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Pt–Sn/Al_2O_3 catalyst for the selective hydrodeoxygenation of esters

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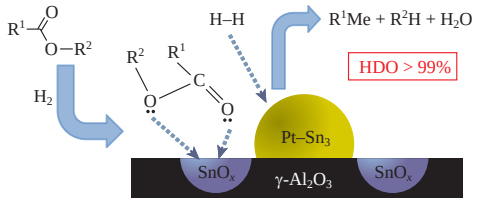
The hydrodeoxygenation of esters over a bimetallic catalyst has been shown to produce hydrocarbons derived from the alkoxy and acyl groups of a parent ester in a quantative yield.



Vegetable oil is renewable feedstock for fuel production.[1] Hydrodeoxygenation (HDO) is the most promising pathway for converting vegetable oils into isoalkanes (so-called green diesel).[2] The main fuel characteristics of green diesel [a high cetane number (75–90), a lower setting point and high oxidation stability] excel those of biodiesel synthesized *via* transesterification and those of petroleum based diesel.[1–3]

Ester deoxygenation proceeds in three general pathways: hydrodeoxygenation, decarbonylation and decarboxylation. Decarboxylation and decarbonylation reactions result in loss of the carbon mass of the reagent; in addition, carbon oxides undergo hydrogenation, which results in expensive hydrogen expenditure on the formation of methane.[4,5] HDO saves valuable carbon mass since the direct hydrogenation of C–O bonds takes place.[6] A condition for the profitability of chemical process and green chemistry requirements is the absence of wastes and by-products. Therefore, an important task is to develop a catalyst that ensures high HDO selectivity of vegetable oils and derivatives.

The aim of this work was to use a catalyst based on the heterometallic precursor $(PPh_4)_3[Pt(SnCl_3)_5]$[7] in the HDO of microalgal oil and a wide range of esters over platinum–tin catalysts. At a temperature of 400 °C, a monometallic Sn/Al_2O_3 catalyst exhibits no activity in oil conversion. Figure 1 shows the composition of the products of microalgal oil mixture conversion over monometallic Pt/Al_2O_3 and bimetallic catalysts with Sn/Pt atomic ratios of 1 : 1; 3 : 1 and 5 : 1, and demonstrates an increase in the yield of C_{18} hydrocarbons with growing tin content of catalysts.†

The bimetallic Pt-Sn_5/Al_2O_3 catalyst with platinum–tin bonds has the highest selectivity in HDO of microalgae oil. Reaction products contain carbon oxide traces, methane and ethane to indicate a nearly complete suppression of decarbonylation and decarboxylation processes. The total yield of a C_3–C_{18} hydrocarbon fraction reaches 99%. The lowest yield of C_{18} hydrocarbons was obtained over monometallic Pt/Al_2O_3. Tin addition to the catalyst increased the yield of C_{18} hydrocarbons. Note that catalysts containing active components at Sn/Pt atomic ratios of 3 : 1 and 5 : 1 obtained by co-impregnation provide the identical yields of products to indicate the key role of the precursor in the catalyst selectivity, while the amount of tin has less influence.

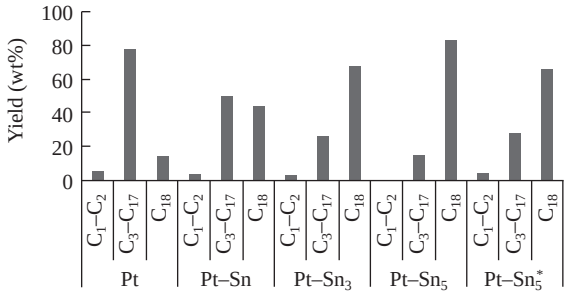


Figure 1 The yield of the products of algal oil mixture conversion over catalysts with various Sn/Pt ratios. Pt–Sn_5^* was prepared by the co-impregnation of $(PPh_3)_2PtCl_2$ and $SnCl_2$; Pt–Sn_5 was prepared by the impregnation of $(PPh_4)_3[Pt(SnCl_3)_5]$.

† As initial substrates, a mixture of three algae oils (40% *Luminaria*, 30% *Botryococcus brunii* and 30% *Phaeodactyum tricormutum*) from BUNGE (Canada) and nonyl propionate, ethyl acetate, methyl oleate, methyl palmitate, methyl myristate, methyl benzoate and benzyl acetate were used. The fatty acid composition of the microalgae oil was analyzed *via* the transesterification of oil with methanol and GC-MS analysis of fatty acid methyl esters. The fatty acid composition was the following (wt%): palmitic (C_{16} : 0), 4.5; stearic (C_{18} : 0), 0.2; oleic (C_{18} : 1), 54.2; linoleic (C_{18} : 2), 32.5; linolenic (C_{18} : 3), 2.9; and others, 5.7.

The support γ-Al_2O_3 was impregnated with Pt and Sn in different ratios. $(PPh_3)_2PtCl_2$, $SnCl_2$ and $(PPh_4)_3[Pt(SnCl_3)_5]$ were used as precursors. The platinum content of the catalysts was 0.4 wt%. The metal content of synthesized catalysts was determined by ICP AES. The catalysts were pretreated in hydrogen at 450 °C for 10 h.

Catalytic tests were performed using a PID Eng&Tech microcatalytic unit with a 10 cm^3 reactor (D_{in} = 9.12 mm, L = 153 mm) at 400 °C, VHSV = 1.2 h^{-1}, a hydrogen to substrate molar ratio of 100 : 1 and a pressure of 50 atm.

The reaction products were analyzed by GC (Varian 3600) and GC-MS (Automass-150 Delsi Nermag). Low concentrations of CO (< 0.4 vol%) in gaseous products were determined using a Riken Keiki RI-550A gas analyzer with an IR cell.

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Table 1 Parameters of the deoxygenation of esters over the $Pt–Sn_5/Al_2O_3$ catalyst.[a]

Substrate	Income/ mmol	Outcome/mmol		*S* (%) R^1Me	*S* (%) R^2H
		R^1Me	R^2H		
Ethyl acetate	404	798		98.8	
Nonyl propionate	173	168	172	97.1	99.4
Methyl oleate	94	90	94	95.8	100.0
Methyl palmitate	104	100	104	96.2	100.0
Methyl myristate	116	112	116	96.6	100.0
Methyl benzoate	199	190	199	95.5	100.0
Benzyl acetate	172	170	170	99.2	99.2

[a]*S* is the selectivity for hydrocarbon formation.

To determine the possible effect of the carboxylate fragments of esters and to confirm the possibility of their selective HDO in the presence of a $Pt–Sn_5/Al_2O_3$ catalyst based on a heterometallic precursor, the transformation of individual ethyl acetate, nonyl propionate, methyl oleate, methyl palmitate, methyl myristate, methyl benzoate and benzyl acetate was carried out.

Products of the reaction of 404 mmol of ethyl acetate contain 798 mmol of an ethane–ethylene fraction, which corresponds to 98.8% selectivity for HDO (Table 1). Based on the example of ethyl acetate transformation, it is impossible to unambiguously estimate the selectivity of the carboxylate fragment conversion and that of the alkyl alcohol fragment one. For the evaluation of HDO selectivity, nonyl propionate was used as a starting reactant.

As follows from the distribution of nonyl propionate conversion products, the alkyl group reacts with 99.4% selectivity and the carboxyl fragment turns into the corresponding hydrocarbon with 97.1% selectivity (Table 1). Such results are consistent with those observed for the microalgal oil mixture (Figure 1). Therefore, the catalyst selectivity for alkane formation from the alkyl fragment derived from alcohol is higher than that from the acyl group of the initial ester.

Currently, scientific interest is focused on the direct extraction of microalgae with supercritical methanol in order to produce fatty acid methyl esters in one stage.[8,9] The main components of vegetable oils, including microalgae oils, are oleic (C_{18}), palmitic (C_{16}) and myristic (C_{14}) acids. Therefore, we studied the transformation of methyl esters of these acids and found that the alkyl fragment underwent HDO with selectivity close to 100%. The selectivity of the formation of hydrocarbons containing the number of carbon atoms equal to that of the initial carboxylate fragments, within the experimental error, tends to increase with decreasing the carbon chain length. However, the selectivity is reduced due to the cracking of C–C bonds formed by the aliphatic hydrocarbons rather than the intensification of the decarbonylation and decarboxylation reactions.

In the reaction of methyl benzoate, a decrease in the selectivity of carboxylate fragment HDO was observed. Among the conversion products, carbon oxides and methanol were found. At the same time, the selectivity of the formation of toluene and ethane from benzyl acetate was close to 100%. Thus, the carboxylate fragment structure of an ester dramatically affects the HDO selectivity. The selectivity of methyl benzoate HDO decreased due to the intensification of decarboxylation and decarbonylation processes caused by a decrease in the bond-braking energy down to 96 kcal mol^{-1} for C_{ar}–COOMe from 107–144 kcal mol^{-1} for $C_nH_{2n+1}CH_2$–COOMe.[10,11]

Thus, the $Pt–Sn_5/Al_2O_3$ catalyst based on a heterometallic precursor exhibits a high selectivity in HDO of algal oil and a wide range of esters, the processes of decarbonylation and decarboxylation being completely inhibited.

As follows from the published characterization of the test catalyst,[12–15] its high selectivity for deoxygenation is likely determined by two important factors, namely, the particle size and structure of the platinum–tin precursor. Small sizes of both tin oxide and metallic alloy clusters, which were detected in the catalyst by TEM and XPS,[12] provide their interaction with only ester oxygen atoms as the most active centers of the substrate. The interaction between these clusters and unsaturated bonds in the hydrocarbon chain of the acyl group is sterically hindered.

The heterometallic complex used as the precursor of active metals comprises a direct bond between platinum and tin atoms, which probably favors the generation of adjoining tin-containing (SnO_x) and intermetallic centers ($PtSn_3$) on the support surface. Such clusters are believed to have the greater ability for the chemisorption of esters by oxygen atoms followed by their reduction with hydrogen than for the cracking of hydrocarbon fragments.

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