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MNP@perfluorinated superacid polymers: a family of bifunctional catalysts for the selective, one-pot conversion of vegetable substrates in water

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Abstract:	Innovative catalysts aimed at the sustainable, multistep conversion of renewable plant derivatives to high added-value chemicals with high selectivity are strongly awaited. In this work we describe the rational design to a new versatile family of bifunctional catalytic materials, based on the combination of supported metal nanoparticles and the superacid, perfluorinated Aquivion® PFSA polymer. The heterogeneous catalysts were tested in the one-pot, one-stage conversion of (+)-citronellal to (-)-menthol and levulinic acid to γ-valerolactone in the water phase, showing high activity and full selectivity under mild reaction conditions. The results are discussed in terms of catalyst microstructure.
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Dear Editor,

sustainable conversion of vegetable biomass-derived compounds requires complex reaction sequences to be performed efficiently in cascade, in one-pot and in one-stage. A potential solution to this is to use heterogeneous catalysts featuring continuous arrays of specialized active sites, namely acid and metal single-sites, provided that good site-accessibility and resistance under reaction conditions is ensured. Perfluorinated polymers are known for their exceptional chemical and thermal resistance, however rarely investigated as support for catalytically active species. In the present work, we devised a new family of bifunctional heterogeneous catalysts by the incorporation of a variety of metal nanoparticles onto a perfluorinated PFSA matrix endowed with immobilized acid sites with strength comparable to that of sulfuric acid. A detailed study on the catalytic activity and selection of these materials for targeted applications is reported. Results were analyzed by decoupling the catalysts performance in monofunctional steps and discussed in terms of catalyst microstructure. The catalytic, direct conversion of levulinic acid to γ-valerolactone and (+)-citronellal to (-)-menthol in the water phase were tested as representative processes for vegetable biomass valorisation, showing high activity and full selectivity under mild reaction conditions. The scientific work was complemented by in-depth catalyst characterization, catalyst reuse studies and comparison with literature known systems.

We believe that the present paper is of interest to those working in the field of new catalytic materials and sustainable production processes, while the catalysts family proposed largely applicable to the conversion processes of a variety of biomass-derived substrates. Therefore, we would be delighted if you may consider this manuscript for publication to ChemCatChem as full paper.

thanks for your time and attention,
Pierluigi Barbaro

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MNP@perfluorinated superacid polymers: a family of bifunctional catalysts for the selective, one-pot conversion of vegetable substrates in water

Carmen Moreno-Marrodan,[a] Francesca Liguori,[a] Pierluigi Barbaro,*[a] Stefano Caporali,[b] Luca Merlo[c] and Claudio Oldani[c]

Abstract: Innovative catalysts aimed at the sustainable, multistep conversion of renewable plant derivatives to high added-value chemicals with high selectivity are strongly awaited. In this work we describe the rational design to a new versatile family of bifunctional catalytic materials, based on the combination of supported metal nanoparticles and the superacid, perfluorinated Aquivion® PFSA polymer. The heterogeneous catalysts were tested in the one-pot, one-stage conversion of (+)-citronellal to (-)-menthol and levulinic acid to γ-valerolactone in the water phase, showing high activity and full selectivity under mild reaction conditions. The results are discussed in terms of catalyst microstructure.

Introduction

Chemicals production from not-critical, renewable raw materials is of great relevance in the process industry aimed at reducing its dependence from petrochemical sources.[1,2] Vegetable biomass is key to this due to the large non-edible portion and the availability from municipal and agricultural wastes, biorefinery residues or from alternative farming,[3,4] thus to have limited competition with the food industry.[5] Methods to convert plant derivatives into added value products have been developed involving complex reaction sequences of two or more metal-catalysed reduction and acid-catalysed (e.g. hydrolysis, dehydration, esterification) steps.[6,7] However, most processes have been achieved using multiple reactor units, harsh conditions or strong mineral acids, which requires considerable time, space and energy inputs, while corrosion and neutralization issues are often associated.[8] Moreover, a multitude of compounds can be generated, therefore intermediate workups, troublesome purifications procedures or use of organic solvents may be needed, with significant drawbacks in terms of costs, efficiency and waste emissions. The development of alternative methods that comply with sustainability criteria is thus highly desirable.[9,10] The target is to attain 100% selectivity at high conversion level in a one-pot, one-stage under the mildest possible reaction conditions.[11]

Efficient multireaction processes are commonly carried out by living organisms through bifunctional biological catalysts, i.e. enzymes.[12,13] Some synthetic homogeneous acid–metal bifunctional catalysts have been obtained by mimicking these natural systems. However, their selectivity is often poor because of the lack of a continuous array of specialized active sites.[14,15] In addition, heterogeneous catalysts are preferred by industry due to the easier catalyst reuse and product separation.[16] A potential solution is to use a combination of well-defined supported acid and metal sites acting under the same conditions,[17,18] notably metal catalysts onto solid acids, hereinafter referred to as *truly bifunctional catalysts*.[19,20] A number of excellent reviews on bifunctional heterogeneous catalysts have appeared in the literature,[21,22] including for the conversion of vegetable biomass.[23,24] Among the various solid acids catalysts available on the market, Brønsted acid-type sulfonated polymers, e.g. Amberlyst®, Dowex®, Nafion®, have shown unsurpassed versatility and efficiency in several applications on the large-scale.[25,26] A reason for this is their satisfactory chemical and thermal resistance and the availability in different morphologies (shape, size and porosity), strength and number of acidic sites. The appropriate combination of these properties allows for the selection of the best catalyst for each application. In spite of that, with the exception of Amberlyst CH® (a conventional, macroreticular styrene-DVB copolymer bearing 1 wt % Pd and 4.8 meq g^{-1} sulfonic groups, used for MIBK synthesis),[27,28] no bifunctional catalyst based on the above materials have been commercialized so far.[29]

A family of perfluorinated, fluorosulfonic acid resins has recently become available from Solvay Specialty Polymers S.p.A under the name Aquivion® PFSA (Scheme 1).[30,31] These polymers feature an acidic strength comparable to that of sulfuric acid (Hammett acidity ca. -12),[32] while showing remarkable thermal resistance and chemical inertness that allow to withstand highly aggressive reaction conditions, including strongly acidic and reductive environments.[33,34] In addition, due to the shortest side chain, Aquivion displays a higher crystallinity, ionic conductivity and glass transition temperature (T_g 140 °C) compared to its fluorinated congeners Nafion®, Flemion® and Aciplex®.[35] Aquivion® has been reported for applications as proton conductor in fuel cells[36,37] and as solid acid catalyst, either alone[38,39] or supported (onto carbon, silica, ceria).[40,41]

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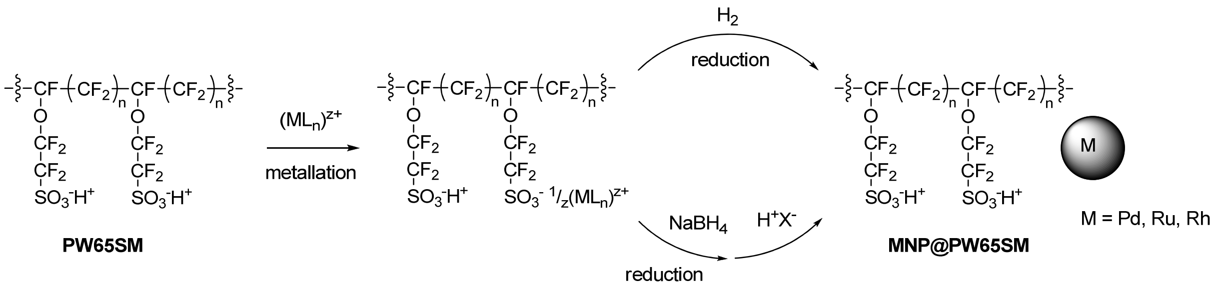


Scheme 1. Schematic representation of the structure and the synthetic procedure for MNP@PW65SM Aquivion® catalysts.

Table 1. Selected properties and labeling scheme for representative MNP@PW65SM catalysts prepared.

Metal	Precursor	Reduction method	Acid washing [a]	Catalyst label	Metal loading [wt%] [b]		MNP size [c] [nm]
					M	Na	
Pd	$Pd(NO_3)_2$	H_2 [d]	-	Pd@PW65SM-H2	1.34	< 0.05	2.3 ± 0.5
Rh	$[Rh(NBD)_2]BF_4$	H_2 [e]	-	Rh@PW65SM-H2	1.30	< 0.05	3.9 ± 0.9
		$NaBH_4$	-	Rh@PW65SM-BH4	1.21	3.29	3.4 ± 0.7
		$NaBH_4$	TfOH	Rh@PW65SM-OTf	1.22	< 0.05	2.5 ± 0.6
Ru	$Ru(NO)(NO_3)_x(OH)_y$	H_2 [e]	-	Ru@PW65SM-H2	2.02	< 0.05	2.1 ± 0.6
		$NaBH_4$	-	Ru@PW65SM-BH4	1.79	3.19	3.4 ± 0.5
		$NaBH_4$	TfOH	Ru@PW65SM-OTf	1.78	< 0.05	3.2 ± 0.8

[a] TfOH = CF_3SO_3H. [b] From ICP-OES. [c] From TEM. [d] 1 bar H_2, room temperature. [e] 20 bar H_2, 120 °C.

Herein we report the synthesis and characterization of a new class of bifunctional, heterogeneous catalysts based on Aquivion-supported metal nanoparticles (MNP, M = Pd, Ru, Rh). This catalysts family has been rationally designed to achieve the effective, multistep conversion of biomass derivatives by a single catalytic body, through the combination of key properties: a polymeric, perfluorinated solid support material (for catalyst resistance), a solid acid functionality with strength comparable to that of sulphuric acid (for acid catalysis devoid of mineral acids), immobilized metal nanoparticles (for catalytic hydrogenations).

Application of the prepared catalysts to the direct (*i.e. one-stage, one-pot*) conversion of vegetable-derived substrates was explored in the aqueous phase. Two representative processes were selected to this purpose: the synthesis of γ-valerolactone (GVL) from levulinic acid and the synthesis of (-)-menthol from citronellal. Motivations for these choices are multiple. GVL is an important platform bio-molecule for access to a variety of uses and derivatives. The synthesis of GVL requires a hydrogenation-lactonization reactions sequence, usually under relatively high temperatures and H_2 pressures. (-)-Menthol is a high-volume market chemical, industrially produced through an isomerization-hydrogenation reactions sequence, however, with severe limitations in term of selectivity and use of organic solvents.

Results and Discussion

Synthesis and characterization of the catalysts

The support material used in the present study was the non-commercial Aquivion® powder having 1.54 mmol g^{-1} proton density (ion-exchange capacity), CF_3 end-capping groups and 354-500 μm grain size range, hereinafter referred as PW65SM. Analogously to other non-crosslinked functionalized polymers,[42,43] the material displays a very low surface area in the dry state (0.3 m^2 g^{-1}) consistent with a gel-type (microporous) structure.[44] Accordingly, the polymer interior is fully accessible only after swelling in an appropriate solvent.[45,46] Insolubility and swelling tests were carried out, showing the best solvents in this respect to be water, THF, toluene and *n*-hexane.[47] After sieving the material, the intermediate fraction size was selected because of the lower internal mass transfer limitations compared to the larger particles size[48,49] and to the better sedimentation and easier recovery compared to smaller particles. Neither Aquivion® pellets nor membranes of the same composition were investigated due to the loss of the native porosity of the raw powdered material upon extrusion.[50] Use of other Aquivion® polymers with lower acid capacity was not examined in detail, owing to the high proton density desired for our applications (*vide infra*) and the lower swelling in water.

Noble metals nanoparticles (Pd, Rh, Ru) were immobilized onto PW65SM by a straightforward, two-steps procedure,[48] taking advantage of the remarkable ion-exchange properties of Aquivion® (Scheme 1).[30,51] Thus, irrespective of the metal, the polymer was first metallated by ion exchange *via* treatment with a solution of an appropriate metal precursor, followed by metal reduction. A systematic study was performed using H_2 or $NaBH_4$ as reducing agents, aimed at highlighting any effect of the reductant on the catalytic performance (*vide infra*). Partial substitution of proton ions in metallated PW65SM was achieved using a mmol metal / meq ion-exchange capacity ratio of 1/10. The procedure resulted in polymers with a typical 1.1-2.5% (w/w) metal loading after reduction (ICP-OES, Table 1), corresponding to a 80-90% metal uptake, a value higher than that usually obtained for conventional ion-exchange resins (50-80%).[52,53,54] Similarly to other polymeric systems, clean reduction of the metallated PW65SM under 1 bar H_2 and room temperature was possible only for the Pd derivative, whereas Ru and Rh required stronger reaction conditions (20 bar H_2, 120 °C). In these latter cases, metal reduction at room temperature could be achieved using an excess of $NaBH_4$,[53, 55] however successive washing with CF_3SO_3H was required after borohydride treatment, in order to remove the sodium ions from the polymer and restore the original protic form of Aquivion.[56,57] The absence of residual sodium in the finished catalysts was ascertained by ICP-OES analysis.[47] Table 1 summarizes the catalysts synthesized and the labelling scheme adopted. Giving priority to a greener procedure whenever possible, palladium catalyst was prepared exclusively following the cleanest approach. Preliminary studies showed that immobilization of Pt nanoparticles onto Aquivion® is also possible using analogous protocols.[51]

The as prepared MNP@PW65SM catalysts were characterized in the solid state by a combination of spectroscopic, diffraction and microscopy techniques. Metal loading was obtained from ICP-OES and EDS. TEM and XRD analysis showed all catalysts to contain embedded MNP of small particle size (Table 1). For any given metal, the nanoparticles size was dependent from the reducing agent used, as expected.[58] Typical diameter dimensions were in the range 2 - 4 nm. Representative size distribution data and TEM images for Pd and Ru catalysts are shown in Figure 1. Figures for the Rh derivatives are reported in the Supporting Information (Figure S2). The small size of the *in-situ* formed MNP is attributable to the stabilization properties of MNP by gel-type functional polymers, thanks to the dual effect of charged functional groups (electrostatic stabilization)[59] and porosity (steric stabilization).[60,61] Limited growth of MNP is also favoured by the atomic level dispersion of the metal precursor within the polymer, as a consequence of the ion-exchange immobilization procedure.[62] TEM and XRD data were consistent within the experimental errors, although partial overlapping of metal peaks with those of the matrix was observed for the Rh and Ru derivatives. XPS measurements were carried out to characterize the oxidation state of the supported MNP in representative catalysts. Figure 2 shows the XPS spectrum of Pd@PW65SM-H2 in the Pd 3d region where the usual palladium doublet is observed. The Pd 3d peaks were deconvoluted into two oxidation states, metallic Pd(0) at lower binding energy (Pd $3d_{5/2}$ 335.1 ± 0.1 eV) and Pd(II) at higher energy (Pd $3d_{5/2}$ 337.2 ± 0.1 eV), with the latest likely due to PdO.[63] No other palladium species were detected. The calculated abundance of the two species was 83.3% for Pd(0) and 16.7% for Pd(II). As it was previously reported,[64] the presence of PdO can be safely attributed to a layer covering the core of metallic palladium particles due to sample manipulation, since the percentage of Pd(0) was increased up to 88.1% after sputtering with Ar, a procedure that removes the most superficial atoms of the nanoparticle.[65] Similar findings were obtained for the XPS spectrum of Ru@PW65SM-H2, that was deconvoluted into two components attributed to Ru(0) (Ru $3d_{5/2}$ 279.9 ± 0.1 eV) and RuO_2 species (Ru $3d_{5/2}$ 281.5 ± 0.1 eV). (Figure 3). The spectrum was complicated by partial overlap with carbon matrix peaks (C 1s) in this case. The XPS spectrum of Rh@PW65SM-H2 was successfully fitted using a single Rh(0) component (Supporting Information, Figure S4). The acid density in the MNP@PW65SM catalysts did not substantially differ from that of the original Aquivion® polymer. Although this could not be demonstrated by conventional TPD / amine desorption experiments due to the limited accessibility of gas reactants to gel-type resin in the dry state,[66] indirect proofs were obtained both from ICP-OES analyses, showing no variation in sulfur loading and a negligible sodium content after acidic rinsing (Table 1), and from the acidic functional tests by means of the catalytic hydrolysis reaction of ethyl lactate (*vide infra*).

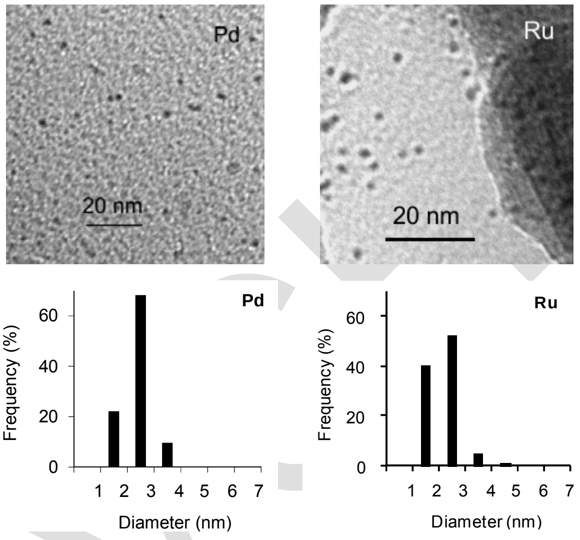


Figure 1. Typical TEM images (top) and MNP size distribution (bottom) for Pd@PW65SM-H2 (left) and Ru@PW65SM-H2 (right).

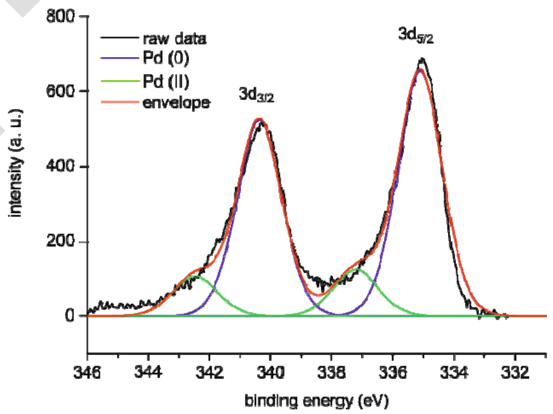


Figure 2. XPS spectrum of Pd@PW65SM-H2 in the Pd 3d region.

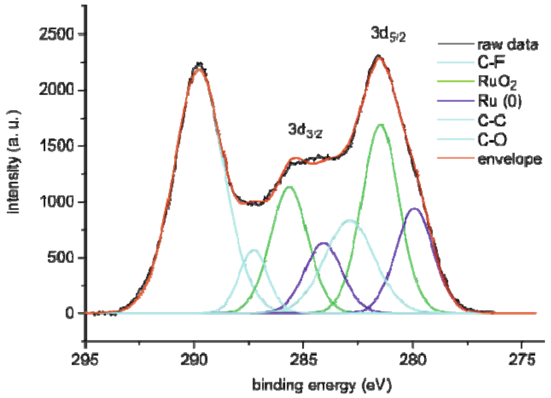
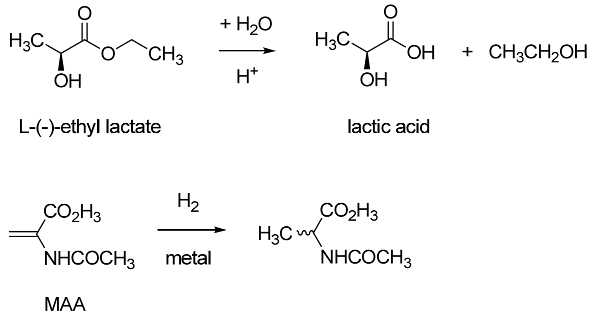


Figure 3. XPS spectrum of Ru@PW65SM-H2 in the Ru 3d region.



Scheme 2. Acid-catalyzed hydrolysis of ethyl lactate and metal-catalyzed hydrogenation of MAA.

Table 2 Selected data for the hydrolysis of ethyl lactate by MNP@PW65SM catalysts.[a]

Entry	Metal	Catalyst	Conversion [%] [b]
1	-	PW65SM	60
2	-	PW65SM-BH4	3
3	Pd	Pd@PW65SM-H2	59
4	Rh	Rh@PW65SM-H2	46
5		Rh@PW65SM-BH4	13
6		Rh@PW65SM-OTf	43
7	Ru	Ru@PW65SM-H2	38
8		Ru@PW65SM-BH4	11
9		Ru@PW65SM-OTf	38

[a] Reaction conditions: 70 °C, 190 rpm stirring rate, ethyl lactate 7.0·10^{-2} M in water, catalyst 40 mg, molar ratio ethyl lactate / Brønsted acid sites = 35:1. [b] After 210 min reaction time.

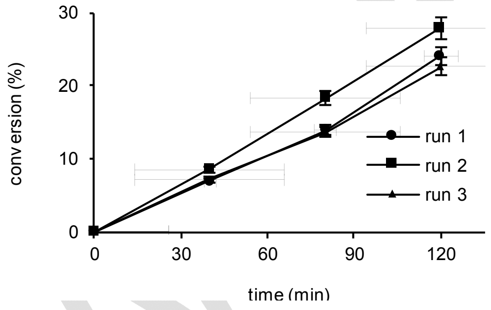


Figure 4. Reuse of Ru@PW65SM-H2 catalyst in the hydrolysis reaction of ethyl lactate. Reaction conditions: 70 °C, 190 rpm stirring rate, ethyl lactate 7.0·10^{-2} M in water, catalyst 40 mg, molar ratio ethyl lactate / Brønsted acid sites = 35:1.

Catalytic reactions

All MNP@PW65SM materials were tested as ‘bifunctional’ heterogeneous catalysts in the aqueous phase using appropriate probe substrates. Benchmark single-step reactions were preliminarily exploited to examine the ‘monofunctional’ catalytic activity, either metallic or acidic, of the prepared materials. Aim of the study was to establish the effect of the preparation method on the catalysts efficiency and to select the best catalyst combination to perform acid-hydrogenation reaction sequences in one-pot. The hydrolysis of ethyl lactate (acid catalysis) and the hydrogenation of methyl 2-acetamidoacrylate (metal catalysis) in the aqueous phase were chosen, respectively, to this purpose (Scheme 2).

In the hydrolysis reaction of ethyl lactate, the activities of the MNP@PW65SM catalysts were compared to that of unmetallated PW65SM under identical conditions. Purpose of the tests was: i) to determine whether the native acidity of Aquivion® is retained upon MNP incorporation, ii) to highlight the effect of both the metal and the proton regeneration treatment on the acidity of the catalysts, iii) to evaluate the catalysts stability under the reaction conditions adopted. Selected results are reported in Table 2. In a reference experiment, the PW65SM catalyst under batch conditions provided a 60% conversion at 70 °C and 210 min reaction time (entry 1). Irrespective of the metal or the reduction method, provided that reduction with $NaBH_4$ is followed by acid washing, activities of MNP@PW65SM species were comparable within the experimental errors and slightly lower than that of PW65SM (entries 3, 4, 6, 7, 9).[47] This indicates that the number and strength of Brønsted acid sites are substantially retained upon incorporation of the metal into Aquivion®, as long as rinsing with strong acids is carried out to restore the protic form of the polymer, whenever an excess of $NaBH_4$ is used as metal reducing agent. As expected, conversions were significantly lower for PW65SM-BH4 (3%) and for MNP@PW65SM-BH4 (<13%) catalysts in which all H^+ ions were replaced with Na^+ during metal reduction (Table 2, entries 2,5, 8). The residual activity can be attributed to the Lewis acid contribution of the metal[67] and to the thermal instability of ethyl lactate, in that case. After reaction completion, the catalysts could be quantitatively recovered by decantation and analysed by TEM and EDS showing no significant changes in the MNP size or in the sulfur content. Metal leaching in solution was below the ICP-OES detection limit (0.2 ppm) in any case. The recovered catalysts could be reused showing only a minor activity drop (ca. 4%). A representative example is reported in graphical format in Figure 4 for Ru@PW65SM-H2 over three consecutive runs. Interestingly, under the same reaction conditions and for the same substrate / acid sites molar ratio, the conversion using the metal-free catalyst PW65SM was significantly higher than that provided by the sulfonated ion exchange resin Dowex (28%), that can be ascribed to the stronger acidity of the Aquivion® material.[68]

Table 3 Selected data for the hydrogenation of MAA by MNP@PW65SM catalysts.[a]

Entry	Metal	Catalyst	Conversion [%] [b]
1	Pd	Pd@PW65SM-H2	77
2	Rh	Rh@PW65SM-H2	62
3		Rh@PW65SM-BH4	61
4		Rh@PW65SM-OTf	65
5	Ru	Ru@PW65SM-H2	21
6		Ru@PW65SM-BH4	7
7		Ru@PW65SM-OTf	7

[a] Reaction conditions: room temperature, 1 bar H_2, 190 rpm stirring, MAA 7.56·10^{-2} M in water, molar ratio MAA / metal = 126:1. [b] Conversion after 90 min reaction time.

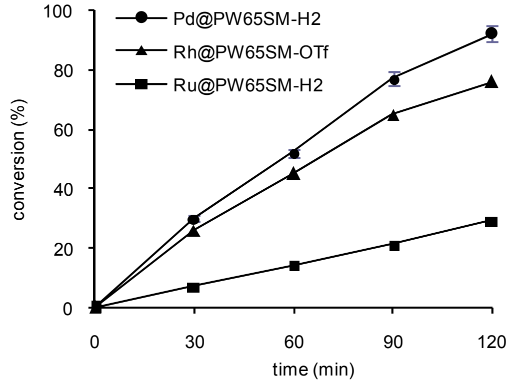


Figure 5. Selected data for the hydrogenation of MAA by MNP@PW65SM catalyst. Reaction conditions: room temperature, 1 bar H_2, water solution, 190 rpm stirring rate, molar ratio MAA / metal = 126:1.

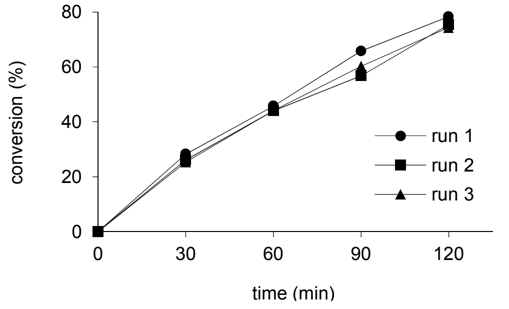


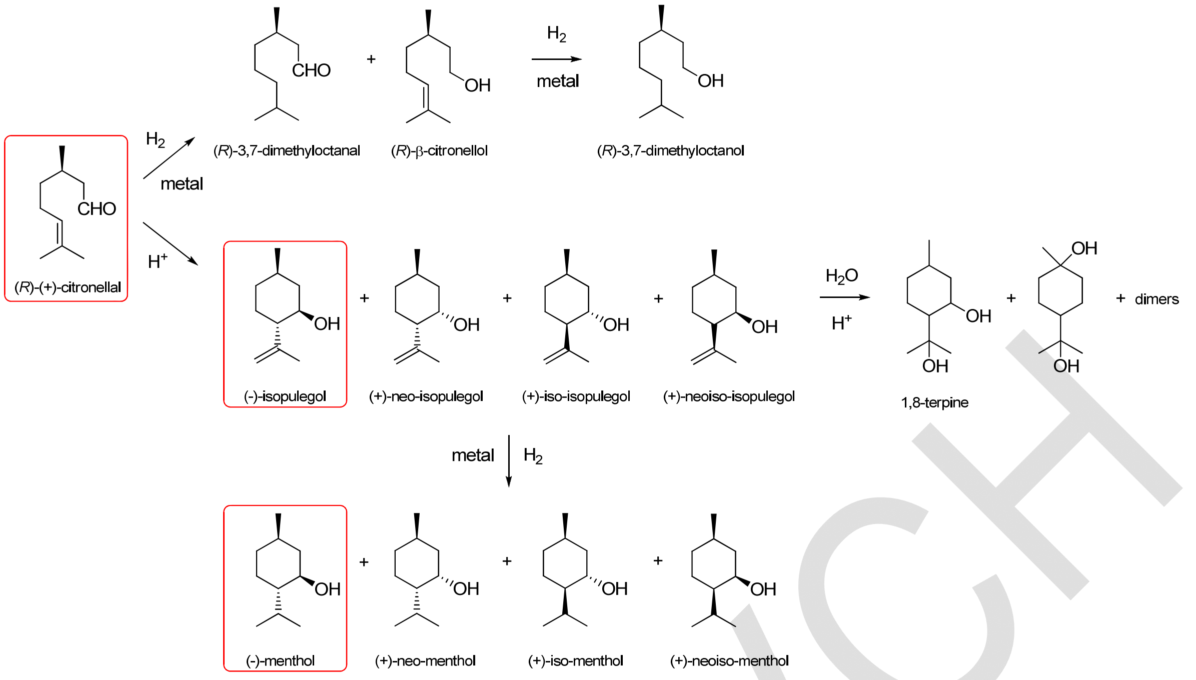
Figure 6. Reuse of Rh@PW65SM-OTf catalyst in the batch hydrogenation of MAA. Reaction conditions: room temperature, 1 bar H_2, water solution, 190 rpm stirring rate, molar ratio MAA / metal = 126:1.

The hydrogenation reaction of the water-soluble olefin methyl 2-acetamidoacrylate (MAA) was used to: i) ascertain the effect of the metal reducing agent on the hydrogenation activity, of MNP@PW65SM catalysts, ii) detect any effect of the acid washing treatment on the catalytic activity, iii) identify the most efficient Aquivion®-supported metal for catalytic hydrogenations. Batch experiments were carried out using an inert reactor, 1 bar H_2 pressure and room temperature. All catalysts showed to be active under these conditions. Representative results are summarized in Table 3 and graphically shown in Figure 5, whereas full data are reported in Figures S9-S11. A perusal of activity data shows that, for any given metal and irrespective of the metal reducing agent, the most active catalysts are those containing metal particles of the smaller size (Table 1), i.e. Rh@PW65SM-OTf in the case of rhodium (Table 3, entry 4) and Ru@PW65SM-H2 in the case of ruthenium (Table 3, entry 5). Comparable activities were generally observed for the catalysts obtained from $NaBH_4$ reduction, irrespective if an acidic washing was performed or not (Table 3, entry 3-4 and 6-7). This evidence rules out any significant poisoning effects of the metal surface by the conjugated anion of the acid used for washings.[57] We must underline, however, that the interpretation of the above findings must be considered with care, since several additional factors, besides MNP size,[69,70] may affect the hydrogenation activity of the catalysts, including shape[71,72] and distribution of embedded MNP[73,74] and the acidity of the support material.[75,76] As expected from the diverse affinities for the C=C bond,[77,78] activities were different for different metals, with catalytic efficiency decreasing in the order Pd > Rh > Ru for the same catalyst type. After completion of the hydrogenation reactions, the catalysts recovered by decantation showed no significant changes of the MNP size by TEM, nor metal leaching in solution was detected by ICP-OES. Catalysts reuse was possible with no significant activity decrease over several consecutive runs. A representative example is reported in Figure 6 for Rh@PW65SM-OTf catalyst. It is worth noticing that Pd@PW65SM-H2 and Rh@PW65SM-H2 show activities comparable to those of the parent Pd@Dowex[48] and Rh@Dowex[79] catalysts based on a gel-type polymeric support. This indicates the full site-accessibility of the Aquivion catalysts thanks to microporosity developed upon swelling. Stability and efficiency of functional resin-supported metal catalyst in hydrogenation reactions was previously attributed to the favourable combination of microporous structure of the support with the narrow size distribution of the immobilized metal particles.[53]

All above findings provide useful information for the selection of the "optimal" bifunctional MNP@Aquivion catalysts. Best compromise between metal and acidic activity is expected for catalysts obtained by H_2 reduction, in the case of Pd and Ru, and by $NaBH_4$ reduction followed by CF_3SO_3H washings, in the case of Rh. It must be noticed that these criteria apply for reaction sequences involving the hydrogenation of C=C bonds, while they may significantly differ for the combination of multistep reactions comprising other processes, e.g. C=O bond reduction. Thus, due to the different affinities,[78] it is expected that Pd will be the best metal option for C=C hydrogenations, while the Ru-based catalyst may be preferred for reaction sequences involving C=O bonds hydrogenations.

The "bifunctional" performance of selected catalysts was then scrutinized in representative two-step reactions of high significance in the valorisation of vegetable biomass derivatives, namely the direct conversion of (*R*)-(+)-citronellal to (-)-menthol and the direct conversion of levulinic acid to GVL.

Conversion of (*R*)-(+)-citronellal to (-) menthol: (-)-Menthol is a highly demanded product for the food and pharmaceutical industry due the characteristic peppermint fragrance and refreshing effect.[80,81] No such properties are featured by the (+)-menthol enantiomer.[82] (-)-Menthol is synthetically produced on a 3000 tons / year scale by the Takasago process, based on five steps starting from myrcene and accounting for ca. 20 % of the overall world market of menthol.[83] The two last steps of the process involve the acid-catalysed cyclization of (+)-citronellal to (-)-isopulegol by stoichiometric amounts of $ZnBr_2$, followed by conventional C=C bond hydrogenation of the latter by Ni catalysts (Scheme S3). The challenge for heterogeneous bifunctional catalysts is to carry out the conversion of citronellal into menthol with high selectivity in one-pot and one-stage. Indeed, under the simultaneous conditions of acid and hydrogenation catalysis, citronellal may undergo a very complex reaction system (Scheme 3). (+)-Citronellal features one stereogenic carbon atom and two prochiral carbon atoms,[84] hence four different isopulegol and menthol diastereoisomers may be produced, in addition to various competitive hydration and hydrogenation reaction products.



Scheme 3 Catalytic reaction pathways for (*R*)-(+)-citronellal under hydrogenation / acid conditions with main potential products.

Table 4 Selected data for the direct conversions of (*R*)-(+)-citronellal to (-)-menthol by MNP@PW65SM catalysts.[a]

Entry	Catalyst	Temp. [°C]	Time [h]	Conv. [%]	Sel. (-)-menthol [b] [%]	Yield [%] (-)-menthol	(-)-isopulegol	others	Productivity[c] [mol g_M^{-1} h^{-1}]x10^2
1	PW65SM	80	24	99	1	1	27	71	-
2	Pd@PW65SM-H2	80	48	100	99	99	0	1	1.9
3	Pd@PW65SM-H2	60	23	100	99	99	0	1	4.7
4	Pd@PW65SM-H2	60	16	99	90	89	10	0	5.6
5	Rh@PW65SM-OTf	80	48	98	19	18	5	75[d]	-
6	Ru@PW65SM-H2	80	48	100	17	17	0	83 [d]	-
7	Pd@Dowex	60	23	97	16	16	1	80	-

[a] Reaction conditions: (+)-citronellal 0.1 M in water, substrate/metal molar ratio = 114:1, H_2 pressure 10 bar. Data from GC analysis. [b] Selectivity to (-)-menthol. [c] Calculated on moles of (-)-menthol product and metal M content. [d] 1,8-Terpine and isomers >90%.

Table 5 Selected literature data for the direct conversions of (±)-citronellal to (±)-menthol by heterogeneous catalysts. [a]

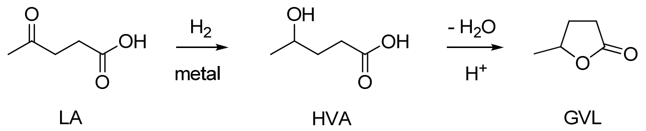
Entry	Catalyst	Type	Solvent	Temp. [°C]	H_2 [bar]	Yield [%] menthol isomers [b]	menthol [c]	Productivity [d] [mol g_M^{-1} h^{-1}]x10^2	Ref.
1	1.3% Pd@PW65SM-H2 [e]	bifunctional	water	60	10	99	(-) 99	4.7	this work
2	1% Ru@H-BEA-25	bifunctional	dioxane	100	15	93	(±) 79	75	[87]
3	2% Pt@H-beta	bifunctional	dioxane	25	20	96	(±) 85	93	[91]
4	3% Ir@H-Beta	bifunctional	cyclohexane	80	8	93	(±) 70	10	[92]
5	Cu@SiO_2 [e]	bifunctional [f]	toluene	90	1	95	(-) 75	3	[90]
6	15% Ru-$ZnBr_2$@SiO_2 [e]	bifunctional	cyclohexane	60	1	90	(-) 85	-	[89]
7	5% Pd-PW@SiO_2 [e]	bifunctional	cyclohexane	70	35	92	(-) 78	21	[94]
8	2% Pt@Ga-MCM-41 [e]	bifunctional	2-propanol	120	- [g]	87	(-) 60	2460	[95]
9	Zr-beta + 15% Ni/MCM-41	mixture [h]	*t*-butanol	80	20	77	(±) 73	5 [i]	[96]
10	0.28% Pd@MIL-101	bifunctional	cyclohexane	80	8	34	(±) 27	6	[97]

[a] Data at full conversion. [b] Sum of menthol isomers: (±)-menthol, (±)-neo-menthol, (±)-iso-menthol and (±)-neoiso-menthol. Racemic mixture for each isomer, unless enantiopure (+)-citronellal was used as substrate. [c] Menthol yield, enantiomer in brackets. [d] Calculated on moles of (-)-menthol product and metal M content. [e] (+)-Citronellal was used. [f] Copper acts as both hydrogenation and acidic site. [g] Microwave-assisted transfer hydrogenation. [h] Mechanical mixture. [i] Based on Ni.

A number of bifunctional MNP@PW65SM catalysts, selected on the basis of the benchmark reactions criterion above described, were tested over concentrated aqueous solutions of (+)-citronellal under identical reaction conditions, namely Pd@PW65SM-H2, Rh@PW65SM-OTf and Ru@PW65SM-H2. In a typical experiment, a mixture of catalyst, (+)-citronellal and water was heated under a selected hydrogen pressure. After stirring for the desired time, the solid was decanted and the resulting clear solution analysed without further treatments by chromatographic, spectrometry and NMR techniques. Representative results are reported in Table 4 in terms of overall conversion and (-)-menthol purity, selectivity and yield. Productivities ($mol_{(-)\text{-menthol}}$ / $weight_{metal}$ x h) were included for comparative purposes. As reference reaction, the metal-free catalyst PW65SM gave 99% citronellal conversion after 24 h at 80 °C and 10 bar H_2, thus confirming the high acid catalytic activity of the Aquivion support (Table 4, entry 1). The reaction resulted in a fully diasteroselective cyclization to (-)-isopulegol (27% yield) and in ca. 71% hydration to 1,8-terpine isomers.[85,86] No traces of other isopulegol isomers were detected. A milky solution with a lower isopulegol content was obtained for longer reaction times, likely due to significant isopulegol degradation to insoluble dimers.[87,88] Use of the Pd@PW65SM-H2 catalyst at 80 °C resulted in full citronellal conversion with 99% selectivity to (-)-menthol after 48 h (Table 4, entry 2). Neither traces of isopulegol or menthol isomers nor other hydrogenation or hydration by-products were observed by GC, GC-Ms and ^1H NMR analysis. Because of the excellent performance, Pd@PW65SM-H2 was examined in a broader temperature range. At 60 °C and shorter reaction times (23 h) the catalyst still showed neither drop of activity nor selectivity (Table 4, entry 3). Conversion was below 100% after 16 h resulting in ca 9:1 ratio (-)-menthol):(-)-isopulegol yield (Table 4, entry 4). In agreement with earlier observations, these findings indicate that, under these conditions, the conversion kinetic involves a diastereoselective citronellal cyclization step, followed by a slower (-)-isopulegol hydrogenation,[89,90] whose rate is higher than that of the competitive hydration reaction. The above results for Pd are in line with our prediction based on the one-step MAA hydrogenation and ethyl lactate hydrolysis reactions. Indeed, the protonated rhodium catalysts showed appreciable activity at 80 °C, but very poor chemo selectivity to (-)-menthol, due to prevalent isopulegol hydration to 1,8 terpine isomers and other degradation products (ca. 80% yield, Table 4, entry 5, and Table S9). On the basis of the MAA hydrogenation findings (Table 3, entry 4 and Figure 5), this is attributable to a less efficient hydrogenation than hydration step in the case of rhodium. Similar results were obtained using the Ru@PWS65SM-H2 catalysts (Table 4, entry 6), which agrees with the low C=C hydrogenation activity of Ru compared to Pd (Table 3, entry 5). It is worth mentioning that, under the same experimental conditions, the literature reported Pd@Dowex catalyst,[48] based on a sulfonated polystyrene support, showed similar activity, but much lower (-)-menthol selectivity (16%, Table 4, entry 7), that can be tentatively attributed to the lower hydrogenation efficiency due to the larger PdNP size in this case (3.7 nm). Irrespective of the metal or the reaction temperature, the Aquivion®-supported catalysts could be quantitatively recovered after cooling down to room temperature and decantation. No significant change of MNP size was highlighted by TEM.

The selectivity observed in the direct conversion of (+)-citronellal to (-)-menthol by Pd@PW65SM-H2 catalyst must be highlighted. No significant amounts of (+)-neo-menthol, (+)-iso-menthol or (+)-neoiso-menthol isomers were detected, thus indicating 100% diastereoselectivity in the cyclization to (-)-isopulegol, as well as fully chemoselective hydrogenation. It is worth noticing that the first step of the Takasago process affords a molar ratio of (-)-isopulegol to the other isopulegol diastereoisomers of 96:4. To the best of our knowledge, Pd@PW65SM-H2 provides *the best yield of (-)-menthol so far reported in the direct catalytic conversion of citronellal*. Other heterogeneous catalysts, either bifunctional or mechanical mixtures, have been described for this reaction, however showing lower stereo or chemo selectivity (Table 5).[20] Although racemic citronellal is usually employed in these studies, which results in (±)-menthol mixtures, they are useful to compare the efficiency of the tested catalysts. Thus, very good chemoselectivity to menthol isomers (93-96% yield at full conversion) and good stereoselectivity to menthol (70-85% yield) have been shown by zeolite-supported Ru,[87] Pt[91] or Ir[92,93] nanoparticles (Table 5, entry 2, 3 and 4). Moderate yields of menthol (60-85%) have been obtained either using Cu onto unfunctionalized silica,[90] Ru onto SiO_2-supported zinc bromide,[89] Pd onto heteropolyacid-silica,[94] or Pt onto Ga-doped silica[95] under microwave-assisted transfer hydrogenation conditions (Table 5, entries 5-8). Lower menthol yields were obtained using either a Zr-beta + Ni@SiO_2 mechanical mixture[96] or a bifunctional MOF catalyst containing coordinatively unsaturated Cr^{3+} sites and palladium nanoparticles[97] (Table 5, entries 9-10). With respect to other literature reported hydrogenation catalysts, Pd@PW65SM-H2 ranks in the low-range reaction rate, the highest productivity value having been observed under hydrogen-transfer conditions using 2-propanol as H-source (Table 5, entry 8).[95] Productivity for Pd@PW65SM-H2 is ca. $5\cdot10^{-2}$ mol g_{Pd}^{-1} h^{-1}, that increases to ca. $20\cdot10^{-2}$ mol g_{Pd}^{-1} h^{-1} if only the surface exposed Pd atoms are considered (23.8% from TEM). However, advantages of Pd@PW65SM-H2 are clear in terms of use of water solvent, milder reaction conditions and (-)-menthol purity, which prevents the need of burdensome downstream purifications.

From the comparison with other catalysts, one can argue that the high (stereo)selectivity of Pd@PW65SM-H2 is attributable to the appropriate combination of efficient metal-site catalysis and strong Brønsted acidity of the Aquivion® PFSA support. A complex combination of other factors, although less evident, may play a role, including porosity of the material,[98,99] balance of Lewis and Brønsted acid sites in the solid catalyst,[88,100,101] nature of the solvent. It is known that the one-pot synthesis of menthol from citronellal is very sensitive to the solvent used.[91] However, this more directly affects the overall conversion rate and the relative rates of acid / metal catalysis, hence the chemoselectivity, rather than stereoselectivity.[102,103] In the case of Sn-beta catalysts, a beneficial effect on the diastereoselectivity by addition of small amounts of water was highlighted, although the way of action could not be ascertained.[104] In the case in our hands, compared to water, use of Pd@PW65SM-H2 in THF resulted in lower (-)-menthol selectivity, at the same conversion level (yield (-)-menthol 73%, Table S9). Reactions carried out in *n*-hexane resulted in very low conversions, that can be tentatively attributed to the low polarity of the solvent.[87] It is clear that use of water solvent is inherently advantageous in terms of environmental impact, whereas it may present some selectivity issues because of the potential formation hydration by-products. However, this issue can be circumvented by selection of the appropriate catalyst, i.e. Pd@PW65SM-H2 in this case.



Scheme 4. Pathway of catalytic conversion of LA to GVL.

Table 6 Selected data for the direct conversions of LA to GVL by MNP@PW65SM catalysts.[a]

Entry	Catalyst	Temp. [°C]	Time [h]	Conv. [%]	Sel.[b] [%]	Prod. [c] [mol g_M^{-1} h^{-1}]
1	PW65SM	70	4	0.0	-	-
2	Pd@PW65SM-H2	70	4	1	> 99	-
3	Rh@PW65SM-OTf [d]	70	4	20	> 99	0.13
4	Ru@PW65SM-H2 [e]	70	4	86	> 99	0.81
5	Ru@PW65SM-H2 [e]	70	7	> 99	99	0.45
6	Ru@PW65SM-H2 [e]	80	4	97	96	0.87
7	Ru@PW65SM-BH4	50	4	26	99	0.27
8	Ru@PW65SM-OTf	50	4	50	99	0.52
9	Ru@Dowex [f]	50	4	29	99	0.30

[a] Reaction conditions: LA 0.43 M in water, substrate/metal molar ratio = 420:1, H_2 pressure 5 bar. Data from GC analysis. [b] Selectivity to GVL. [c] GVL Productivity calculated on metal M content. [d] Substrate/metal molar ratio 320. [e] Substrate/metal molar ratio 380. [f] Data from ref. [118].

Conversion of levulinic acid to γ-valerolactone: GVL is a safe material widely used as solvent, flavour, intermediate in the synthesis of a variety of fine chemicals and as platform for liquid biofuels.[105,106] It can be catalytically produced from levulinic acid (LA),[107,108] a degradation product of lignocellulosic biomass,[109] by a two-step hydrogenation-lactonization process *via* γ-hydroxyvaleric acid (HVA) in one-pot (Scheme 4).[110] Details of the reaction mechanism and kinetic of the aqueous phase catalytic conversion of LA to GVL can be found in the literature.[111,112] The selected "best" bifunctional MNP@PW65SM catalysts above described for each metal were tested in the direct conversion of LA to GVL under various conditions of temperature and H_2 pressure. Operations were carried out in batch using an inert autoclave, real feedstock material, i.e. a concentrated aqueous solution of LA, and the same one-pot, one-stage protocol above described for the conversion of (+)-citronellal. Representative results for experiments carried out using different catalysts are summarized in Table 6. Under the same reaction conditions, the activity of MNP@PW65SM catalysts roughly followed the order Ru (good) > Rh (moderate) > Pd (negligible), which is in fair agreement with the increasing metal affinities toward aliphatic C=O bonds hydrogenation.[113] Thus, while GVL yields were less than 20% using the selected Pd and Rh catalysts (Table 6, entries 2,3), the ruthenium derivative Ru@PW65SM-H2 resulted in 86% yield after 4 hours under 70 °C and 5 bar H_2 (Table 6, entry 4). The ruthenium catalysts were therefore investigated in greater detail. Full conversion could be achieved using the Ru@PW65SM-H2 catalyst upon increase of the reaction time from four to seven hours, while selectivity to GVL remained above 99% (Table 6, entry 5). A productivity of 0.45 mol_{GVL} g_{Ru}^{-1} h^{-1} could be calculated on these basis, that increases to 1.72 mol_{GVL} g_{Ru}^{-1} h^{-1} if the surface-exposed Ru atoms are considered (26%), as inferred from TEM data.[114] Over 4 hours reaction time, an increase of the temperature to 80 °C caused a conversion enhancement to 97% and a slight selectivity decrease to 96%, due to the formation of unidentified GVL degradation products (Table 6, entry 6). In the aqueous-phase synthesis of GVL from LA (Scheme 4), it is known that the HVA lactonization step controls the rate of GVL formation below 70°C, whereas at higher reaction temperatures the LA hydrogenation is rate determining.[112] A solid acid co-catalyst acid may therefore enhance the intramolecular esterification of HVA at low temperatures and, ultimately, the yield of GVL. This has been previously demonstrated using either Ru@C + Amberlyst[110,115] or Ru@graphite + zeolite[116] mechanical mixtures. In the case in our hands, in order to establish the role of the acidic Aquivion® support, we performed a series of experiments at 50 °C using protonated and non-protonated Ru catalysts having the same Ru content and size of embedded RuNP, namely Ru@PW65SM-OTf and Ru@PW65SM-BH4. Thus, while use of Ru@PW65SM-BH4 resulted in 26% LA conversion (Table 6, entry 7), the corresponding acid catalyst Ru@PW65SM-OTf provided a 50% conversion under the same reaction conditions (Table 6, entry 8), which demonstrates a positive contribution from the support. However, since selectivity was invariably above 99%, with no traces of HVA product detected by GC and HPLC analysis, any role of the support on the lactonization step cannot be ascertained. By contrast, these evidences clearly indicate a “proton acceleration” effect on the Ru-catalyzed hydrogenation step, as previously reported for Ru@C + Amberlyst mixtures,[115] and bifunctional Ru@SPES and Ru@Dowex catalysts.[117,118] Notably, at 50 °C the productivity of the Ru@PW65SM-OTf catalyst was ca. 70% higher than that of the literature reported, yet weaker acid, Ru@Dowex congener containing embedded RuNP of comparable size (2.8 ± 0.8 nm) (Table 6, entry 8, 9 and Figure S12), which confirms the benefits of the high acidic strength of Aquivion® on the catalytic activity.[118] Whatever the MNP@PW65SM catalyst, no metal leaching above the ICP-OES detection limit were observed. The catalysts could be quantitatively recovered at the end of the catalytic runs, simply by cooling down the reaction mixture to room temperature and decantation. No significant changes of MNP size were shown by the recovered Ru@PW65SM-H2 catalyst (Table S4, Figure S3). Catalyst reuse was possible, showing minor activity loss (< 10%) after 3 cycles (Figure S13).

Several solid-supported bifunctional catalysts have been described for the conversion of LA to GVL,[107,119] however they often require high temperatures and/or high hydrogen pressures.[112,120,121] To the best of our knowledge, Ru@PW65SM-H2 allows for one of the highest selectivity under the mildest operating conditions ever reported for a heterogeneous catalyst, although with slightly lower reaction rate (Table S8). The above results corroborate that Ru particles of small size together with a considerable density of high strength acid sites are crucial to obtain highly efficient, low-temperature catalysts for the direct conversion of LA to GVL.[122]

Conclusion

Methods for the production of fine chemicals from vegetable derived substrates complying with sustainability criteria are of central relevance to global policies related to environmental protection and mitigation of climate changes.[123,124] Strategies based on direct catalytic conversions may be crucial to this goal, however they require sophisticated catalysts able to operate with diverse metal centres and diverse functional groups, thus to promote multi-step sequential syntheses otherwise unattainable with conventional catalysts.[62] This necessitates a rational design of multifunctional heterogeneous catalysts that considers appropriate chemical compositions, choice of support and active phase properties.[125]

In this paper we described a very simple design to a new family of metal / acid catalysts tailored for the liquid phase direct conversion of plant biomass derivatives, based on readily available materials. We showed that the combination of the specific properties of Aquivion® PFSA (porosity, acidity, thermal and chemical stability) with those of embedded nano-sized noble metal entities (Pd, Rh, Ru) allows for the obtainment of bifunctional catalysts, featuring effective versatility in terms of both supported metals and catalysed reactions. A systematic study of catalyst performance, carried out by decoupling the catalyst activity in separated reaction steps, enabled the prediction of the best bifunctional systems for two important multistep processes, namely the synthesis of GVL and (-)-menthol. Both reactions were attained in the aqueous phase with good conversions and excellent selectivity under mild reaction conditions, with no need for (acidic) additives, intermediate workups or regeneration treatments. Noteworthy, operating conditions could be kept below 70 °C and 10 bar H_2 pressure, which is an important target for sustainable industrial applications.[126,127] The superior performance of the MNP@PW65SM catalysts was attributed to the concurrence of well-defined, strong acidic and MNP hydrogenation sites on the support, with the optimal resistance and appropriate swelling of the fluorinated matrix in water. Lack, for instance, of adequate porosity (e.g. Nafion)[128] or acidity (e.g. Dowex) in polymeric congeners commonly results in lower catalytic activity, due to either the failure of the substrate to access the active sites or the acid-catalysed steps (e.g. dehydration, cyclization) to occur efficiently.

We are confident that the materials described in this work will boost novel catalytic processes for the effective conversion of plant biomass derivatives.

Experimental Section

General information

The Aquivion® material used was the PW65S type, i.e. a coarse powder (PW) containing 1.54 mmol SO_3H/g, equivalent weight 650 g/mol (65), with CF_3 end-capping group stabilizer (S) and 0.3 $m^2\ g^{-1}$ surface area. The material was sieved into four fractions wherein that of size range 354-500 μm, herein identified by the label “M”, was examined throughout the present study.

Synthesis of the catalysts

Step 1: metallation of the polymer. In a typical procedure, a degassed solution of metal precursor (0.088 mmol metal) in the appropriate solvent (17.0 mL) was added under nitrogen via syringe to a degassed suspension of PW65SM (600 mg, 0.924 meq SO_3H, mol ratio SO_3H/metal = 10.5) in the same solvent (17.0 mL). The mixture was stirred at room temperature for 2 h using an orbital stirrer. The resulting solid was decanted, washed with the solvent (3 x 25 mL) before being dried at 50 °C under high vacuum overnight. Step 2: method a) reduction with H_2. The metallated polymer was loaded into an autoclave under nitrogen without solvent. The autoclave was charged with hydrogen (1 bar for Pd, 20 bar for Rh, Ru) and heated at the desired temperature (rt for Pd, 120 °C for Rh, Ru) for 2-6 hours. After that time, the autoclave was cooled to room temperature, depressurized and the black solid obtained stored under nitrogen. Step 2: method b) reduction with $NaBH_4$. In a typical procedure, solid $NaBH_4$ was added in excess (100 mg, 2.64 mmol, 30:1 with respect to the metal) to a degassed suspension of metallated resin (600 mg) in water (15 mL). Bubbles appeared immediately while the resin turned to black and the solution remained colourless. After 2h at room temperature and 250 rpm orbital stirring, the solid was decanted and was washed with degassed water (4 x 25 mL), before being dried under high vacuum at 50°C overnight. The resulting product obtained as black powder was stored under nitrogen. A sample of this material (450 mg, 0.66 mmol exchange sites) was washed twice for 20 min each with a degassed solution of the selected acid in water (0.1 M, 66 ml, 6.6 mmol H^+) under orbital-stirring. The solid was decanted and washed with degassed H_2O until neutral pH. The resin was then dried under high-vacuum for 24h at 50°C.

Catalytic conversion of (*R*)-(+)-citronellal to (-)-menthol

In a typical procedure, the supported catalyst Pd@PW65SM-H2 (60 mg, 1.34 wt % Pd, 0.007 mmol of palladium), was placed under nitrogen into a metal-free autoclave. Neat (*R*)-(+)-citronellal (133.0 mg, 0.86 mmol, substrate/Pd molar ratio 114) was then added under nitrogen. Degassed, deionized water (9.0 mL) was transferred under nitrogen via a Teflon tube into the autoclave. Nitrogen was replaced by hydrogen with three cycles pressurization/depressurization. The autoclave was charged with 10 bar pressure of hydrogen, stirred at 150 rpm and heated to 80 °C using an oil bath. After 48 hours, the reactor was cooled down to room temperature, depressurized and the solution was removed for GC-Ms analysis using a gas-tight syringe. An analogous procedure and identical reaction conditions were used for the other catalysts.

Catalytic conversion of LA to GVL

In a typical procedure, the supported ruthenium catalyst (60 mg, 1.79 wt % Ru, 0.011 mmol of ruthenium), was placed under nitrogen into a metal-free autoclave. A degassed solution of LA in deionized water (10.4 mL, 0.43 M, 4.47 mmol, substrate/Ru molar ratio 420) was added under nitrogen via a Teflon tube. Nitrogen was replaced by hydrogen with three cycles pressurization / depressurization. The autoclave was charged with 5 bar H_2 pressure, stirred at 240 rpm and heated to 70 °C using an oil bath. After 4 hours, the reactor was cooled down to room temperature, depressurized and the solution was removed for GC-Ms and HPLC analysis using a gas-tight syringe. An analogous procedure and identical reaction conditions were used for the other catalysts.

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Keywords: bifunctional catalysts • cascade reactions • biomass conversion • heterogeneous catalysis • Aquivion

‡ Abbreviations: MIBK, methyl isobutyl ketone; THF, tetrahydrofuran; DVB, divinylbenzene; NBD, bicyclo[2.2.1]hepta-2,5-diene; TEM, transmission electron microscopy; XRD, X-ray diffraction; EDS, energy dispersive X-ray spectrometry; ICP-OES, inductively coupled plasma optical emission spectroscopy; XPS, X-ray photoelectron spectroscopy; GC, gas chromatography; GC-Ms, gas chromatography-mass spectrometry; NMR, nuclear magnetic resonance; TPD, temperature programmed desorption.

§ C. Moreno-Marrodan and F. Liguori contributed equally to this work.

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Supporting Information

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