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Catalytic Conversions in Aqueous Media. Part 2. A Novel and Highly Efficient Biphasic Hydrogenation of Renewable Methyl Esters of Linseed and Sunflower Oils to High Quality Biodiesel Employing Rh/TPPTS Complexes

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Abstract An unusual high catalytic activity (TOF = 117,000 h^{-1}) and high catalyst productivity (TON = 9,700) have been achieved in the first example of partial hydrogenation of renewable polyunsaturated crude methyl esters of linseed and sunflower oils catalyzed by water soluble Rh/TPPTS complexes [TPPTS = $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$] in aqueous/organic two-phase systems to afford monounsaturated fatty esters which is biodiesel first generation of improved oxidative stability, energy and environmental performance at a low pour point. This exceptionally high catalytic activity contrast with the general perception that industrially applied water soluble Rh/TPPTS catalysts normally exhibit very low rates in the conversions of higher molecular weight starting materials in aqueous/organic two-phase systems.

Keywords Two-phase catalysis · Aqueous · Hydrogenation · Rhodium · TPPTS · Water soluble · Methyl esters of linseed and sunflower oils · Renewable resources · Biodiesel · Oxidative stability

1 Introduction

Currently there is increasing interest in aqueous-phase organometallic catalysis. The use of aqueous media facilitates recovery and recycling of the catalyst and circumvents the need for organic solvents which provides substantial environmental and economical benefits [1]. Biodiesel [2], which mainly consists of methyl esters of vegetable oils, is steadily gaining significance because of the following advantages over petroleum diesel: it has a negative CO_2 balance, it is renewable, biodegradable, non-toxic, safe (higher flashpoint), low in sulfur, provides engine lubricity, emits less CO, hydrocarbons, particulates and smoke, and has a higher cetane number. The transesterification route of vegetable oils with methanol to methyl esters, i.e., biodiesel first generation, is commercialized in the EU with rapeseed and sunflower oils being the major feedstocks and in the USA with soybean oil feedstock [2]. However, current technology has not solved all problems associated with the use of biodiesel. Challenges remain *inter alia* the production of biodiesel that meets oxidative stability and NO_x emissions requirements. In fact, biodiesel is highly exposed to oxidative processes during storage because it contains polyunsaturated fatty acid methyl esters (FAME). Their relative rates of autoxidation are: 98 for methyl linolenate (MLN, Scheme 1), 41 for methyl linoleate (ML), and 1 for methyl oleate (MO) [3, 7] Therefore, selective hydrogenation of biodiesel to C18:1 FAME substantially increases their oxidative stabilities which makes the addition of synthetic antioxidants superfluous. Moreover, partial hydrogenation of biodiesel increases the energy performance, i.e., the cetane number of the fuel. Knothe [4] reported for ethyl linolenate a cetane number of 22.7, for ML: 38.2, for MO: 59.3, and for methyl stearate: 86.9. Furthermore, selective hydrogenation of biodiesel combats

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For part 1 of this series see Ref. [14].

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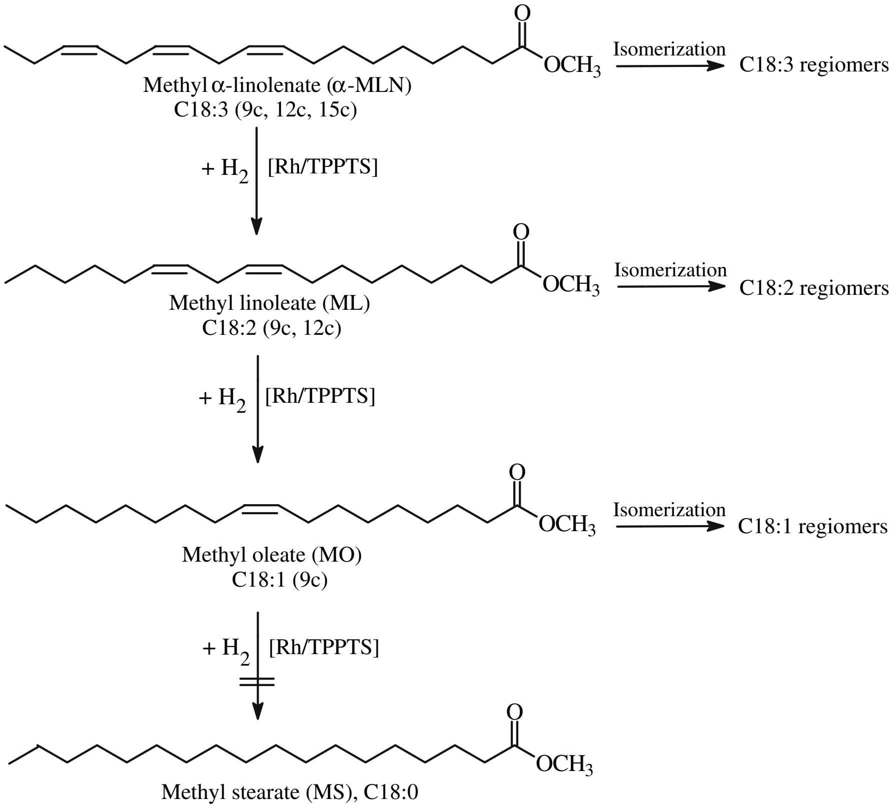
Scheme 1 The simplified pathway of the partial hydrogenation of methyl esters of linseed oil (MELO) and methyl esters of sunflower oil (MESO) catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems. Methyl α-linolenate (α-MLN) and C18:3 regiomers are converted to ML and C18:2 regiomers and finally to MO and C18:1 regiomers containing a small amount of the final product methyl stearate (MS)



its NO_x-effect: the increase of NO_x emissions observed in most studies of biodiesel [5]. Conventional B20 blends (20% biodiesel in petrodiesel) produced a NO_x increase of 3–5% compared to petrodiesel. These studies [5] also showed that NO_x emissions decreased with decreasing unsaturation. Szybist et al. [5b] used a B20 blend where the biodiesel portion contained 76% of MO and could even eliminate the biodiesel NO_x-effect. Falk and Meyer-Pittroff [6] described the partial hydrogenation of biodiesel catalyzed by a heterogeneous nickel B113W system and could increase its oxidative stability at a low pour point. More recently, Moser et al. [7] partially hydrogenated soybean oil using a commercial heterogeneous Ni-based Nysosel 645 catalyst and after transesterification with methanol could improve the oxidative stability of the biodiesel product. An economic analysis suggested that the cost increase regarding the hydrogenation step would be US$ 0.04/l and partially hydrogenated biodiesel deserve consideration as a potential biofuel [7]. We have investigated the partial hydrogenation of polyunsaturated crude methyl esters of linseed and sunflower oils to afford selectively monounsaturated fatty esters catalyzed by water soluble Rh/TPPTS complexes in aqueous/organic two-phase systems in order to improve the quality of biodiesel in terms of increased oxidative stability, higher energy performance and elimination of the NO_x-effect at a low pour point [8]. To our knowledge, this is the first example of a hydrogenation of esters of renewable vegetable oils catalyzed by water soluble transition metal complexes in aqueous/organic two-phase systems.

2 Experimental

2.1 Materials

Linseed oil and sunflower seed oil (from *Helianthus annuus*) were purchased from Aldrich and Fluka, respectively, and were used without any further purification. $RhCl_3 \cdot 3H_2O$ was purchased from Acros Organics. Dodecyltrimethylammonium chloride (DTAC) was purchased from Acros Organics and used without any further purification. TPPTS was prepared according to the procedure of Hoechst AG, Werk Ruhrchemie [9] and isolated with purity higher than 98%. Hydrogen (quality 5.0) was purchased from Messer Hellas (Athens) and was used without further purification. Distilled demineralized water was deoxygenated in an ultrasound bath under high vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times.

2.2 Typical Transesterification Reaction of Vegetable Oils with Methanol

In a typical transesterification reaction of sunflower oil: A 1,000-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a thermometer and a condenser was charged with 322.0 g of sunflower oil and a solution of 203.0 g methanol containing 3.22 g of NaOH. The mixture was stirred at 55 °C for 70 min. The course of the reaction was followed by thin layer chromatography. The reaction mixture was then cooled and further stirred for 4.5 h at room temperature. After phase separation resulted in the isolation of the methyl esters of sunflower oil (MESO) and the glycerol. The glycerol phase (bottom layer) was removed and kept in a separate container. The MESO phase (top layer) was washed with distilled water several times (pH = 7.0), dried over Na_2SO_4 to obtain 230 g of MESO mixture which was used as starting material in the hydrogenation reaction without any purification by distillation. Methyl esters composition of sunflower oil was determined by gas chromatography (vide infra) and is given in Table 1. The same procedure was used for the transesterification of linseed oil and the composition of the methyl esters of linseed oil (MELO) was determined by gas chromatography and is given also in Table 1.

2.3 Typical Hydrogenation Procedure

In a typical hydrogenationreaction of MESO: 1.32 mg (0.005 mmol) $RhCl_3 \cdot 3H_2O$ and 9.24 mg (0.015 mmol) TPPTS, (TPPTS/Rh molar ratio = 3) were dissolved in 15 mL deaerated distilled demineralized water within 1 min of stirring. This aqueous catalyst solution, having a rhodium concentration of 34 ppm, with 15.15 g (75.0 mmol of C=C units) of MESO mixture which results a two-phase system with a volume ratio of aqueous/organic phase = 1.5/1.6, were charged into an Autoclave Engineers autoclave (100 mL) which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of C=C units/Rh was 15,000. After a number of pressurizing–depressurizing cycles with hydrogen to remove the last traces of argon/air, the autoclave was pressured and contents were heated with stirring (stirring rate = 850 rpm). At the reaction temperature of 120 °C the hydrogen partial pressure was 50 bar and the reaction time 5 min. After the reaction the autoclave was cooled to room temperature, vented of hydrogen and the reaction mixture removed. The upper organic layer was easily separated from the lower aqueous layer containing the catalyst and dried over sodium sulfate. The organic layer containing the products was analyzed by gas chromatography (GC) after addition of eicosane or methyl heptadecanoate as internal standards.

2.4 Analyses

$^{31}P\{^1H\}$NMR spectra (121 MHz, referenced to external 85% H_3PO_4) were recordered on a Varian Unity Plus 300/54 spectrometer. The purity of the ligand TPPTS was determined by quantitative $^{31}P\{^1H\}$NMR analysis in D_2O at 25 °C. δ TPPTS = −5.4 ppm. The various *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated FAME isomers contained in the starting materials and products were identified by comparison of GC and gas chromatography/mass spectrometry (GC/MS) analytic data with data for authentic samples. GC/MS was measured on a Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap MS. The GC was equipped with a flame ionization detector (FID) and a SP-2560 capillary column (100 m × 0.25 mm i.d. × 0.2 µm film thickness) which was purchased from Supelco (Athens, Greece). The SP-2560 capillary column is one of the columns used in the recently approved American Oil Chemists' Society (AOCS) official method Ce 1h-05 for the determination of *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method [10]. Carrier gas was He at 230 kPa. The oven temperature was initially at 170 °C for 0 min and then increased to 220 °C at 1 °C/min. The injector and detector temperatures were set at 220 and 230 °C, respectively. GC analyses were run on a Shimadzu GC-14B equipped with a FID detector and a SP-2560 capillary column with conditions as described above in GC/MS analyses.

3 Results and Discussion

Typical results obtained in the partial hydrogenation of crude MELO and crude MESO to a mixture of monounsaturated (C18:1) esters (Scheme 1) at 70–120 °C and 10–100 bar H_2 pressure in the presence of water soluble Rh/TPPTS catalysts at low rhodium concentrations in water ([Rh] = 34 ppm) in aqueous/organic two-phase systems are given in Table 1. Despite of the propensity of MLN to autoxidize the European Biodiesel Standard EN 14214 sets a limit of 12% of MLN in biodiesel fuel in order not to exclude high-oleic rapeseed oil, the major feedstock in the EU [2c]. Furthermore, we chose MELO because it mainly consists of α-MLN and constitutes a good model to investigate the whole spectrum of the reaction: C18:3 → C18:2 → C18:1 $\nrightarrow$ C18:0. One of the aims of partial hydrogenation to C18:1 FAME is to avoid deterioration in low-temperature behavior of biodiesel such as on the pour point. To preserve fluidity it is mandatory not to increase the melting point of the mixture that depends on both the amount of methyl stearate (MS, C18:0) and the extend of

Table 1 Hydrogenation of crude MELO and crude MESO catalysed by Rh/TPPTS complexes in aqueous/organic two-phase systems at 34 ppm Rh in the aqueous solution[a]

Run	Starting material	C=C/Rh molar ratio	P/Rh molar ratio	Surfactant	Organic solvent	T (°C)	P_{H_2} (bar)	t (min)	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	*cis*-C18:1 (total) (mol%)	*trans*-C18:1 (total) (mol%)	MS (mol%)	TOF[b] (h^{-1})	TON[c]
–	MELO 1[d]	–	–	–	–	–	–	–	56.8[e]	16.7[f]	22.5[g]	22.5[g]	–	4.0	–	
1	MELO 1	500	3	DTAC	*n*-Hexane	70	10	120	0.4	9.5	71.7	43.1	28.6	18.4	160	320
2	MELO 1	500	4	DTAC	*n*-Hexane	70	10	120	0.7	8.3	79.1	51.4	27.7	11.9	160	320
3	MELO 1	500	5	DTAC	*n*-Hexane	70	10	120	0.5	18.2	68.6	38.0	30.6	12.7	140	280
4	MELO 1	500	6	DTAC	*n*-Hexane	70	10	120	0.7	22.4	67.7	34.7	33.0	9.2	140	280
5	MELO 1	500	8	DTAC	*n*-Hexane	70	10	120	30.0	19.6	43.0	36.4	6.6	7.4	65	130
6	MELO 1	500	4	DTAC	*n*-Hexane	80	10	120	0.5	8.8	79.8	37.3	42.5	10.9	160	320
7	MELO 1	500	4	DTAC	*n*-Hexane	90	10	120	1.4	8.2	79.3	45.6	33.7	11.1	160	320
8	MELO 1	1000	4	DTAC	*n*-Pentane	70	10	10	41.2	21.3	33.2	31.4	1.8	4.3	930	150
9	MELO 1	1000	4	DTAC	Diethyl ether	70	10	10	1.2	22.0	67.2	54.2	13.0	9.6	3300	550
–	MELO 2[d]	–		–	–	–	–	–	65.8[e]	13.3[f]	18.5[g]	18.5[g]	–	2.4	–	–
10	MELO 2	3000	4	DTAC	Diethyl ether	70	40	10	2.0	26.5	62.2	47.3	14.9	9.3	11400	1900
11	MELO 2	3000	4	DTAC	Diethyl ether	70	70	10	0.8	10.1	67.0	39.8	27.2	22.1	12200	2000
12	MELO 2	3000	4	DTAC	Diethyl ether	70	100	10	0.6	10.6	63.9	35.9	28.0	24.9	12200	2000
13	MELO 2	10000	4	DTAC	Diethyl ether	80	100	10	0.7	24.5	64.0	46.3	17.7	10.8	39000	6500
–	MESO 1[d]	–	–	–	–	–	–	–	–	69.2[f]	27.8[g]	27.8[g]	–	3.0	–	–
14	MESO 1	1000	5	DTAC	Diethyl ether	100	70	10	–	40.4	44.6	38.0	6.6	15.0	1700	280
15	MESO 1	1000	4	–	Diethyl ether	110	50	10	–	11.6	65.1	45.2	19.9	23.3	3400	560
16	MESO 1	10000	4	–	Diethyl ether	110	50	10	–	56.8	36.7	33.5	3.2	6.5	7400	1200
17[h]	MESO 1	10000	3	–	Diethyl ether	120	50	10	–	9.6	63.9	31.7	32.2	26.5	35700	5900
18[h]	MESO 1	10000	3	–	–	120	50	10	–	10.8	67.0	35.9	31.1	22.2	35000	5800
19[h]	MESO 1	20000	3	–	–	120	50	5	–	38.6	52.1	36.0	16.1	9.3	73300	6100
–	MESO 2[d]	–	–	–	–	–	–	–	–	68.8[f]	28.4[g]	28.4[g]	–	2.8	–	–
20[h]	MESO 2	17500	3	–	–	120	50	5	–	20.0	64.7	40.0	24.7	15.3	107000	8900
21[h]	MESO 2	15000	3	–	–	120	50	5	–	6.0	68.3	35.8	32.5	25.7	117000	9700
–	MESO 3[d]	–	–		–	–	–	–	–	66.2[f]	30.0[g]	30.0[g]	–	3.8	–	–
22[h]	MESO 3	17000	5	–	–	110	40	10	–	39.3	50.7	40.5	10.2	10.0	27400	4500
23[h,i]	MESO 3	17000	Recycled catalyst	–	–	110	40	10	–	39.8	51.6	43.0	8.6	8.6	27000	4500

Table 1 continued

[a] Reaction conditions: 2.63 mg (0.01 mmol) $RhCl_3 \cdot 3H_2O$; except runs 17–23, 1.32 mg (0.005 mmol) $RhCl_3 \cdot 3H_2O$; 24.63 mg (0.04 mmol) TPPTS (P/Rh molar ratio = 4); 31.66 mg (0.12 mmol) DTAC (DTAC/TPPTS molar ratio = 3); except runs 8–14, DTAC/TPPTS = 2; 30 mL deaerated distilled demineralized water; except runs 17–23, 15 mL of water; 163.3 mg (1.2 mmol) KH_2PO_4, pH = 7.0 adjusted with 5% aqueous NaOH. Addition of MELO dissolved in 10 mL of organic solvent results a two-phase system with a volume ratio of aqueous/organic phase = 3/1.1–3/2.6; except run 13, 18.8 mL diethylether (aqueous/organic phase = 3/3.5). Runs 14–23: aqueous/organic phase = 1.5/2.2–1.5/1.1. Runs 14 and 15: 10 mL diethylether, run 16: 18.8 mL diethylether, run 17: 6.2 mL diethylether. Stirring rate = 770–850 rpm. In all runs: no decomposition of the catalyst and no formation of black metallic aggregates

[b] Defined as mole of hydrogenated C=C units in C18:3, C18:2, and C18:1 starting material mixtures and all other regiomers per mole of rhodium per hour

[c] Defined as mole of hydrogenated C=C units in C18:3, C18:2, and C18:1 starting material mixtures and all other regiomers per mole of rhodium

[d] Crude MELO and MESO except of α-MLN, ML, MO, and MS further contained 3.4–5.5% of methyl palmitate (C16:0) and 0.4–0.6% of methyl behenate (C22:0) which were ignored in the experiments

[e] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c)

[f] Methyl linoleate (ML), C18:2 (9c, 12c)

[g] Methyl oleate (MO), C18:1 (9c)

[h] No buffer was added, pH = 4.3

[i] The aqueous catalyst layer (15 mL) of run 22 after separation was re-used with addition of 18.108 g (85.0 mmol) MESO 3

cis/trans and positional isomerization. For example the melting point of MS is +39.1 °C, of MO: −19.9 °C and of methyl elaidate (C18:1, 9t): +10.0 °C.

3.1 Catalytic Hydrogenation Reactions of MELO using Water Soluble Rh/TPPTS Complexes in Aqueous/Organic Two-phase Systems

The selectivity of monounsaturated (C18:1) ester regiomers in the Rh/TPPTS-catalyzed micellar hydrogenation of MELO is strongly influenced by the amount of TPPTS added to rhodium precursor (runs 1–5). Total contents in C18:1 regiomers up to 79.1% were achieved in the micellar hydrogenation of crude MELO using Rh/TPPTS catalysts at a TPPTS/Rh molar ratio of 4 at 70 °C and 10 bar with addition of cationic surfactant DTAC and *n*-hexane in aqueous/organic two-phase systems (run 2). The selectivity toward C18:0 regiomers could be slightly increased to 79.8% at a temperature of 80 °C (run 6). Under these conditions, however, the catalytic activity remained low (TOF up to 160 h^{-1}). The activity could be increased (TOF = 930 h^{-1}) using *n*-pentane (run 8) and much higher catalytic activity (TOF = 3,300 h^{-1}) was obtained with diethylether (run 9) in the hydrogenation of MELO using Rh/TPPTS complexes at 70 °C, 10 bar and a C=C units/Rh molar ratio of 1,000 in aqueous/organic biphasic system. Unfortunately the amount of *trans*-C18:1 isomers formed was substantial (up to 42.5%). The effect of H_2 partial pressure in the Rh/TPPTS-catalyzed hydrogenation of MELO is shown in runs 1–12. High catalytic activities (TOF = 39,000 h^{-1}) were achieved in the Rh/TPPTS catalyzed hydrogenation of MELO at 80 °C, 100 bar H_2 pressure and a C=C units/Rh molar ratio of 10,000 with addition of DTAC and diethylether in aqueous/organic two-phase systems (run 13).

3.2 Catalytic Hydrogenation Reactions of MESO using Water Soluble Rh/TPPTS Complexes in Aqueous/Organic Two-phase Systems

Biphasic hydrogenation reactions of crude MESO were carried out using Rh/TPPTS catalysts in the presence (run 14) and absence of DTAC (run 15) at a C=C units/Rh molar ratio of 1,000 within 10 min which showed that reasonable activities (TOF = 3,400 h^{-1}) could be achieved in the absence of surfactant. Fell et al. [11] hydroformylated ω-alkenecarboxylic acid methyl esters using Rh/TPPTS catalysts in aqueous/organic two-phase systems and could shown that lower and mid range starting materials up to C10:1 were converted without any addition of surfactant whereas terminally unsaturated esters higher than C11:1 could be effectively converted only by adding cationic surfactants. In order to explain the results of runs 14 and 15 we assume that lecithin which is present in sunflower oil and thus in crude MESO acts as an inherent zwitterionic surfactant and therefore in run 15 micellar catalysis may also be operative. The effect of pH on the hydrogenation was studied in a series of experiments in mixtures buffered with KH_2PO_4/NaOH at pH = 7.0 (runs 1–16) and unbuffered mixtures at pH = 4.3 (runs 17–23). Biphasic hydrogenation of MESO in the presence (run 16) and absence of buffer (run 17) at a C=C units /Rh molar ratio of 10,000 within 10 min showed that the hydrogenation reaction proceeds smoothly (TOF = 35,700 h^{-1}) in the absence of buffer at pH = 4.3. Hydrogenation reactions of MESO were carried out in the presence (run 17) and absence of diethylether (run 18), which showed that the absence of diethylether caused a minor decrease in catalytic activity from 35,700 to 35,000 TOFs per hour.

Exceptionally high catalytic activities (TOF = 117,000 h^{-1}) and high catalyst productivity (TON = 9,700) were achieved in the hydrogenation of crude MESO using Rh/TPPTS catalysts at a C=C units/Rh molar ratio of 15,000, 120 °C, 50 bar H_2 and [Rh] = 34 ppm in water to obtain a total content of 68.3% in C18:1 regiomers within 5 min without addition of surfactant and organic solvent in aqueous/organic two-phase systems (run 21). To our knowledge, this is the highest catalytic activity exhibited so far by water soluble transition metal TPPTS complexes in aqueous/organic two-phase systems. Indeed, this unusual high catalytic activity in water is even more remarkable when one considers that MESO is a mixture of higher molecular weight, functionalized, olefins/dienes and furthermore that it contains internal C=C units. We note that an intrinsic limitation of aqueous/organic biphasic catalysis is generally the significantly lower rates compared to analogous reactions in organic media [1]. This exceptionally high catalytic activity observed in the biphasic Rh/TPPTS-catalyzed hydrogenation of higher molecular weight MESO starting materials contrasts with the general perception that industrially applied water soluble Rh/TPPTS catalysts normally exhibit very low rates in the conversions of higher molecular weight starting materials in aqueous/organic two-phase systems due to mass transfer limitations resulting from the lower solubility of higher molecular weight starting materials in water [1]. This exceptional rate enhancement achieved in the hydrogenation of MESO (run 21) alternatively may be explained by invoking interactions between the solvent water and catalytic intermediate species in the biphasic system. We assume that water probably shifts the equilibrium of chelated catalytic intermediates where both C=C units and esters groups of MESO are coordinated towards non-chelated catalytic complexes, occupy the vacant coordination and also hydrogen bonding stabilizes the non-chelated species which obviously facilitates subsequent steps in the catalytic cycle. Chelated catalytic intermediates with involvement of interactions with the solvent water have been proposed in Rh/TPPTS-catalyzed hydroformylation reactions of acrylic esters in order to explain the relative high catalytic activities (TOF ~ 1,700 h^{-1}) obtained in aqueous/organic two-phase systems [12]. Increasing the C=C units/Rh molar ratio to 17,500 (run 20) and 20,000 (run 19) the catalytic activity decreased to 107,000 and 73,300 TOFs per hour with total contents in C18:1 esters isomer mixture of 64.7 and 52.1%, respectively.

Although the catalyst is added as a rhodium(III) salt (usually $RhCl_3 \cdot 3H_2O$) the actual catalyst is a rhodium (I) TPPTS complex, i.e., $RhCl(TPPTS)_3$, formed in situ from $RhCl_3 \cdot 3H_2O$ with TPPTS under homogeneous hydrogenation conditions in aqueous media [13, 14]. Dynamic light scattering studies of the Rh/TPPTS catalytic system in aqueous media have proven its homogeneous nature [14]. An alternative explanation regarding the nature of the catalytic active species namely the formation of catalytic active Rh(0) nanoparticles by reducing $RhCl_3 \cdot H_2O$ with hydrogen and stabilizing in the organic phase with surfactant FAME starting materials which posses a lower *Hydrophilic–Lipophilic Balance* (HLB) could be excluded because a recycling experiment of the aqueous phase containing the Rh/TPPTS catalyst showed that the catalytic activity remained high in a consecutive run (runs 22, 23). If catalytic Rh(0) nanoparticles with FAME as protective dispersants were formed in the organic phase than these catalytic species would be separated off during decantation and no catalytic activity would be observed by re-using the aqueous phase in the biphasic hydrogenation of a new portion of MESO as described in run 23.

No black rhodium metal aggregates were observed in all biphasic hydrogenation reactions presented here which indicates that the Rh/TPPTS catalyst remains intact without decomposition after the reaction in the aqueous layer which is a clear solution.

4 Conclusions

We have shown that the partial hydrogenation reaction of renewable polyunsaturated crude methyl esters of linseed and sunflower oils to their monounsaturated counterparts using water soluble transition metal complexes as catalysts proceeds smoothly in aqueous/organic two-phase systems. Unexpected high catalytic activity and high catalyst productivity were achieved with Rh/TPPTS complexes which is the highest activity exhibited so far by water soluble transition metal TPPTS complexes in biphasic systems.

High contents to monounsaturated fatty esters regiomers were obtained which is biodiesel first generation of improved oxidative stability, energy and environmental performance. The Rh/TPPTS catalyst after the reaction could be easily recovered by a simple phase separation and a recycling experiment of the aqueous catalyst layer showed that the catalytic activity remained high in a consecutive run. Hence, we are currently investigating the scope of this useful aqueous/organic biphasic catalytic hydrogenation reaction of renewable methyl esters of vegetable oils.

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