “Researches and developments on priority directions of scientific-technological complex of Russia for 2014-2020”, unique number RFMEFI57514X0052.

References

Hasheminejad M., Tabatabaei M., Mansourpanah Y., Mahdi Khatami far, Azita Javani, 2011, Upstream and downstream strategies to economize biodiesel production, Bioresources Technology, 102, 461-468

R.P. John, G.S. Anisha, K.M. Nampoothiri, A. Pandey, 2011, Micro and macroalgal biomass: a renewable source for bioethanol, Bioresources Technology, 102, 186-193

Demirbas A. 2008. Biodiesel: A realistic fuel alternative for diesel engines, Springer-Verlad London Ltd., London, United Kingdom

Mäki-Arvela P., Rozmyslowicz B., Lestari S., Simakova O., Eränen K., Salmi T., Murzin D.Yu., 2011, Catalytic Deoxygenation of Tall Oil Fatty Acid over Palladium Supported on Mesoporous Carbon, Energy and Fuels, 25, 2815-2825

Chistyakov A. V., Gubanov M. A., Tsodikov M. V., 2013, The Direct Conversion of Rapeseed Oil towards Hydrocarbons over Industrial Catalysts, Chemical Engineering Transactions, 32, 1093-1098

Mikulec J., Cvengros J., Joríková L., Banic M., Kleinová A., 2009, Diesel production technology from renewable sources – second generation biofuels, Chemical Engineering Transactions, 18, 475-480

Kovács S., Boda L., Leveles L., Thernesz A., Hancsók J., 2010, Catalytic Hydrogenating of Triglycerides for the Production of Bioparaffin Mixture, Chemical Engineering Transactions 21, 1321-1326

Tsodikov M. V., Murzin V. Yu., Chistyakov A. V., Yandieva F. A., Gubanov M. A., Zharova P. A., Shapovalov S. S., Tikhonova O. G., Pasynskii A. A., Paul S., 2014, Dumeignil F.The Direct Ethanol Conversion to Hydrocarbons over Pt-Containing Catalysts, Chemical Engineering Transactions, 37, 583-588