

A Remarkable Effect of Aluminum on the Novel and Efficient Aqueous-Phase Hydrogenation of Levulinic Acid into γ-Valerolactone Using Water-Soluble Platinum Catalysts Modified with Nitrogen-Containing Ligands

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Abstract

The catalytic performance of novel water-soluble platinum catalysts modified with various nitrogen-containing and phosphine ligands in the hydrogenation reaction of levulinic acid (LA) into γ -valerolactone (GVL) has been studied in environmentally attractive, green, aqueous monophasic systems. The presence of the Lewis acid aluminum enormously increases the catalytic activity of water-soluble platinum catalysts modified with nitrogen-containing ligands in the LA hydrogenation reaction and high catalytic activities up to 3540 TOF's per hour with a quantitative selectivity towards GVL have been achieved using Na₂PtCl₆·6H₂O precursors modified with the bidentate bathophenanthrolinedisulfonic acid disodium salt (BPhDS) ligand and low amounts of AlCl₃·6H₂O promotors (molar ratio of AlCl₃·6H₂O/Pt = 0.17) in aqueous media. This unprecedented increase in catalytic activity with aluminum promotors for water-soluble transition metal catalytic systems in aqueous-phase hydrogenation reactions has not been described until now in the literature. The apparent activation energy of platinum catalyst modified with the monodentate nitrilotriacetic acid trisodium salt ligand in aqueous media metal and amounts to a relative low value of 73.04 kJ mol⁻¹ when one considers that in the LA hydrogenation reaction this catalyst reduces a less reactive keto group into alcohol functionality. A recycling experiment of the Pt/BPhDS/Al catalyst from the aqueous monophasic LA hydrogenation reaction mixture followed by biphasic recovery of the catalyst in active form from organic reaction products by extraction and simple phase separation of an aqueous/organic two-phase system formed after addition of diethyl ether has shown that the Pt/BPhDS/Al catalyst is stable without loss of activity and selectivity in a consecutive run.

Graphical Abstract



Keywords Aqueous-phase hydrogenation · Levulinic acid · Platinum · Aluminum · Water-soluble ligands

Extended author information available on the last page of the article

1 Introduction

Because of the broad range of potential industrial applications there is increasing interest in catalysis in aqueous media [1–5]. Water-soluble rhodium catalytic complexes modified with the sodium salt of trisulfonated triphenylphosphine [TPPTS, $P(C_6H_4$ -m-SO₃Na)₃, Fig. 1], for example, is applied industrially in the hydroformylation of propene employing aqueous/organic two-phase systems [1, 2]. The use of water circumvents the need for organic solvents and facilitates recovery and recycling of the catalyst which can provide substantial economic and environmental benefits and water is a non-toxic, non-inflammable, safe, inexpensive, abundantly available and a green solvent [1–5]. The polarity of water makes it an ideal solvent to convert polar biomass raw materials with high oxygen content such as hydrophilic carbohydrates and their derivatives by water-soluble transition metal catalytic complexes in aqueous monophasic systems followed



Fig. 1 Structures of the water-soluble ligands triphenylphosphinetrisulfonic acid trisodium salt (TPPTS), nitrilotriacetic acid trisodium salt (NTA·Na₃), 2,2'-bipyridine-4,4'-dicarboxylic acid (BPyDCA), bathophenanthrolinedisulfonic acid disodium salt (BPhDS), ethylenediaminetetraacetic acid tetrasodium salt (EDTA·Na₄), 2,6-pyridinedicarboxylic acid (2,6-PyDCA), 3-pyridinesulfonic acid (3-PSA), 3,4-pyridinedicarboxylic acid (3,4-PyDCA), 2,2'-biquinoline-

4,4'dicarboxylic acid dipotassium salt (BQC), 2-aminoethanesulfonic acid (Taurine), bathocuproinedisulfonic acid disodium salt (BCDS), sulfanilic acid sodium salt (SANa), diethylenetriaminepentaacetic acid pentasodium salt (DTPA·Na₅), nitrilotris(methylphosphonic acid) (NTPA), tris(2-pyridyl)phosphine (T₂PyP) and 1,3,5-triaza-7-phosphaadamantane (PTA)

by biphasic recovery of the catalyst in active form from organic reaction products by simple phase separation of an aqueous/organic two-phase system formed after external addition of an organic solvent such as diethyl ether.

Nowadays, there is growing interest in the use of hydrophilic carbohydrates and their platform chemical derivatives from renewable biomass because of their far reaching applications as attractive industrial feedstocks for biorefineries to produce biofuels and bio-based chemicals according to the principles of Green-Sustainable Chemistry and because they contribute to lower greenhouse gas emissions [6-14]. Today, levulinic acid (LA, Scheme 1) is considered as a versatile and key platform chemical of central relevance in the development of biorefineries of the future with many potential industrial applications. LA is readily available from both C₆ and C₅ carbohydrates and the most famous industrial continuous process for the production of LA is the Biofine process which was developed by BioMetics Inc. in the earlies 1990s and proceeds with sulfuric acid catalyzed hydrolysis of e.g lignocellulose [8, 10, 15]. The GFBiochemicals company after revision and redesign of the process engineering of Biofine has developed on commercial scale a process for the production of LA directly from biomass with the capacity 10,000 MT/a of LA [12, 16, 17]. Other companies producing LA are Golden Race Group [16] and DuPont [18] and is expected that the higher production capacity will cause a reduction in the LA price from 5 to 8 US\$ per Kg which is currently, to lower than 1 US\$ per Kg [18]. The last years, the hydrogenation reaction of LA into γ -valerolactone (GVL, Scheme 1) is a very active research field and various heterogeneous catalysts [11, 14, 18-24], catalytic nanoparticles [25-27] and conventional apolar homogeneous transition metal catalytic complexes have been developed for this reaction in the absence or presence of organic or aqueous solvents [28-33]. GVL is an important C₅ platform chemical for the production of advanced biofuels, bio-based fine chemicals and polymers and could be also used as an additive for gasoline, as a sustainable polar aprotic solvent and as a food additive [10-12, 14, 16, 19, 20, 23, 26, 34, 35].

The aqueous-phase catalytic hydrogenation reaction of LA into GVL employing water-soluble transition metal catalytic complexes has been described by several research groups started with the pioneer work of Joó et al. [36] in the presence of water-soluble Ru/TPPMS complexes $[TPPMS = PPh_2(C_6H_4 - m - SO_3Na)]$. Horváth et al. [37, 38] used water-soluble Ru(acac)₃/TPPTS catalysts in the aqueous monophasic hydrogenation of LA to yield 95% GVL which was isolated after extraction by means of a biphasic system formed with addition of ethyl acetate. Heeres et al. [39, 40] investigated the biphasic catalytic hydrogenation of LA into GVL by water-soluble RuCl₃·3H₂O/TPPTS systems to observe a conversion of 82% of LA in a dichloromethane/ water two-phase system. In a recycling experiment, however, the RuCl₃·3H₂O/TPPTS catalyst was partially deactivated because in the first run the conversion of LA was 81% and in the followed catalyst recycling experiment only 55% of LA were converted [39]. Delhomme et al. [41] described the hydrogenation of LA into GVL catalyzed by RuCl₃·3H₂O or Ru(acac)₃ precustors modified with water-soluble phosphine ligands such as TPPTS, TPPMS, PTA (Fig. 1) in aqueous monophasic systems to achieve a maximum catalytic activity of TOF = 210 h^{-1} with RuCl₃·3H₂O/TPPTS catalysts and an activity of TOF = 202 h^{-1} using Ru(acac)₃/TPPTS with a conversion of LA of 99% and selectivity towards GVL of 97%. Fu et al. [42, 43] disclosed the hydrogenation of LA to GVL using pentamethylcyclopentadienylirid ium(III) catalysts modified with water-soluble ligands such as 4,4'-dicarboxy-2,2'-bipyridine and 4,4'-dihydroxy-2,2'bipyridine and found high catalytic activities up to 12,200 TOFs per hour in aqueous monophasic systems.

Recently, we reported [44] the aqueous-phase hydrogenation of LA into GVL employing water-soluble ruthenium catalysts modified with various nitrogen-containing ligands and the recovery of such catalysts in a biphasic system formed after addition of diethyl ether. We now report the novel and efficient aqueous-phase hydrogenation of LA into GVL using water-soluble platinum catalysts modified with nitrogen-containing and phosphine ligands and an enormous increase in catalytic activity observed in the presence of the Lewis acid aluminum in the aqueous reaction mixture as well as the recovery of the catalyst in active form from organic reaction products by extraction and a simple phase separation of the biphasic system formed after addition of diethyl ether without any loss of the catalytic activity and selectivity. To our knowledge, this is the first example of a hydrogenation reaction of LA into GVL using water-soluble platinum catalysts in aqueous media and the unprecedented increase in catalytic activity with aluminum promotors for water-soluble transition metal catalytic systems

Scheme 1 Selective hydrogenation of levulinic acid (LA) into γ-valerolactone (GVL) catalyzed by water-soluble platinum catalysts modified with nitrogen-containing ligands in aqueous media



in aqueous-phase hydrogenation reactions has not been described until now in the literature.

2 Experimental

2.1 Materials

Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and used without further purification. 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. Levulinic acid (LA) with a purity of 98% was purchased from Alfa Aesar and used without any further purification. y-valerolactone (GVL) and valeric acid (VA) were obtained from Alfa Aesar. 1,4-Pentanediol (1,4-PDO) and N,N-dimethylformamide (DMF) were purchased from Aldrich. Na₂PtCl₆·6H₂O, PtCl₂, Pt(NH₃)₄Cl₂·H₂O, $PtO_2 \cdot H_2O$ and $Pt(acac)_2$ were purchased from Alfa Aesar. TPPTS was prepared according to literature procedures [45–52] and isolated with purity higher than 98%. Tris(2pyridyl)phosphine (T₂PyP) was prepared according to the procedure of the group of Wilkinson [53] with purity higher than 99%. Nitrilotriacetic acid trisodium salt (NTA·Na₃), bathocuproinedisulfonic acid disodium salt (BCDS), ethylenediaminetetraacetic acid tetrasodium salt (EDTA \cdot Na₄) and 2,2'-bipyridine-4,4'-dicarboxylic acid (BPyDCA) were purchased from Alfa Aesar; bathophenanthrolinedisulfonic acid disodium salt (BPhDS), 2-aminoethanesulfonic acid (Taurine), 3-pyridinesulfonic acid (3-PSA), 2,6-pyridinedicarboxylic acid (2,6-PyDCA) and 3,4-pyridinedicarboxylic acid (3,4-PyDCA) were obtained from Acros Organics; nitrilotris(methylphosphonic acid) (NTPA) and diethylenetriaminepentaacetic acid pentasodium salt (DTPA·Na₅) were obtained from Fluka; 2,2'-biquinoline-4,4'dicarboxylic acid dipotassium salt (BQC), sulfanilic acid sodium salt (SANa) and 1,3,5-triaza-7-phosphaadamantane (PTA) were purchased from Aldrich. All nitrogen containing ligands mentioned, were used without any further purification. NaI and NaCl were purchased from Alfa Aesar; AlCl₃·6H₂O was obtained from Sigma Aldrich; NaH₂PO₄·H₂O and MgCl₂·6H₂O were purchased from Merck.

2.2 Procedure of a Typical Catalytic Hydrogenation Experiment

First, the autoclave was thoroughly cleaned and followed by numerous series of treatment of the autoclave at elevated temperatures (150 °C) and pressures (60 bar of H_2) within 1 h each time using an aqueous solution of BPhDS (Fig. 1) in the absence of any transition metals in order to be sure that no memory effects of the autoclave regarding previous transition metal catalytic systems are still operative. After this procedure, the hydrogenation reactions of LA were carried out in the presence of water-soluble platinum catalysts modified with nitrogen-containing ligands and phosphines in aqueous monophasic systems. The catalytic hydrogenation experiment of LA of entry 4/2 of Table 4 was carried out with the following procedure. The water-soluble Na₂PtCl₆·6H₂O/BPhDS/AlCl₃·6H₂O catalyst precursor was first synthesized by dissolving under stirring of 2.81 mg (0.005 mmol) Na₂PtCl₆·6H₂O, 2.86 mg (0.005 mmol) BPhDS (molar ratio BPhDS/Pt = 1) and 0.21 mg (0.00085 mmol) AlCl₃·6H₂O (molar ratio AlCl₃·6H₂O/ Pt = 0.17) under argon in 20 ml deaerated demineralized water within 10 min of time at room temperature. After addition of 2.322 g (20 mmol) LA to the aqueous catalyst solution under stirring for further 5 min the reaction mixture at room temperature, having a platinum concentration of 44 ppm, was charged into an Autoclave Engineers autoclave of a nominal volume of 100 ml which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of LA/Pt was 4000. After a number of pressurisingdepressurising cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured and contents were heated with stirring (stirring rate = 880 rpm). The heating time to reach a reaction temperature of 150 °C was 20 min. At the reaction temperature of 150 °C the hydrogen partial pressure was 60 bar and the reaction time 1 h. After the reaction the autoclave was cooled (within 20 min) to room temperature, vented of hydrogen and the aqueous reaction mixture having a pH value of 2.91 was removed. The product mixture was analyzed by gas chromatography (GC) after addition of N,N-dimethylformamide as standard and the obtained results are given in entry 4/2 of Table 4. Emphasis has been placed in all reaction described in Tables 1, 2, 3 and 4 in order to obtain reproducible results.

2.3 Analyses

The purity of the TPPTS ligand was determined by quantitative ³¹P{¹H}NMR analysis in D₂O at 25 °C. δ TPPTS = -5.4 ppm. ³¹P{¹H}NMR spectra (121 MHz, referenced to external 85% H₃PO₄) were recordered on a Varian Unity Plus 300/54 spectrometer. The hydrogenation product γ -valerolactone (GVL) and the side products 1,4-pentanediol (1,4-PDO) and valeric acid (VA) 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 an Agilent 6890N GC coupled with an Agilent 5975B MS. The GC was equipped with a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness). Carrier gas was He with 2 ml min⁻¹. Injector system: pulsed splitless. The injector

Table 1	Effect of reaction time	, platinum precursor	, molar ratio e	of the ligand	to platinum an	nd of the nat	ure of the l	igand on th	e platinum-cata-
lyzed hy	drogenation of levulini	c acid (LA) into γ-va	lerolactone (G	GVL) in comp	letely aqueous	s medium			

Entry	Catalyst precursor	t (h)	L/Pt molar	Conversion	Selectivity	$TOF^{a}(h^{-1})$		
			ratio	LA (mol%)	GVL (mol%)	1,4-PDO (mol%)	VA (mol%)	
1/1 ^{b,c}	Na2PtCl6·6H2O/BPhDS	1	1	50	99.6	0.4	_	151
1/2 ^{b,c}	Na2PtCl6·6H2O/BPhDS	1.6	1	75	99.5	0.5	_	136
1/3 ^b	Na2PtCl6·6H2O/BPhDS	3	1	100	99.3	0.7	_	100
1/4 ^{b,d}	Na2PtCl6·6H2O/BPhDS	6	1	100	99.2	0.8	_	50
1/5 ^c	Na2PtCl6·6H2O/BPhDS	1	1	13	99.2	0.8	_	63
1/6 ^c	PtCl ₂ /BPhDS	1	1	13	98.0	1.0	1.0	52
1/7 ^c	Pt(NH3)4Cl2·H2O/BPhDS	1	1	9	96.5	3.5	_	44
1/8 ^c	PtO2·H2O/BPhDS	1	1	8	97.4	1.3	1.3	38
1/9 ^c	Pt(acac) ₂ /BPhDS	1	1	3	92.4	3.8	3.8	13
1/10 ^c	Na2PtCl6·6H2O/BPhDS	1	2	7	95.5	3.0	1.5	33
1/11 ^c	Na2PtCl6·6H2O/BPhDS	1	3	5	96.0	2.0	2.0	25
1/12 ^c	Na2PtCl6·6H2O/BPhDS	1	4	3	94.2	2.9	2.9	17
1/13 ^e	Na2PtCl6·6H2O/NTA·Na3	1	2	96	97.4	2.6	_	287
1/14 ^{c,e}	Na2PtCl6·6H2O/BPyDCA	1	1	92	99.6	0.4	-	277
1/15 ^{c,e}	Na2PtCl6·6H2O/BPhDS	1	1	91	98.5	1.5	_	273
1/16 ^{c,e}	Na2PtCl6·6H2O/EDTA·Na4	1	1	76	98.07	0.87	1.06	227
1/17 ^e	Na2PtCl6·6H2O/2,6-PyDCA	1	2	74	98.2	1.8	-	222
1/18 ^e	Na2PtCl6·6H2O/3-PSA	1	2	56	98.92	0.48	0.6	167
1/19 ^e	Na2PtCl6·6H2O/3,4-PyDCA	1	2	55	98.7	0.7	0.6	163
1/20 ^{c,e}	Na2PtCl6·6H2O/BQC	1	1	54	96.54	1.11	2.35	162
1/21 ^e	Na2PtCl6·6H2O/Taurine	1	2	51	98.6	1.4	-	154
1/22 ^{c,e}	Na2PtCl6·6H2O/BCDS	1	1	28	98.5	1.0	0.5	83
1/23 ^e	Na2PtCl6·6H2O/SANa	1	2	22	96.1	1.8	2.1	67
1/24 ^e	Na2PtCl6·6H2O/DTPA·Na5	1	1	20	98.3	1.0	0.7	61
1/25 ^e	Na2PtCl6·6H2O/TPPTS	1	2	10	94.2	3.2	2.6	31
1/26 ^e	Na2PtCl6·6H2O/NTPA	1	2	3	94.7	2.6	2.7	8
1/27 ^e	Na ₂ PtCl ₆ ·6H ₂ O/T ₂ PyP	1	1	3	94.9	2.5	2.6	8
1/28 c,e	Na2PtCl6·6H2O/PTA	1	2	2	95.5	1.5	3	5

Reaction conditions: T = 140 °C; $P_{H_2} = 50$ bar; 2.81 mg (0.005 mmol) Na₂PtCl₆·6H₂O; 0.2905 g (2.5 mmol) of LA (molar ratio of LA/Pt=500); 20 ml of deairated demineralised water; pH of the aqueous catalyst phase after the reaction = 2.72–3.80; [Pt]=48 ppm; black precipitate presumed to be metallic platinum; stirring rate = 880 rpm

^aDefined as mole of GVL, 1,4-PDO and VA produced per mole of platinum per hour

^b5.62 mg (0.01 mmol) Na₂PtCl₆·6H₂O; 0.348 g (3 mmol) of LA (molar ratio of LA/Pt=300); [Pt]=96 ppm.

^cMinor amount of metallic platinum

 $^{d}P_{H_{2}} = 60$ bar

 $^{e}T = 150 \text{ °C}; P_{H_2} = 60 \text{ bar}; 2.81 \text{ mg} (0.005 \text{ mmol}) \text{ Na}_2 \text{PtCl}_6 \cdot 6\text{H}_2\text{O}; 0.1742 \text{ g} (1.5 \text{ mmol}) \text{ of LA} (\text{molar ratio of LA/Pt} = 300)$

and detector temperatures were set at 300 °C and 250 °C, respectively. Ms quad: 150 °C, MS source: 230 °C. The oven temperature was initially at 60 °C for 0 min and then increased to 240 °C with a rate of 10 °C min⁻¹. The GC analyses were run on a Shimadzu GC-14B equipped with a FID detector and a HP-Innowax capillary column (30 m × 0.251 mm i.d. × 0.50 µm film thickness) which was purchased from Agilent Technologies. Carrier gas was N₂ at 100 kPa. The oven temperature was initially at 120 °C for 0 min and then increased to 240 °C at 10 °C min⁻¹. The injector and detector temperatures both were set at 240 °C.

Entry	Catalyst precursor	T (°C)	P _{H2} (bar)	LA/Pt molarratio	Conversion	Selectivity			$TOF^{a}(h^{-1})$
					LA (mol%)	GVL (mol%)	1,4-PDO (mol%)	VA (mol%)	
2/1 ^b	Na2PtCl6·6H2O/NTA·Na3	110	50	500	12	98.4	0.8	0.8	62
2/2 ^b	Na2PtCl6·6H2O/NTA·Na3	120	50	500	20	98.2	0.7	1.1	99
2/3 ^b	Na2PtCl6·6H2O/NTA·Na3	130	50	500	57	97.3	1.2	1.5	285
2/4	Na2PtCl6·6H2O/NTA·Na3	140	50	500	67	98.4	0.7	0.9	337
2/5	Na2PtCl6·6H2O/NTA·Na3	150	50	500	100	99.2	-	0.8	500
2/6	Na2PtCl6·6H2O/NTA·Na3	150	20	900	44	98.7	-	1.3	399
2/7	Na2PtCl6·6H2O/NTA·Na3	150	30	900	46	98.0	-	2.0	410
2/8	Na2PtCl6·6H2O/NTA·Na3	150	40	900	77	97.1	-	2.9	689
2/9	Na2PtCl6·6H2O/NTA·Na3	150	50	900	97	96.9	-	3.1	870
2/10	Na2PtCl6·6H2O/NTA·Na3	150	50	800	100	98.0	-	2.0	800
2/11	Na2PtCl6·6H2O/NTA·Na3	150	50	1000	75	98.7	-	1.3	750
2/12	Na2PtCl6·6H2O/NTA·Na3	150	50	1100	62	98.6	-	1.4	686
2/13	Na2PtCl6·6H2O/NTA·Na3	150	50	1200	57	96.8	-	3.2	679
2/14	Na2PtCl6·6H2O/NTA·Na3	150	50	1500	41	98.5	-	1.5	612

Table 2 Effect of temperature, dihydrogen pressure and of the molar ratio of C=O units/Pt on the hydrogenation of levulinic acid (LA) into γ -valerolactone (GVL) in completely aqueous medium

Reaction conditions: t=1 h; 2.81 mg (0.005 mmol) Na₂PtCl₆·6H₂O; 2.74 mg (0.01 mmol) NTA·Na₃ (molar ratio NTA·Na₃/Pt=2); 0.2905 g (2.5 mmol) of LA (molar ratio of LA/Pt=500); 20 ml of deaerated demineralised water; pH of the aqueous catalyst phase after the reaction = 2.94–3.86; [Pt]=48 ppm; black precipitate presumed to be metallic platinum; stirring rate = 880 rpm

^aDefined as mole of GVL, 1,4-PDO and VA produced per mole of platinum per hour

^bMinor amount of metallic platinum

3 Results and Discussion

3.1 Hydrogenation of LA into GVL Using Water-Soluble Platinum Catalysts Modified with Nitrogen-Containing Ligands in Aqueous Media

Homogeneous transition metal catalytic systems applied in the hydrogenation of LA which contains two functional groups (-C=O and -CO₂H) under mild reaction conditions typical for homogeneous catalysis usually are capable to hydrogenate selectively the more reactive functionality among them which is the carbonyl moiety into the alcohol group to form the intermediate 4-hydroxyvaleric acid which subsequently readily undergoes dehydration to yield by highly favorable intramolecular esterification the C_5 cyclic ester product namely GVL (Scheme 1). Due to the high oxygen content and, therefore, the hydrophilicity of levulinic acid the hydrogenation on its C=O group should be carried out in aqueous media. In various studies [27, 54–56] it is proved that the presence of the aqueous solvent has a beneficial effect in LA hydrogenation reactions to GVL catalyzed by heterogeneous and nanoparticles ruthenium based catalytic systems. A joint experimental and theoretical study with DFT calculations for the hydrogenation reaction of LA to GVL catalyzed by heterogeneous ruthenium catalysts in

THF and water have shown that the presence of H-bonded water molecules dramatically reduces the energetic span of the reaction pathway thus enhancing the catalytic activity in the aqueous medium [54]. Another study emphasized that addition of water accelerated the rates in Ru/C-catalyzed hydrogenation reactions of LA to GVL [94]. Moreover, with ruthenium(0) nanoparticle catalysts the highest conversions in LA hydrogenation reactions to GVL were observed in the presence of the aqueous solvent whereas in organic solvents such as 1.4-dioxane, THF, ethanol and methanol significantly lower yields were obtained in this reaction [27, 56]. Heterogeneous platinum based catalytic systems have been usually applied under forcing conditions in the hydrogenation of LA beyond GLV to produce valeric acid (VA, Scheme 2) which in the presence of alcohols under acidic conditions yields alkyl valerates well known as valeric biofuels [57-60]. Lange et al. [57, 58] hydrogenated in the gas-phase LA into GVL over Pt/TiO₂ catalysts with a productivity of 10 $g_{GVL} g_{cat}^{-1} h^{-1}$ and selectivity to GVL over 95 mol% with negligible deactivation over 100 h at 200 °C and 40 bar hydrogen. In the next gas-phase transformation step GVL was hydrogenated over Pt/H-ZSM-5 catalysts into VA with a productivity of 2 $g_{VA} g_{cat}^{-1} h^{-1}$ and selectivity towards VA over 90 mol% at 250 °C and 10 bar H₂ pressure. This performance could be kept for more than 1500 h with catalyst regeneration at 400 °C and 10 bar hydrogen

Entry	Catalyst precursor	Water (ml)	Salts	Salt/Pt molar ratio	LA/Pt	pH value	Conversion	Selectivity			$TOF^{a}\left(h^{-1}\right)$
					molar ratio		LA (mol%)	GVL (mol%)	1,4-PDO (mol%)	VA (mol%)	
3/1 ^b	Na2PtCl6.6H2O/NTA·Na3	20	. 1	1	2000	3.26	41	98.3	I	1.7	816
3/2	Na2PtCl ₆ ·6H2O/NTA·Na3	40	I	I	2000	3.18	67	99.1	I	0.9	1338
3/3	Na2PtCl6.6H2O/NTA-Na3	40	NaI	100	2000	3.01	4	97.5	I	2.5	80
3/4	Na2PtCl ₆ ·6H2O/NTA·Na3	40	NaCl	100	2000	3.07	26	98.1	I	1.9	528
3/5°	Na2PtCl6.6H2O/NTA·Na3	40	$MgCl_2.6H_2O$	50	2000	3.13	52	98.6	0.6	0.8	1036
3/6	Na2PtCl6.6H2O/NTA-Na3	40	AICl ₃ ·6H ₂ O	33	2000	2.26	84	9.66	I	0.4	1682
3/7	Na2PtCl ₆ ·6H2O/NTA·Na3	40	AICI ₃ $\cdot 6H_2O$	17	2000	2.55	100	7.66	I	0.3	2000
3/8	Na2PtCl6.6H2O/NTA·Na3	40	AICl ₃ ·6H ₂ O	17	3000	2.52	67	98.8	I	1.2	2007
3/9°	Na2PtCl ₆ ·6H2O/NTA·Na3	40	AICl ₃ ·6H ₂ O/NaH ₂ PO ₄ ·H ₂ O	17/100	3000	2.70	2	94.7	I	5.3	57
$3/10^{d}$	Na2PtCl ₆ ·6H2O/NTA·Na3	40	AICl ₃ ·6H ₂ O/NaH ₂ PO ₄ ·H ₂ O	17/100	3000	7.03	1	80	I	20	15
3/11 ^{c,d}	Na2PtCl ₆ .6H2O/NTA·Na3	40	AlCl ₃ $\cdot 6H_2O$	17	3000	10.40	1	90.9	I	9.1	33
Reactic	on conditions: $T = 150 \circ C$; $P_{\rm E}$	$f_1^{4} = 50$ bar; t	= 1 h; 1.40 mg (0.0025 mmol) N	a ₂ PtCl ₆ .6H ₂ O; 1.37	mg (0.005	mmol) NTA	-Na ₃ (molar ra	atio NTA·Na ₃ //	Pt=2); [Pt]:	= 12 ppm; blac	k precipitate
^a Define	ed to be inetained platinum, s ad as mole of GVL, 1,4-PDO	and VA proc	duced per mole of platinum per h	our							
^b [Pt]=	24 ppm										
°Minor	amount of metallic platinum	_									
3 MHdp	as adjusted with 5% aqueous	NaOH									

aqueous medium and recycling experiments of the water-soluble catalyst in aqueous/organic two-phase systems

Entry	Catalyst precursor	L/Pt	LA/Pt	Al/Pt	Conversion	Selectivity			$TOF^{a}(h^{-1})$
		molar ratio	molar ratio	molar ratio	LA (mol%)	GVL (mol%)	LA (mol%)	GVL (mol%)	
4/1	Na ₂ PtCl ₆ ·6H ₂ O/BPhDS/ AlCl ₃ ·6H ₂ O	1	4000	17	23	99.1	0.9	_	910
4/2	Na ₂ PtCl ₆ ·6H ₂ O/BPhDS/ AlCl ₃ ·6H ₂ O	1	4000	0.17	89	100	-	_	3540
4/3	Na ₂ PtCl ₆ ·6H ₂ O/BPhDS/ AlCl ₃ ·6H ₂ O	2	4000	0.17	42	98.6	0.9	0.5	1670
4/4 ^b	Na ₂ PtCl ₆ ·6H ₂ O/BPhDS/ AlCl ₃ ·6H ₂ O	3	4000	0.17	26	99.7	0.3	_	1040
4/5 ^b	Na ₂ PtCl ₆ ·6H ₂ O/BPhDS/ AlCl ₃ ·6H ₂ O	3	1000	0.17	100	100	-	_	1000
4/6 ^{b,c}	Recycled catalyst	3	1000	0.17	100	99.2	0.8	-	1000

Reaction conditions: T=150 °C; $P_{H_2}=60$ bar; t=1 h; 2.81 mg (0.005 mmol) Na₂PtCl₆·6H₂O; 20 ml of deairated demineralised water; pH of the aqueous catalyst phase after the reaction=2.59–3.0; [Pt]=44–47 ppm; black precipitate presumed to be metallic platinum; stirring rate=880 rpm

^aDefined as mole of GVL, 1,4-PDO and VA produced per mole of platinum per hour

^bMinor amount of metallic platinum

^cThe aqueous catalyst layer (20 ml) of entry 4/4, after extraction with 5 ml of diethyl ether and separation of the upper organic phase, was reused with addition of a new portion of 0.581 g (5 mmol C=O units) of LA



Scheme 2 Hydrogenation of LA beyond GLV to produce 1,4-pentanediol (1,4-PDO) and valeric acid (VA) catalyzed by water-soluble platinum catalysts modified with nitrogen-containing ligands in aqueous media

pressure. The final step is esterification of VA with alcohols to valeric acid esters by an acidic ion-exchange resin catalyst. Lange et al. [57, 58] further reported the one-step conversion of GVL into valeric esters over Pt or Pd/TiO₂ catalysts with a selectivity of 20–50 mol% pentyl valerate at 275–300 °C. The group of Shimizu [59] described the one-pot hydrogenation of LA catalyzed by Pt/H-ZSM-5 at 200 °C and 8 bar H₂ pressure to yield under solvent-free conditions up to 99 mol% of VA and with methanol as solvent changed the selectivity resulting to 87 mol% of methyl

valerate. Gu et al. [60] also synthesized Pt/H-ZSM-5 catalyst and applied in the aqueous-phase hydrogenation of LA at 200 °C and 10 bar hydrogen pressure to yield up to 91.4 mol% of VA.

We chose water-soluble nitrogen-containing ligands to modify platinum catalysts and applied in the LA hydrogenation reaction in aqueous media because nitrogen-containing ligands have the great advantage that they are low price compounds and because such catalytic systems have not been applied until now in aqueous-phase catalytic conversions at all and because of the superior activity of palladium catalysts modified with nitrogen-containing ligands compared with TPPTS benchmark modifier in the hydrogenation reaction of renewable polyunsaturated methyl esters of soybean oil into their monounsaturated counterparts in aqueous/ organic two-phase micellar systems [61] and also because of the higher catalytic activity exhibited ruthenium catalysts modified with water-soluble nitrogen-containing ligands in the aqueous-phase hydrogenation reaction of LA into GVL compared with ruthenium catalysts modified with watersoluble phosphines such as TPPTS and T₂PyP (Fig. 1) in aqueous media [44]. To our knowledge, the only example of an aqueous-phase catalytic hydrogenation reaction using water-soluble Pt/TPPTS catalysts is the selective hydrogenation of polyunsaturated methyl esters of vegetable oils into their monounsaturated counterparts with low formation of undesired trans-isomers in aqueous/organic two-phase systems [62]. Moreover, we chose water-soluble nitrogencontaining ligands such as BPhDS, taurine etc. (Fig. 1) to modify platinum catalysts for the hydrogenation of LA to GVL because such catalytic systems are not susceptible to air oxygen and palladium catalysts modified with nitrogencontaining ligands such as BPhDS and taurine have been applied even in aerobic oxidation reactions of terminal olefins to methyl ketones in aqueous media [63, 64].

We have studied the influence of operating reaction parameters such as the reaction time, nature of platinum precursors, molar ratio of ligand/platinum, nature of ligands, temperature, hydrogen pressure, the molar ratio of LA/Pt, added aqueous solvent, salts, the pH value and the molar ratio of AlCl₃·6H₂O/Pt on the hydrogenation reaction of LA in order to achieve high catalytic activities and selectivities to GVL and performed recycling experiments to prove the stability of the water-soluble platinum catalyst modified with nitrogen-containing ligands and aluminum in aqueous media.

3.1.1 Effect of Reaction Time

First, we investigated the influence of the reaction duration on the hydrogenation of LA catalyzed by water-soluble Na₂PtCl₆·6H₂O catalysts precursors modified with the nitrogen-containing ligand bathophenanthrolinedisulfonic acid disodium salt (BPhDS, Fig. 1) at molar ratios of LA/Pt=300 and of ligand/platinum=1, a reaction temperature of 140 °C, 50 bar H₂ pressure and addition of 20 ml of deairated demineralized aqueous solvent with a platinum concentration of 96 ppm in water in the absence of any added organic solvent (Table 1, entries 1/1–1/4). The hydrogenation of LA started immediately with hydrogen consumption without an induction period of the reaction. Therefore, no prereduction of the Pt/BPhDS catalyst was carried out and only made sure that the reaction conditions were well chosen in order to obtain reproducible results. All the following experiments were carried out systematically without a prior prereduction of the Pt/BPhDS catalyst. The conversion of LA increases with increasing reaction time from 1 up to 6 h to give values from 50 up to 100 mol% with very high selectivities towards GVL from 99.2 up to 99.6 mol% in aqueous media (Table 1, entries 1/1-1/4). Even at a longer reaction time of 6 h the selectivity of GVL remained high (99.2 mol%) with a small formation of the side product 1,4-pentanediol (1,4-PDO) of only 0.8 mol% (entry 1/4) which is obtained from Pt/ BPhDS-catalyzed hydrogenation of GVL (Scheme 2). The reaction pathway for the formation of 1,4-PDO from GVL hydrogenation has been described by Geilen et al. [33] and involves hydrogenation of the C=O bond of GVL to form the cyclic hemiacetal compound which is in equilibrium with the open 4-hydroxypentanal form followed by further hydrogenation of the carbonyl functional group to yield 1,4-PDO (Scheme 2). After the hydrogenation reaction with a duration of 1 and 1.6 h a minor amount of metallic platinum was observed indicating to a minor extent decomposition of the Pt/BPhDS catalyst (entries 1/1, 1/2) whereas at longer reaction times from 3 up to 6 h larger amounts of metallic platinum were formed at the end of the reaction (entries 1/3, 1/4).

3.1.2 Effect of Platinum Precursor and of BPhDS/Pt Molar Ratio

The water-soluble Na₂PtCl₆·6H₂O/BPhDS and $Pt(NH_3)_4Cl_2 \cdot H_2O/BPhDS$ catalyst precursors were synthesized by dissolving under stirring Na₂PtCl₆·6H₂O or Pt(NH₃)₄Cl₂·H₂O with BPhDS under argon in 20 ml deairated demineralized water within 10 min of time at room temperature. After addition of LA to the aqueous catalyst solution under stirring for further 5 min at room temperature the reaction mixture was than charged into an Autoclave Engineers autoclave and was further proceeded as described in Sect. 2.2. The synthesis of the catalyst precursors PtCl₂/ BPhDS, PtO₂·H₂O/BPhDS and Pt(acac)₂/BPhDS was carried out with a different procedure due to the low solubility of these platinum precursors in water at room temperature. The autoclave was direct loaded under argon with the platinum precursor, BPhDS, deairated demineralized water and LA and subsequently was closed. After a number of pressurising-depressurising cycles with hydrogen to remove last traces of air oxygen under stirring, the autoclave was pressured and contents were heated with stirring. The synthesis of these water-soluble platinum catalyst precursors takes place under the reaction conditions namely a temperature of 140 °C and a hydrogen pressure of 50 bar. In the aqueousphase hydrogenation reaction of LA in the presence of watersoluble platinum catalysts modified with BPhDS ligands the catalytic activity of platinum precursors decreased in the order: $Na_2PtCl_6 \cdot 6H_2O > PtCl_2 > Pt(NH_3)_4Cl_2 \cdot H_2O > Pt$ $O_2 \cdot H_2O > Pt(acac)_2$ to give TOF values of 63 h⁻¹, 52 h⁻¹, 44 h⁻¹, 38 h⁻¹ and 13 h⁻¹, respectively, at molar ratios of LA/Pt = 500 and of ligand/platinum precursor = 1, a reaction temperature of 140 °C, 50 bar H₂ pressure and addition of 20 ml of deairated demineralized aqueous solvent with a platinum concentration of 48 ppm in water within 1 h of reaction time (Table 1, entries 1/5–1/9). With the water-soluble platinum catalysts precursors Na₂PtCl₆·6H₂O/BPhDS and Pt(NH₃)₄Cl₂·H₂O/BPhDS the selectivity towards GVL was 99.2 and 96.5 mol%, respectively, with a formation of only one side product namely 1,4-PDO with a selectivity of 0.8 mol% and 3.5 mol%, respectively (entries 1/5,1/7). In contrast, using the water-soluble PtCl₂/BPhDS, PtO₂·H₂O/ BPhDS and Pt(acac)₂/BPhDS catalyst precursors the selectivity of GVL was 92.4-98.0 mol% and of 1,4-PDO from 1.0 up to 3.8 mol% with, however, formation of a second side product namely valeric acid (VA, Scheme 2) which was obtained with a selectivity from 1.0 up to 3.8 mol% (entries 1/6, 1/8 and 1/9). According to the mechanism proposed by the group of Dumesic [65, 66] protonation of GVL leads to ring-opening of GVL through intermedites bearing carbenium ions to produce pentenoic acid which is subsequently hydrogenated to yield VA (Scheme 2). After the hydrogenation reactions with all applied water-soluble platinum catalyst precursors a minor amount of metallic platinum was observed indicating to a minor extent decomposition of the Pt/BPhDS catalysts (entries 1/5-1/9).

We further investigated the influence of the molar ratio of L/Pt on the hydrogenation of LA catalyzed by water-soluble Na₂PtCl₆·6H₂O precursors modified with the nitrogencontaining ligand BPhDS at a molar ratio of LA/Pt=500, a reaction temperature of 140 °C, 50 bar H₂ pressure and addition of 20 ml of deairated demineralized aqueous solvent with a platinum concentration of 48 ppm in water within 1 h of reaction time (Table 1, entries 1/5 and 1/10-1/12). As expected, the highest catalytic activity with a turnover frequency (TOF) of 63 h⁻¹ was obtained at a low BPhDS/ Pt molar ratio of 1 (entry 1/5) whereas at increasing ligand/ platinum molar ratios the catalytic activity decreases to give at a molar ratio of BPhDS/Pt = 4 a TOF value of 17 h^{-1} (entry 1/12). This lower catalytic activity at higher BPhDS/ Pt molar ratios could probably be rationalized by assuming that a competition between the free BPhDS ligand and the C=O units of LA for a coordination site on platinum takes place which may lead to a retardation in the activation of the LA hydrogenation reaction. Similarly, the group of Joó [67] also observed a retarding effect of excess of water-soluble TPPMS ligand added to ruthenium precursor in Ru/TPPMS-catalyzed hydrogenation reactions in aqueous media. Moreover, the group of Sheldon [63, 64] has shown in Pd/BPhDS-catalyzed aerobic oxidation reactions of terminal olefins to methyl ketones in aqueous media that the best results were also obtained at a BPhDS/Pd molar ratio of 1. The Pt/BPhDS-catalyzed hydrogenation reaction of LA is highly selective to give at the low L/Pt molar ratio of 1 a selectivity towards GVL of 99.2 mol% (entry 1/5) and at the higher molar ratio of BPhDS/Pt=4 the selectivity to GVL remained relative high (94.2 mol%) with a formation of 2.9 mol% of both side products 1,4-PDO and VA (entry 1/12). After the hydrogenation reactions a minor amount of metallic platinum formation was observed at the molar ratios of BPhDS/Pt=1–4 indicating to a minor extent decomposition of the Pt/BPhDS catalysts (entries 1/5 and 1/10–1/12).

3.1.3 Effect of the Nature of Ligands

Table 1, entries 1/13–1/28 show the activity and selectivity of in-situ formed water-soluble platinum catalysts in the hydrogenation of LA as a function of different phosphines, P^N chelating and various nitrogen-containing ligands (Fig. 1) in aqueous media. The highest catalytic activity $(TOF = 287 h^{-1})$ with a conversion of LA of 96.0 mol% and selectivities towards GVL of 97.4 mol% and 1,4-PDO of 2.6 mol% in the hydrogenation reaction of LA was achieved with Na₂PtCl₆·6H₂O precursors modified with water-soluble nitrilotriacetic acid trisodium salt (NTA·Na₃) ligands (Fig. 1) at molar ratios of LA/Pt = 300 and NTA \cdot Na₂/Pt = 2, a reaction temperature of 150 °C under 60 bar hydrogen pressure within 1 h of reaction time and addition of 20 ml of deairated demineralized water with a platinum concentration of 48 ppm in the aqueous phase (Table 1, entry 1/13). In contrast, the catalytic activity exhibited the Na₂PtCl₆·6H₂O precursor modified with the TPPTS benchmark ligand (Fig. 1) was much lower (TOF=31 h^{-1}) with a conversion of LA of 10.0 mol% and selectivity to GVL of 94.2 mol%, to 1,4-PDO of 3.2 mol% and to VA of 2.6 mol% under the same conditions in this hydrogenation reaction (Table 1, entry 1/25). Catalytic activities in the range from 277 to 222 TOF's per hour with high selectivities towards GVL of 99.6–98.07 mol% were obtained with Na₂PtCl₆·6H₂O precursors modified with water-soluble 2,2'-bipyridine-4,4'-dicarboxylic acid (BPyDCA, Fig. 1), bathophenanthrolinedisulfonic acid disodium salt (BPhDS), ethylenediaminetetraacetic acid tetrasodium salt (EDTA·Na₄) and 2,6-pyridinedicarboxylic acid (2,6-PyDCA) ligands in the hydrogenation of LA in aqueous medium (Table 1, entries 1/14–1/17). The catalytic hydrogenation activity exhibited Na₂PtCl₆·6H₂O precursors modified with the watersoluble nitrogen-containing ligands 3-pyridinesulfonic acid (3-PSA), 3,4-pyridinedicarboxylic acid (3,4-PyDCA), 2,2'-biguinoline-4,4'dicarboxylic acid dipotassium salt (BQC), 2-aminoethanesulfonic acid (Taurine), bathocuproinedisulfonic acid disodium salt (BCDS), sulfanilic acid sodium salt (SANa) and diethylenetriaminepentaacetic acid pentasodium salt (DTPA·Na₅) were in the range of

167 and 61 TOF's per hour and the selectivities to GVL of 98.92–96.1 mol% (Table 1, entries 1/18–1/24) which are still higher than the catalytic activity (TOF = 31 h^{-1}) exhibited the Na₂PtCl₆·6H₂O/TPPTS catalyst (Table 1, entry 1/25). Using the water-soluble ligands nitrilotris(methylphosphonic acid) (NTPA), tris(2-pyridyl)phosphine (T_2PyP) and 1,3,5-triaza-7-phosphaadamantane (PTA) as modifiers of Na₂PtCl₆·6H₂O precursors the catalytic LA hydrogenation activities obtained were very low from 8 to 5 TOF's per hour (Table 1, entries 1/26-1/28). After the hydrogenation reaction of LA into GVL catalyzed by Na₂PtCl₆·6H₂O precursors modified with water-soluble BPyDCA, BPhDS, EDTA·Na₄, BQC, BCDS and PTA ligands a formation of a minor amount of metallic platinum was observed indicating to a minor extent decomposition of the catalyst (entries 1/14-1/16, 1/20, 1/22 and 1/25) whereas in the presence of the other water-soluble ligands more metallic platinum was formed after the reaction. In general, in the aqueousphase hydrogenation reaction of LA the catalytic activities exhibited Na₂PtCl₆·6H₂O precursors modified with watersoluble phosphines such as TPPTS and PTA were much lower with 31 and 5 TOF's per hour, respectively (Table 1, entries 1/25 and 1/28) compared with the catalytic activities exhibited with nitrogen-containing ligands such as NTA·Na₃, BPyDCA and BPhDS with 287, 277 and 273 TOF's per hour, respectively (entries 1/13-1/15). In order to explain the higher catalytic activities exhibited water-soluble platinum catalysts modified with nitrogen-containing ligands compared with their platinum phosphine counterparts in the aqueous-phase hydrogenation reaction of LA to GVL we consider the mechanistic study by Geilen et al. [68] for the homogeneous LA hydrogenation reaction catalyzed by [Ru(TriPhos)H]⁺ in ionic liquids. In this reaction mechanism [68] hydride transfer from the Ru-H group of the catalyst to the carbon atom of coordinated C=O functionality of the starting material LA takes place followed by protonation of the resulting Ru-OR moiety via σ -bond metathesis from a nonclassical coordinated dihydrogen molecule, η^2 -H₂, regenerating at the same time the catalytically active classical ruthenium hydride, namely the Ru-H functionality. Geilen et al [68] mentioned that the heterolytic cleavage of the nonclassical coordinated dihydrogen molecule η^2 -H₂ and the associated protonation of the Ru-OR group may be assisted by basic centers or solvents which may reduce the energy barrier for both the cleavage and protonation steps even further. According to this mechanism [68] the results obtained in the aqueous-phase platinum-catalyzed LA hydrogenation reaction were rationalized by assuming that in the presence of nitrogen-containing compounds which act both as ligands to platinum and as bases their N-atoms facilitates both steps the heterolytic cleavage of coordinated dihydrogen molecule η^2 -H₂ and the associated protonation of the Pt-OR group to obtain GVL with higher reaction rates compared

with platinum catalysts modified with phosphines because phosphines are weaker bases compared with their nitrogencontaining counterparts. Moreover, in the aqueous-phase platinum-catalyzed hydrogenation reaction of LA the nature of the highly polar aqueous medium could also facilitate both steps the heterolytic cleavage of coordinated dihydrogen molecule and the associated protonation of the Pt-OR moiety to obtain GVL as described in the above mentioned reaction mechanism [68].

3.1.4 Effect of Temperature, Hydrogen Pressure and Molar Ratio LA/Pt

The catalytic activity in the Na₂PtCl₆·6H₂O/NTA·Na₃-catalyzed hydrogenation of LA to GVL increases with increasing temperature from 110 °C up to 150 °C to give TOFs from 62 up to 500 h^{-1} with conversions of LA from 12 up to 100 mol%, respectively, and high selectivities to GVL from 97.3 up to 99.2 mol% with 1,4-PDO formations of 0.7 up to 1.2 mol% and VA formations from 0.8 up to 1.5 mol% at a molar ratio of LA/Pt = 500 and NTA·Na₂/Pt = 2 under 50 bar H₂ pressure and a platinum concentration of 48 ppm in water within 1 h reaction time in aqueous medium (Table 2, entries 2/1-2/5). Using the Na₂PtCl₆·6H₂O/NTA·Na₃ catalytic system after the hydrogenation reaction a formation of a minor amount of metallic platinum was observed at reaction temperatures from 110 up to 130 °C indicating to a minor extent decomposition of the catalyst (entries 2/1-2/3) whereas at higher temperatures of 140 °C and 150 °C more metallic platinum was formed after the reaction (entries 2/4 and 2/5). The apparent Arrhenius parameter of the activation energy of the Pt/NTA·Na₃-catalyzed hydrogenation reaction of LA in aqueous media was calculated from results obtained from hydrogenation reactions carried out at temperatures 110-150 °C and are summarized in Table 2, entries 2/1-2/5. The apparent activation energy which was calculated with these data (Fig. 2) amounts to a relative low value of 73.04 kJ/mol when one considers that in the LA hydrogenation reaction this catalyst reduces a less reactive keto group into alcohol functionality.

The hydrogen pressure has a pronounced effect on the activity in the Na₂PtCl₆·6H₂O/NTA·Na₃-catalyzed hydrogenation reaction of LA and is shown in Table 2, entries 2/6–2/9. The catalytic activity increased from TOF=399 h⁻¹ up to TOF = 870 h⁻¹ and the selectivity towards GVL decreased from 98.7 mol% down to 96.9 mol% with increasing hydrogen partial pressure from 20 to 50 bar at a reaction temperature of 150 °C, molar ratios of LA/Pt=500 and of NTA·Na₃/Pt=2 and a platinum concentration of 48 ppm in water within 1 h reaction time in the aqueous monophasic system. At the low hydrogen pressure of 20 bar the selectivity to VA was 1.3 mol% and with increasing pressure the

Fig. 2 Calculation of the apparent Arrhenius parameter of the activation energy of the hydrogenation reaction of LA catalyzed by water-soluble Pt/NTA·Na₃ catalysts in aqueous media



selectivity to VA increased to give under 50 bar hydrogen pressure 3.1 mol% of VA (entries 2/6–2/9).

The effect of LA/Pt molar ratio in the Na₂PtCl₆·6H₂O/ NTA·Na₃-catalyzed hydrogenation of LA to GVL in aqueous media is shown in Table 2, entries 2/9-2/14. The catalytic activity increased from TOF = 800 h⁻¹ to TOF = 870 h⁻¹ while the selectivity to GVL decreased from 98.0 mol% to 96.9 mol% with increasing molar ratios of LA/Pt from 800 to 900 at a reaction temperature of 150 °C, 50 bar hydrogen pressure, a molar ratio of NTA·Na₃/Pt = 2 at a platinum concentration of 48 ppm in water within 1 h in the hydrogenation of LA in aqueous media (Table 2, entries 2/10 and 2/9). Raising the LA/Pt molar ratio higher has a negative effect on the reaction rate in the aqueous-phase hydrogenation of LA. Thus, the catalytic activity decreased from TOF = 750 h⁻¹ down to TOF = 612 h⁻¹ with increasing LA/Pt molar ratios from 1000 up to 1500 (entries 2/11–2/14).

3.1.5 Effect of Added Aqueous Solvent, Salts and of the pH Value

The amount of added aqueous solvent has a pronounced effect on the activity in the Na₂PtCl₆·6H₂O/NTA·Na₃-catalyzed hydrogenation reaction of LA and is shown in Table 3, entries 3/1 and 3/2. The catalytic activity increased from TOF = 816 h⁻¹ to TOF = 1338 h⁻¹ with increasing amount of added water as a solvent from 20 to 40 ml at a low platinum concentration of 24 and 12 ppm, respectively, a reaction temperature of 150 °C, 50 bar hydrogen pressure, molar ratios of LA/Pt = 2000 and of NTA·Na₃/Pt = 2 within 1 h reaction time in the aqueous monophasic system (entries 3/1 and 3/2). The effect of higher catalytic activity at higher amount of added water could probably be explained by the nature of the highly polar aqueous medium which could facilitate both steps the heterolytic cleavage of coordinated dihydrogen molecule on catalytically active platinum key intermediates and the associated protonation of the Pt-OR moiety to obtain GVL which were suggested according to the reaction mechanism of Geilen et al. [68] for the Rucatalyzed LA hydrogenation and were used to explain our results and mentioned in detail in part Sect. 3.1.3.

Addition of a salt with a strongly coordinating anion such as NaI has a detrimental effect on the catalytic activity of the Na₂PtCl₆·6H₂O/NTA·Na₃ system to obtain a TOF value of 80 h^{-1} (Table 3, entry 3/3) compared with the high activity of TOF = 1338 h^{-1} exhibited by the Na₂PtCl₆·6H₂O/ NTA·Na₃ in the absence of the salt (entry 3/2) in the hydrogenation reaction of LA at a reaction temperature of 150 °C under 50 bar of hydrogen pressure and molar ratios of LA/ Pt = 2000, $NTA \cdot Na_3/Pt = 2$ and NaI/Pt = 100, addition of 40 ml of deairated demineralized water with a platinum concentration of only 12 ppm in water within 1 h of reaction time. In the presence of NaCl, containing the same cation but a less strongly coordinating anion compared to NaI, the catalytic activity increased to obtain 528 TOF's per hour in the Na₂PtCl₆·6H₂O/NTA·Na₃-catalyzed hydrogenation of LA in aqueous medium (entry 3/4). Compared to the low catalytic activities (TOF values 80 and 528 h^{-1}) exhibited Na₂PtCl₆·6H₂O/NTA·Na₃ catalysts in the LA hydrogenation in the presence of monovalent alkali metal salts NaI and NaCl at molar ratios of salt/Pt = 100 (entries 3/3 and 3/4) the addition of the bivalent alkaline earth metal salt, MgCl₂·6H₂O, at a molar ratio of MgCl₂·6H₂O/Pt = 50, gives rise to an increase in catalytic activity to reach 1036 TOF's per hour (entry 3/5).

The hydrogenation of LA catalyzed by Na₂PtCl₆·6H₂O/ NTA·Na₃/AlCl₃·6H₂O systems is influenced by the pH value of the aqueous phase (Table 3, entries 3/8–3/11). The highest catalytic activity (TOF=2007 h⁻¹) was achieved under acidic conditions at pH 2.52 in the absence of any added buffer (entry 3/8) whereas with addition of NaH₂PO₄·H₂O at pH 2.70 the activity drops to 57 TOFs per hour (entry 3/9). This high decrease in catalytic activity from 2007 down to 57 TOF's per hour could probably be explained with the increased ionic strength of the solution due to the presence of added $NaH_2PO_4 \cdot H_2O$ salt at a molar ratio of salt/Pt = 100. It is well known in the field of aqueous-phase catalysis that addition of different salts as a means to increase the solution ionic strength gives rise to a dramatic drop in catalytic activity of e.g. water-soluble Rh/TPPTS catalysts in aqueous-phase hydroformylation reaction of olefins [69], water-soluble Pd/TPPTS catalysts in aqueous-phase carbonylations reactions of 5-hydroxymethylfurfural (HMF) [70–72] and of 1-(4-isobutylphenyl)ethanol to yield ibuprofen [73, 74] and of water-soluble Pt/TPPTS, Ru/TPPTS and Rh/TPPTS catalysts in aqueous-phase hydrogenation reactions of polyunsaturated methyl esters of vegetable oils into their monounsaturated counterparts and of benzene into cyclohexane [62, 75-80]. The hydrogenation reaction of LA catalyzed by Na₂PtCl₆·6H₂O/NTA·Na₃/AlCl₃·6H₂O systems was carried out with addition of NaH₂PO₄·H₂O salt under acidic conditions at pH 2.70 (entry 3/9) in order to be able to study the effect of pH value under similar conditions because for the adjustment of pH 7.03 it is necessary to add the NaH₂PO₄·H₂O salt to create the NaH₂PO₄/NaOHbuffer. The catalytic activity was slightly lower under neutral conditions at pH 7.03 adjusted by a NaH₂PO₄/NaOH-buffer $(TOF = 15 h^{-1}, entry 3/10)$ and slightly increased under basic conditions at pH 10.40 to give a TOF of 33 h^{-1} (entry 3/11).

3.1.6 Effect of AlCl₃·6H₂O Addition and of Molar Ratio Al/Pt on LA Hydrogenation Reaction

In the presence of the trivalent salt AlCl₃·6H₂O at a molar ratio of $AlCl_3 \cdot 6H_2O/Pt = 33$, the catalytic activity considerably increased in the Na₂PtCl₆·6H₂O/NTA·Na₃-catalyzed hydrogenation reaction of LA in water to reach a value of 1682 TOF's per hour (entry 3/6). At a lower molar ratio of AlCl₃·6H₂O/Pt = 17 the activity in the Na₂PtCl₆·6H₂O/ NTA·Na₃-catalyzed LA hydrogenation reaction further increased to achieve a value of $TOF = 2000 h^{-1}$ (entry 3/7) and at the higher molar ratio of LA/Pt = 3000 the activity in Na₂PtCl₆·6H₂O/NTA·Na₃/AlCl₃·6H₂O-catalyzed LA hydrogenation reaction could be slightly increased up to $TOF = 2007 h^{-1}$ in the aqueous medium (entry 3/8). In the presence of Na₂PtCl₆·6H₂O/BPhDS catalysts after the hydrogenation reaction of LA a minor amount of metallic platinum was observed indicating to a minor extent decomposition of the catalyst (entry 1/15) whereas with Na2PtCl6·6H2O/NTA·Na3 catalysts more metallic platinum was formed after the reaction indicating to a higher extent decomposition of this catalyst (entry 1/13). Therefore, we selected the more stable Na₂PtCl₆·6H₂O/BPhDS catalyst to investigate further the influence of the molar ratio of AlCl₃· $6H_2O/Pt$ at the higher molar ratio of LA/Pt = 4000 in the aqueous medium (Table 4, entries 4/1 and 4/2). In the Na₂PtCl₆·6H₂O/BPhDS/AlCl₃·6H₂O-catalyzed hydrogenation reaction of LA at 150 °C under 60 bar of hydrogen and molar ratios of LA/Pt = 4000, BPhDS/Pt = 1 and AlCl₃·6H₂O/Pt = 17, addition of 20 ml of deairated demineralized water with a platinum concentration of 44 ppm in water within 1 h of reaction time the catalytic activity was TOF = 910 h⁻¹ (entry 4/1) whereas at the lower molar ratio of AlCl₃·6H₂O/Pt = 0.17 an exceptionally high catalytic activity was achieved which was as high as 3540 TOF's per hour (entry 4/2).

This remarkable effect of the enormous increase in catalytic activity in water in the presence of aluminum in the Na₂PtCl₆·6H₂O/BPhDS-catalyzed LA hydrogenation could probably be rationalized by assuming that the Lewis acid aluminum strongly influences platinum catalytic active key intermediates species in the way that it facilitates the step of heterolytic cleavage of coordinated dihydrogen molecule, η^2 -H₂, on platinum and also the protonation step of the Pt-OR moiety to yield GVL in the way that aluminum may facilitates the formation of the classical platinum hydride, Pt-H, functionality. These platinum catalytically active key intermediates were suggested according to the reaction mechanism of Geilen et al. [68] for the Ru-catalyzed LA hydrogenation and were used to explain our results as mentioned in detail in part Sect. 3.1.3. It may also be possible that aluminum salts of levulinic acid are formed in the highly polar aqueous medium which promotes their coordination on platinum and also the formation of the above mentioned platinum catalytic active key intermediate species and in this way increase the rates in the LA hydrogenation reaction. We cannot exclude, however, an alternative mechanism involving the ability of aluminum to abstract an anionic ligand such as Cl⁻ from coordination sphere of platinum complex rendering that complex cationic with formation of a corresponding non-coordinating aluminate counter anion and in this way enormously increases the rates in the LA homogeneous hydrogenation reaction. It is well known in the literature that the presence of the Lewis acid aluminum could facilitate the abstraction of an anionic ligand from coordination sphere of a transition metal catalytic complex rendering that complex cationic with formation of a corresponding non-coordinating aluminate counter anion and in this way considerably increases the rates in the homogeneous catalytic reaction. For example, Williams et al. [81] applied highly efficient homogeneous $Pd(PPh_3)_2(OAc)_2$ catalysts with Al(OTf)₃ promotors instead of the classical Brønsted acid cocatalysts in the methoxycarbonylation of styrene and explained the high catalytic activity by assuming that the Lewis acid Al(OTf)₃ dissociates the acetate anionic ligand from the coordination sphere of the palladium complex making that complex cationic with formation of a noncoordinating aluminate $[(AcO)Al(OTf)_3]^-$ counter anion.

It should be also mentioned that, the higher catalytic activity exhibited Na₂PtCl₆·6H₂O/NTA·Na₃ catalysts in the LA hydrogenation to GVL in water in the presence of AlCl₃·6H₂O with TOF = 1682 h⁻¹ (entry 3/6) compared with the activity of TOF = 1036 h⁻¹ (entry 3/5) in the presence of MgCl₂·6H₂O could probably be explained because aluminum is a stronger Lewis acid compared to magnesium.

3.1.7 Recycling Experiments of the Pt/BPhDS/Al Catalyst

In the aqueous-phase catalytic hydrogenation reaction of LA in the presence of Na₂PtCl₆·6H₂O/BPhDS/AlCl₃·6H₂O catalysts at the molar ratio of BPhDS/Pt=1 after the reaction an amount of metallic platinum was formed indicating to an extent decomposition of the catalyst (entry 4/2). Therefore, we carried out hydrogenation reactions of LA at higher BPhDS/Pt molar ratios in order to increase the stability of the Na₂PtCl₆·6H₂O/BPhDS/AlCl₃·6H₂O catalyst in the polar aqueous medium. At a molar ratio of BPhDS/ Pt=2 the catalytic activity was $TOF=1670 h^{-1}$ with some decomposition of the catalyst after the reaction (entry 4/3) whereas at the higher molar ratio of BPhDS/Pt = 3 the catalytic activity was lower (TOF = 1040 h^{-1}) with, however, a minor amount of metallic platinum formation after the reaction indicating a higher stability of the catalyst under these reaction conditions in the aqueous reaction mixture (entry 4/4). Therefore, the recycling experiments of the Na₂PtCl₆·6H₂O/BPhDS/AlCl₃·6H₂O catalyst were carried out at a molar ratio of BPhDS/Pt = 3 due to the higher stability of the in-situ formed water-soluble platinum/bidentate ligand/aluminum catalyst in the aqueous medium.

A recycling experiment with a consecutive run were carried out in the hydrogenation of LA in order to get more information for the stability of Pt/BPhDS/Al catalysts in the aqueous medium (Table 4, entries 4/5 and 4/6). 2.81 mg (0.005 mmol) Na₂PtCl₆·6H₂O, 8.58 mg (0.015 mmol) BPhDS (molar ratio BPhDS/Pt = 3) and 0.21 mg (0.00085 mmol) AlCl₃·6H₂O (molar ratio $AlCl_3 \cdot 6H_2O/Pt = 0.17$) were dissolved under argon in 20 ml of deairated demineralized H₂O and the mixture was stirred for about 10 min at room temperature to give a clear, red coloured, solution. After addition of 0.581 g (5 mmol) LA to the aqueous catalyst solution under stirring for further 5 min the aqueous reaction mixture, having a ruthenium concentration of 47 ppm, was charged into an Autoclave Engineers autoclave of a nominal volume of 100 ml which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of LA/Pt was 1000. After a number of pressurizing-depressurizing cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured and contents were heated with stirring (stirring rate = 880 rpm). The heating time to reach a reaction temperature of 150 °C was 20 min. At the reaction temperature of 150 °C the hydrogen partial pressure was 60 bar and the reaction time 1 h. After the reaction the autoclave was cooled (within 20 min) to room temperature, vented of hydrogen and the aqueous reaction mixture was removed. A sample of 100 mg was taken from the aqueous reaction mixture and was analyzed by gas chromatography (GC) after addition of N,N-dimethylformamide as standard (entry 4/5). Subsequently, 5 ml of diethyl ether were added to the 20 ml of the aqueous reaction mixture to create a biphasic system. The Pt/BPhDS/Al catalyst was easily recovered from reaction products by intensive extraction using a separatory funnel being shaken very well by hands for 5 min and a simple phase separation of the lower aqueous red coloured layer from the upper organic product uncoloured layer. The lower aqueous layer containing the Pt/BPhDS/Al catalyst after addition of a new portion of 0.581 g (5 mmol) of LA (molar ratio of LA/Pt = 1000) was re-used under the same hydrogenation reaction conditions. After the recycling hydrogenation experiment a minor amount of metallic platinum was observed indicating to a minor extent decomposition of the catalyst and the pH value of the aqueous catalyst solution was 3.0. The catalytic activity remained unchanged high (TOF = 1000 h^{-1}) using the recycled Pt/BPhDS/A1 catalyst in the aqueous-phase hydrogenation experiment of entry 4/6 compared with the first hydrogenation reaction of LA of entry 4/5 catalyzed by the same Pt/BPhDS/Al system (TOF = 1000 h^{-1}). These results have shown that the platinum catalyst modified with the nitrogen-containing bidentate ligand BPhDS with aluminium promotors is stable without loss of activity and selectivity which is remarkable when one considers that reaction parameters such as the temperature of 150 °C and the acidic aqueous medium (pH = 3.0) are rather demanding conditions for a homogeneous catalytic hydrogenation reaction.

It is relevant to point out, that after the hydrogenation reaction it is necessary to add low amounts such as 5 ml of diethyl ether to 20 ml of the aqueous catalytic reaction mixture to create a biphasic system in order to extract the reaction products in the upper organic layer from the lower aqueous catalyst layer for the recovery and recycling of the Pt/BPhDS/Al catalyst. If higher amounts such as 10 ml of diethyl ether were added for the extraction of 20 ml aqueous reaction mixture the catalytic activity dramatically decreases in the consecutive LA hydrogenation run mainly due to the diethyl ether and to a lesser extent of the GVL and 1,4-PDO products [LA was not present because of the quantitative conversion in the first run (entry 4/5)] which are inevitably dissolved in small amounts in the highly polar aqueous catalyst solution which gives rise to a drop in the polarity of the LA hydrogenation reaction mixture.

4 Conclusions

The work presented in this paper demonstrated again the high potential of green aqueous-phase catalysis through a new application in the field of utilization of levulinic acid (LA) a renewable biomass based polar platform chemical of central relevance in the development of biorefineries of the future in a sustainable way. We have disclosed a novel hydrogenation reaction of LA into γ -valerolactone (GVL) catalyzed by water-soluble platinum catalysts modified with various nitrogen-containing and phosphine ligands in environmentally attractive, green, aqueous monophasic systems. Interestingly, the presence of the Lewis acid aluminum enormously increases the catalytic activity of water-soluble platinum catalysts modified with nitrogen-containing ligands in the LA hydrogenation reaction and high catalytic activities up to 3540 TOF's per hour with a quantitative selectivity towards GVL have been achieved using Na₂PtCl₆·6H₂O catalysts precursors modified with the bidentate bathophenanthrolinedisulfonic acid disodium salt (BPhDS) ligand and low amounts of AlCl₃·6H₂O promotors (molar ratio of AlCl₃· $6H_2O/Pt = 0.17$) in aqueous media. A recycling experiment of the Pt/BPhDS/Al catalyst from the aqueous monophasic LA hydrogenation reaction mixture followed by biphasic recovery of the catalyst in active form from organic reaction products by extraction and simple phase separation of an aqueous/organic two-phase system formed after addition of diethyl ether has shown that the catalyst is stable without loss of activity and selectivity in a consecutive run. Hence, we are currently investigating the scope of this useful catalytic hydrogenation reaction.

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