#### Journal of Catalysis xxx (xxxx) xxx





Journal of Catalysis



journal homepage: www.elsevier.com/locate/jcat

# Boosting levulinic acid hydrogenation to value-added 1,4-pentanediol using microwave-assisted gold catalysis

F. Bucciol<sup>a</sup>, S. Tabasso<sup>b</sup>, G. Grillo<sup>a</sup>, F. Menegazzo<sup>c</sup>, M. Signoretto<sup>c</sup>, M. Manzoli<sup>a,\*</sup>, G. Cravotto<sup>a</sup>

<sup>a</sup> Department of Drug Science and Technology and NIS – Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via P. Giuria 9, Turin 10125, Italy <sup>b</sup> Department of Chemistry, University of Turin, Via P. Giuria 7, Turin 10125, Italy

<sup>c</sup> CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM Consortium RU Ve, Via Torino 155, 30170 Venezia Mestre, Italy

#### ARTICLE INFO

Article history: Received 5 July 2019 Revised 26 September 2019 Accepted 27 September 2019 Available online xxxx

Keywords: Hydrogenation Levulinic acid 1,4-Pentanediol Microwave reactor Gold catalyst

#### ABSTRACT

Microwave (MW) -assisted levulinic acid (LA) hydrogenation has been performed over two gold catalysts (commercial 1 wt% Au/TiO<sub>2</sub> by AUROlite<sup>™</sup> and 2.5 wt% Au/ZrO<sub>2</sub>, prepared using deposition-precipitation). MW-assisted LA hydrogenation was carried out in water and in solvent-free conditions via (i) H-transfer and (ii) molecular H<sub>2</sub>. Au/TiO<sub>2</sub> promoted complete LA conversion and the further reduction of the produced GVL to 1,4-pentanediol (1,4-PDO) in the presence of 50 bar H<sub>2</sub> at 150 °C (4-hour reaction). Interestingly, selectivity to 1,4-PDO was complete at 200 °C. Extended characterisation highlighted the cooperative role played by the gold nanoparticles and the support, onto which activated hydrogen atoms spillover to react with LA. This results in the remarkable activity of Au/TiO<sub>2</sub>. Both catalysts showed structural and morphological stability under reaction conditions. It was possible to reactivate the Au/TiO<sub>2</sub> catalyst by MW-assisted oxidation, paving the way for catalyst recycling directly inside the MW reactor.

#### 1. Introduction

Levulinic acid (LA) is one of the most promising platform chemicals that can be obtained from biomass. It can be converted into high value-added molecules that can be used as green solvents and biofuel additives in the pharmaceutical industry and in the synthesis of biopolymers [1,2]. Nowadays, most research studies focus on the hydrogenation of LA or levulinic esters (LEs) into  $\gamma$ -valerolactone (GVL), another versatile chemical, due to the preferable intramolecular esterification of LA [3–5].

The important commercial value of diols in the biodegradablepolyester and organic-synthesis industries means that several bio-derived chemicals, such as glycolide, oxalic acid, lactic acid, succinic acid and furfuryl alcohol etc., have been studied for the production of diols [6–11].

However, there are not many reports on the further hydrogenation of GVL to 1,4-PDO. This may be due to the high stability of the lactone ring structure in GVL, which makes further hydrogenation processes difficult and requires a new catalytic system if the transformation is to be performed. 1,4-PDO is an important raw material in the chemical industry and the produced 1,4-PDO can be employed not only as a monomer for the production of polyesters,

\* Corresponding author. E-mail address: maela.manzoli@unito.it (M. Manzoli).

https://doi.org/10.1016/j.jcat.2019.09.041 0021-9517/© 2019 Elsevier Inc. All rights reserved. but also as a platform chemical for the synthesis of organic solvents and medicines [12]. Several bimetallic catalysts, such as Ru-Re/C [13], Rh-Mo/SiO<sub>2</sub> [14], and Ir-MoO<sub>x</sub>/SiO<sub>2</sub> [15], have been developed for the catalytic hydrogenation of LA or LEs. However, low selectivity to 1,4-PDO (42.3% to 82.0%) raises the costs of the process. Therefore, a non-noble metal catalyst such as Cu was prepared for the direct hydrogenation of LA to 1,4-PDO [16]. Unfortunately, the yield of 1,4-PDO was 22.0% even at a higher temperature (200 °C). The highest 1,4-PDO yield obtained from LA or LEs is 82.0% in heterogeneous catalytic systems [13]. Complete ethyl levulinate reduction to 1,4-PDO has been obtained at 160 °C using 1,4-dioxane as the solvent (6 h reaction time) with 60 bar H<sub>2</sub> over a CuAlZn catalyst [17]. However, its toxicity and environmental impact mean that the use of 1,4-dioxane as a solvent should be avoided, according to Green Chemistry principles [18].

Although the medium can interfere with LA hydrogenation to GVL [19], the reaction generally proceeds with high yields under a H<sub>2</sub> atmosphere in the presence of a number of solvents, such as water [20], tetrahydrofuran [21], 1,4-dioxane [19,22], and alcohols [23], as well as under solvent-free conditions [19,24,25]. The reaction also takes place via catalytic transfer hydrogenation over metal oxides, and using supported metal catalysts with either formic acid [26,27], or alcohols [28] as hydrogen donors. The reaction was reported to achieve GVL yields of 82.0–93.0% together with traces of methyltetrahydrofuran (MTHF) (<3.0%), at 250 °C, via

both catalytic hydrogen-transfer hydrogenation and in the presence of 40 bar H<sub>2</sub>. In the latter case, only the combination of both sources of hydrogen guaranteed significant MTHF yields [29].

Based on these premises, the possibility of efficiently converting LA to 1,4-PDO in the presence of a catalyst that requires no solvent (solvent-free conditions) is still highly desirable, but a significant challenge.

Microwaves (MW) are currently used as a non-conventional enabling technology for the promotion of fast chemical transformations by producing rapid internal heating, which has been hypothesised to originate from the direct interaction between the electromagnetic field and specific molecules, intermediates, or even transition states in the reaction medium [30]. Indeed, there is still much debate on discerning between thermal effects, caused by the rapid heating and the high bulk-reaction temperatures that are reached under MW dielectric heating, and other specific or non-thermal effects. Such effects, which are not linked to a macroscopic change in reaction temperature, involve non-uniform heating at the surface of heterogeneous catalysts and the production of hot spots by MW irradiation, resulting in non-equilibrium local heating that is localised at the surface of the metal nanoparticles present on catalysts [31].

In this study, we will focus on MW-assisted LA hydrogenation over gold catalysts (commercial 1 wt% Au/TiO<sub>2</sub> by AUROlite<sup>M</sup> and 2.5 wt% Au/ZrO<sub>2</sub> prepared by deposition–precipitation) to produce 1,4-pentanediol (1,4-PDO).

#### 2. Experimental

#### 2.1. Materials

The commercial gold 1 wt% on titanium dioxide (AUROliteTM, catalogue number 79-0165, CAS number 7440-57-5) was provided by Strem Chemicals INC. and sold in collaboration with Project AuTEK for research purposes [32]. The gold itself is deposited on the support via a proprietary process that yields gold nanoparticles of about 2–3 nm. The catalyst is in the form of extrudates, that were crushed in a mortar until a very fine powder was obtained before the catalytic activity tests. It was compared with a 2.5 wt% Au/ZrO<sub>2</sub> catalyst to investigate the effect of the nature of the support on the catalytic activity and selectivity.

ZrOCl<sub>2</sub> (Fluka) was used as received for sample synthesis.

#### 2.1.1. Preparation of the Au/ZrO<sub>2</sub> catalyst

 $Zr(OH)_4$  was prepared via precipitation from  $ZrOCl_2 \cdot 8H_2O$  at constant pH = 8.6, then aged under reflux conditions for 20 h at 90 °C and washed free from chloride (AgNO<sub>3</sub> test). Afterwards, the obtained zirconium hydroxide was calcined in air (30 mL/min) at 650 °C for 4 h [33].

Gold was added by deposition-precipitation at pH = 8.6 in order to obtain 2.5 wt% Au. The oxide was suspended in an aqueous solution of HAuCl<sub>4</sub>·3 H<sub>2</sub>O for 3 h and the pH was controlled by the addition of NaOH (0.5 M). After filtration, the sample was dried at 35 °C for 16 h and finally calcined in flowing air (30 mL/min) for 3 h at 500 °C. The main features of the  $Au/TiO_2$  and  $Au/ZrO_2$  as-prepared catalysts are summarised in Table 1.

#### 2.2. Characterisation methods

Both the freshly prepared and used catalysts were characterised by transmission electron microscopy (TEM) and high resolution (HR-) TEM measurements. A side entry Jeol JEM 3010 (300 kV) microscope equipped with a LaB<sub>6</sub> filament and fitted with X-ray EDS analysis by a Link ISIS 200 detector was employed. The samples, in the form of powders, were deposited on a copper grid, coated with a porous carbon film. All digital micrographs were collected using an Ultrascan 1000 camera and the images were processed using Gatan digital micrograph software. Gold-particle size distributions were obtained by counting a statistically representative number of particles (>250 and at least 150 for the used and calcined catalysts) for each sample. The mean particle diameter ( $d_m$ ) was calculated as:

$$d_m = \sum d_i n_i / \sum n_i$$

where  $n_i$  is the number of particles of diameter  $d_i$ . Moreover, on the basis of each particle-size distribution, the corresponding metal Specific Surface area (Au SSA,  $m^2/g$ ) for the supported metal particles (supposed to be spherical) was calculated using the formula:

$$SSA = 3\sum n_i r_i^2 / (\rho_{Au} \sum n_i r_i^3) m^2 / g$$

where  $r_i$  is the mean radius of the size class containing  $n_i$  particles, and  $\rho_{Au}$  is the volumetric mass of Au (19.3 g/cm<sup>3</sup>). The Au SSA values obtained for the AuRO and AuZ as-prepared catalysts are reported in Table 1.

X-ray powder diffraction patterns were collected on a PW3050/60 X'Pert PRO MPD diffractometer, from PANalytical, working in Bragg–Brentano geometry, and using a high-powered ceramic tube PW3373/10 LFF with a Cu anode (Cu K<sub> $\alpha$ 1</sub> radiation  $\lambda$  = 1.5406 Å), which was equipped with a Ni filter to attenuate  $K_{\beta}$ . Scattered photons were collected by a real-time multiple strip (RTMS) X'celerator detector. Data were collected in the  $10^{\circ} \le 2\theta \le 90^{\circ}$  angular range, with  $0.02^{\circ} 2\theta$  steps. The powdered samples were examined in their as-received form and posed in a spinning sample holder in order to minimise the preferred orientations of crystallites.

Diffuse Reflectance (DR) UV–Vis-NIR spectra were run at r.t. on a Varian Cary 5000 spectrophotometer, working in the 50,000–4000 cm<sup>-1</sup> range of wavenumbers, with the powders placed in a quartz cell. DR UV–Vis-NIR spectra are reported in the Kubelka-Munk function  $f(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$ ;  $R_{\infty}$  = reflectance of an "infinitely thick" layer of the sample.

FTIR experiments were performed on the samples in selfsupporting pellets that were introduced into the cells. This technique allows thermal treatments to be performed in controlled atmospheres and spectrum scanning to be carried out at controlled temperatures (from –196 °C to room temperature). The FTIR spectra were taken on a Perkin Elmer 2000 spectrometer (equipped with a cryogenic MCT detector). CO adsorption measurements were carried out at low temperature, i.e. the samples were cooled

#### Table 1

Gold loading, catalyst Specific Surface Area (SSA), Au mean diameter and Au SSA of Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub> as-prepared catalysts.

Catalyst	Label	Gold loading (wt%)	SSA (m <sup>2</sup> /g)	Au mean diameter (nm)**	Au SSA (m <sup>2</sup> /g)***
AuTiO <sub>2</sub>	AuRO	1	60*	$2.3 \pm 0.6$	35.3
Au/ZrO <sub>2</sub>	AuZ	2.5	40–50**	$2.4 \pm 0.7$	29.3

Provided by Strem Chemicals INC.

\*\* See the Supporting information.

\*\*\*\* Obtained via HR-TEM measurements.

at -196 °C before CO adsorption. The spectra were normalised with respect to the density of the pellets. Pyridine-adsorption experiments were performed at room temperature. In this case, the spectra were normalised with respect to the density of the pellets and to the surface area of the supports. The spectrum of the sample, before the introduction of the probe, was subtracted from each spectrum.

The adsorption of the pyridine (py) probe molecules was ensured by the use of the expanded vapours of liquid py at room temperature. Before the experiments, the liquid was deaerated using on-line freeze-pumpthaw cycles performed at the temperature of liquid-nitrogen (-196 °C). Prior to the CO– and pyridineadsorption experiments, the samples were submitted to outgassing at r.t. for 1 h to remove water, due to its exposure to air. The FTIR spectra were normalised with respect to the density of the pellets and the surface areas of the supports.

A Pyris Perkin Elmer instrument was used to perform TGA analyses. The samples were heated from 35 °C to 700 °C in a nitrogen atmosphere at a temperature ramp of 10.00 °C/min in an 80.0 mL/min N<sub>2</sub> flow.

#### 2.3. Catalytic tests

MW-assisted LA hydrogenation tests were carried out in a SynthWAVE (MLS GmbH, Milestone Srl) reactor, which houses a closed MW-cavity. LA hydrogenation was performed under both solvent-free conditions and in the presence of  $H_2O$ , used as a solvent. Moreover, the reaction was carried out using two methods: (i) H-transfer; and (ii) in the presence of molecular  $H_2$ . Methanol (MeOH), 2-propanol (2-PrOH) and formic acid (FA) were chosen as H-donors.

In a typical experiment, the Au-supported catalyst (100 mg, AuRO or 40 mg, AuZ) was added to 0.25 mmol of substrate (LA or

GVL). As for the H-transfer tests, either 10 mL of alcohol or  $50 \,\mu\text{L}$  of FA were added and the mixture was heated under MW and magnetic stirring for 4 h at 150 °C. After cooling, the crude reaction was filtered and the catalyst was washed three times with water (2 mL). After the evaporation of the solvents under vacuum, the mixture was analysed by GC–MS.

When using molecular hydrogen, the catalyst/substrate mixture (100 mg AuRO/0.25 mmol or 40 mg Au/Z/0.25 mmol) was heated in a  $H_2$  atmosphere at different pressures under MW and magnetic stirring to the required temperature for the required time. After cooling, 5 mL of water were added to the crude reaction and sonicated for 30 sec. at 40 kHz and then 2 min. at 120 kHz (Weber GmbH MG 200 TFDMF). The mixture was filtered and the catalyst was washed three times with water (2 mL). After the solvent was evaporated under vacuum, the mixture was analysed by GC–MS.

GC–MS analyses were performed on a GC Agilent 6890 (Agilent Technologies – USA), fitted with an Agilent Network 5973 mass detector, using an HP-5 column (30 m long capillary column, an i.d. of 0.25 mm and a film thickness of  $0.25 \mu$ m).

After reaction the catalyst was subsequently thermally treated and recycled as described in detail in section 3.4.

#### 3. Results and discussion

#### 3.1. On the as-prepared catalysts

HR-TEM analyses were carried out on the as-prepared AuRO and AuZ catalysts, and the results are summarised in Fig. 1.

Gold nanoparticles with a spherical shape were quite homogeneously dispersed on both supports (a and c). In particular, the Au nanoparticles have a mean diameter of  $2.3 \pm 0.6$  nm when supported on titania, whereas a mean diameter of  $2.4 \pm 0.7$  nm was



Fig. 1. HR-TEM representative images and Au particle-size distributions of the AuRO (a and b) and AuZ (c and d) as-prepared catalysts. The Au nanoparticles are highlighted by coloured arrows. Instrumental magnification: 300,000×.

#### F. Bucciol et al./Journal of Catalysis xxx (xxxx) xxx

obtained for the zirconia-supported nanoparticles (Fig. 1b and 1d, respectively).

The particle-size distributions are quite narrow in both cases, indicating that the largest fraction of nanoparticles have sizes in the 2–3 nm range and that the deposition-precipitation method provided high gold dispersion.

Moreover, the corresponding metal Specific Surface area (Au SSA,  $m^2/g$ ) for the supported metal particles (supposed to be spherical) was calculated (see Table 1) on the basis of each particle size distribution. It was found that the AuRO catalyst has a metal SSA equal to  $35.3 \text{ m}^2/g$ , whereas a value  $29.3 \text{ m}^2/g$  was obtained for the AuZ catalyst.

In addition, the HR-TEM measurements performed on the AuRO catalyst highlighted the lattice fringes that correspond to the interplanar distances related to the  $(1\ 1\ 0)$  and  $(2\ 0\ 0)$  planes of the rutile (JCPDS file number 00-001-1292) and anatase (JCPDS file number 00-001-0562) phases. On the other hand, the  $(-1\ 1\ 1)$  and  $(1\ 1\ 1)$  planes, related to monoclinic ZrO<sub>2</sub> (JCPDS file number 00-001-0750), and the  $(2\ 0\ 0)$  and  $(2\ 1\ 1)$  planes, due to the presence of zirconia in the tetragonal phase (JCPDS file number 00-002-0733), were observed for the AuZ sample.

These results indicate that the  $TiO_2$  support is made up of a mixture of rutile and anatase, whilst zirconia is a mixture of monoclinic and tetragonal phases, in agreement with the XRD patterns of the as-prepared samples shown in Fig. 2a and 2b, respectively.

Despite no peaks related to gold were observed (for the sake of clarity, the position of the 111 main peak of the cubic phase is indicated by the orange line at 2 Theta 38.2°, JCPDS file number 00-001-1172) the presence of crystalline Au cannot be neglected, because the metal loading is low and the position of the (1 1 1) peak is very close to that of the peaks of both titania and zirconia supports.

Diffuse reflectance UV–Vis-NIR analyses were carried out to investigate the electronic properties of the supported Au nanoparticles. As for the AuRO sample, the gold nanoparticles gave a broad absorption, with a maximum around 18300 cm<sup>-1</sup> that is due to the localised surface plasmon resonance (LSPR) of the supported gold [34] (violet curve in Figure S-1 in the Supporting Information). In addition, the plasmonic band is not well defined and the blueshifted component is due to the presence of small Au nanoparticles [35–37], with a component at higher wavenumbers indicating that gold species of heterogeneous size are present. In the case of AuZ (wine-coloured curve), the LSPR absorption band is more intense, appears narrower and has a slightly different maximum position (18450 cm<sup>-1</sup>).

*In situ* FTIR experiments were performed on the AuRO (Figure S-2a in the Supporting Information, bold line) and AuZ

(Figure S-2c, bold orange line) as-prepared samples, which had previously been outgassed for 1 h at room temperature. The spectra were collected after 3.0 mbar CO was introduced at -196 °C, and during heating in CO (fine orange lines). The AuRO (bold line in Figure S-2b) and AuZ (Figure S-2c, bold violet line) catalysts were then re-cooled at -196 °C in the same CO atmosphere, the spectra were also recorded during the heating (violet fine lines in Figures S-2b and S-2c) in this case.

A sharp peak at 2177 cm<sup>-1</sup>, due to CO on the Ti<sup>4+</sup> sites [38,39], and a band at  $2150 \text{ cm}^{-1}$  (CO in interaction with the OH groups of the support) with a shoulder at 2127 cm<sup>-1</sup>, which can be assigned to CO on  $Au^{\delta^+}$  sites [40], were produced after the first inlet of CO at low temperature onto the as-prepared AuRO catalyst (bold orange line in Figure S-2a). These absorptions progressively decreased in intensity when the temperature increased (fine orange lines) leaving a weak band at 2113 cm<sup>-1</sup>, due to CO on Au<sup> $\delta^+$ </sup> sites [40]. These positively charged gold sites, which originate from the final calcination during preparation, are readily reduced by the CO probe when the AuRO catalyst is re-cooled in the same atmosphere, as indicated by the new symmetric band at 2098 cm<sup>-1</sup>, which can be assigned to CO that is adsorbed onto Au<sup>0</sup> sites [41]. Quite similar spectroscopic features can be observed in the AuZ sample that underwent the experiment that was reported in Fig. 3c; the reduction of the Au<sup> $\delta$ +</sup> sites (bands at 2119 and 2014 cm<sup>-1</sup>) to Au<sup>0</sup> sites (band at  $2098 \text{ cm}^{-1}$ ) by the CO probe. In particular, the position and shape of the final band at 2098 cm<sup>-1</sup> indicate that very similar exposed Au sites are present on both catalysts. It is worth noting, above all, that the gold sites revealed by CO display the same type of reactivity toward the probe.

#### 3.2. Microwave-assisted LA hydrogenation over gold catalysts

Microwave-assisted LA hydrogenation tests were carried out and the reaction was performed under solvent-free conditions, and in the presence of  $H_2O$ , used as the solvent. LA hydrogenation was accomplished by: (i) H-transfer, with the addition of a Hdonor (methanol, 2-propanol or formic acid); and (ii) in the presence of molecular  $H_2$ . As for option (i), using FA or 2-PrOH as the H-donors, the catalytic tests gave low yields to GVL (<15.0%). In addition, when MeOH was employed, the methyl ester was the only product observed in the presence of both catalysts (data not shown). The reaction was then performed in the presence of  $H_2$ under solvent-free conditions and the results are summarised and compared with literature data in Table 2.

It was observed that low LA conversion (27.0%) and GVL yield (4.8%) were obtained in the presence of the AuZ catalyst after 4 h at 150 °C. Moreover, despite LA conversion of 98%, a very low



**Fig. 2.** Comparison of the XRD patterns of the AuRO (a) and AuZ (b) catalysts collected on the as-prepared samples and after reaction under different conditions. The position of the (1 1 1) main peak of the Au cubic phase is indicated with an orange line. A: anatase phase; R: rutile phase; M: monoclinic phase and T: tetragonal phase.

F. Bucciol et al./Journal of Catalysis xxx (xxxx) xxx



**Fig. 3.** FTIR spectra collected after the adsorption of pyridine on AuRO (a) and AuZ (b), performed by expanding the vapors of the liquid probe at room temperature (orange line) and subsequent outgassings up to 30 min (from black fine lines down to wine-coloured line). FTIR spectra collected upon adsorption of 10 mbar H<sub>2</sub>O at room temperature on preadsorbed py (blue line) on AuRO (c) and AuZ (d) and upon outgassing at increasing times (fine black lines) up to 30 min (cyan line).

Table 2
Comparison of the results obtained for different catalysts in the microwave-assisted LA hydrogenation carried out in the presence of $H_2$

Catalyst	Amount (mg)	time (h)	T (°C)	H <sub>2</sub> (bar)	Substrate	Substrate/catalyst ratio (mmol/mg)	solvent	Conversion (%)	Yield, GVL (%)	Yield, 1,4-PDO (%)
AuZ	40	4	150	50	LA	0.25:40	solvent-free	27	4.8	0
	40	4	200	50	LA	0.25:40	solvent-free	100 <sup>a</sup>	1.4	8.7
AuRO	100	4	150	50	LA	0.25:100	solvent-free	98	6.0	1.8
	100	4	200	50	LA	0.25:100	solvent-free	100	0	100
CuZnAl*	50	6	160	60	EL**	1:50	1,4-dioxane	100	2.0	98

\* Data taken from Ref. [17].

\*\* EL: ethyl levulinate.

<sup>a</sup> several high molecular-weight compounds, and 0.8% pentanoic acid.

GVL yield (6.0%) was achieved over the AuRO catalyst under the same conditions. It is worth noting that 1,4-PDO was also produced (with 1.8% yield) with this catalyst. Complete conversion was reached over both catalysts by increasing the temperature to 200 °C and the formation of 1,4-PDO was also observed in the presence of AuZ. However, the yields of GVL and 1,4-PDO still remained low with AuZ (6.0% and 1.8%, respectively), due to the formation of several high molecular weight compounds, and 0.8% pentanoic acid. Interestingly, 1,4-PDO was produced with a 100% yield over the AuRO catalyst.

These data are of pivotal importance because they highlight the synergic role played by the supported gold catalyst and MW irradiation to promote the further reduction of GVL to 1,4-PDO by opening the GVL lactone-ring structure. This process appears to be the rate-determining step of the reaction. Indeed, it has previously been reported that GVL can be produced from the MW-assisted reduction of LA and methyl levulinate at 160 °C for 25 min using *i*-propanol as the H-donor and in the presence of a 5 wt% Ru/C catalyst [42]. The best results were 43.0% LA conversion and 41.0%

yield to GVL. The Au-Pd and Ru-Pd bimetallic alloys supported on TiO<sub>2</sub> were shown to be active in LA hydrogenation to GVL, and Ru-Pd/ TiO<sub>2</sub> was extremely selective toward GVL (99%), due to the isolation of Ru sites by palladium [43]. In another paper, Au catalysts supported on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and TiO<sub>2</sub> were tested in the gas-phase continuous catalytic conversion of (aqueous) LA giving 100% yield to GVL under stoichiometric conditions ( $H_2/LA = 1$ ). The authors demonstrated that GVL was formed via hydrogenation/dehydration with 4-hydroxypentanoic acid (4-HPA) as the intermediate [44]. Zhu et al. have used a zirconia-supported gold catalyst combined with a ZSM-5 zeolite to convert hemicellulose into GVL, without using acids, in the presence of 2-propanol at 120 °C (10 bar N<sub>2</sub>) [45]. This process gave 61.5% GVL after 24 h. Prati et al. have investigated the activity of 1 wt% bimetallic Au-Ir/TiO<sub>2</sub> and Au-Ru/TiO<sub>2</sub> catalysts and observed that, in the case of iridium, the addition of gold led to a drastic drop in activity, although it enhanced selectivity to GVL (>99%) [46]. In particular, only 12.0% of LA conversion was obtained after 6 h of reaction. On the other hand, Au-Ru/TiO<sub>2</sub> (86.0% after 3 h) provided higher

activity than monometallic Ru/TiO<sub>2</sub>, while also maintaining full selectivity to GVL.

To the best of our knowledge, this is the first time that LA has been converted to 1,4 PDO over Au-based catalysts. A comparison with the results of Huo *et al.* is shown in Table 2 [17]; this paper deals with complete ethyl levulinate conversion and yields 1,4-PDO after 6 h at 160 °C over a CuZnAl catalyst, using 1,4-dioxane as the solvent and a 1:50 substrate/catalyst ratio (mmol/mg).

The effect of other parameters, such as reaction time, the nature of the employed substrate and the use of water as the solvent, were investigated by carrying out LA hydrogenation in the presence of the AuRO catalyst. The data reported in Table 3 clearly indicate that the reaction must be performed for 4 h, because LA conversion decreased from 100% to 58% and the 1,4-PDO yield was lowered to 19.6% when the reaction time was reduced to 2 h. Moreover, the choice to start from GVL did not lead to any improvement in catalytic performance; it gave conversions and yields that were lower than those accomplished when using LA as the substrate.

The use of water as the solvent strongly inhibited the reaction over the AuRO catalyst. It led to a lower yield to 1,4-PDO (18.3%) than under solvent-free conditions, and a partial stop of hydrogenation to GVL (4.6%). This effect was even more evident when performing GVL hydrogenation, since no conversion was observed. There are reports that aqueous phase GVL dehydrogenation can lead to  $\alpha$ -angelica lactone [47] and/or LA [48]. This indicates that inhibition by water can play a role in the reversibility of these reactions, as they proceed through an hydration/dehydration equilibrium step (Scheme 1). In a paper dealing with LA hydrogenation to GVL using formic acid as the H-donor in the presence of a number of 5 wt% Ru catalysts supported on carbon, the authors observed that higher conversion values were attained when lower amounts of water were used. This was due to easier diffusion to the active sites of the catalysts, resulting in the faster decomposition of the H-donor [49]. Given the same Au-particle size and exposed gold sites in the AuRO and AuZ catalysts, these findings indicate that the sites of the support have a role to play.

#### 3.2.1. Effect of the nature of the support

Information on the nature, amount and strength of the acid sites exposed at the surface is required to investigate the role that the support plays in MW-assisted LA hydrogenation. For the sake of clarity, the surface of metal oxides consists of coordinatively unsaturated (cu) cations  $(M^{n+})$  and oxide  $(O^{2-})$  ions [50]. In order to reduce the coordinative unsaturation of the surface sites, water dissociative adsorption occurs, forming terminal OH-groups [51]. In this frame, the in situ FTIR spectroscopy of small adsorbed base molecules, such as pyridine (py), is a powerful tool with which to characterise the nature, strength and concentration of acid sites [52]. In particular, the py probe can distinguish between Lewis and Brønsted acidity, giving rise to specific IR absorption bands [53]. It has been reported that the adsorption/desorption of py at room temperature produces two bands in the  $1700-1400 \text{ cm}^{-1}$ mid-IR range. The former (broad, and of medium intensity) is observed at  $\sim$ 1540 cm<sup>-1</sup> and the latter (sharp, and of low intensity) is centred at ~1445 cm<sup>-1</sup>. These bands are associated with the 19b ring mode of py, assigned to the py species adsorbed on Brønsted protonic sites (py-B), and to py species on coordinatively unsaturated  $M^{n+}$  Lewis sites (py-Lewis), respectively [54,55]. Therefore, the exposed acid sites of the supports were probed by Py adsorption and subsequent desorption. The experiments were performed at room temperature on the as-prepared catalysts, which had previously been submitted to outgassing at room temperature for 30 min. Fig. 3 compares the *in situ* FTIR spectra of py adsorbed on the AuRO (a) and AuZ (b) catalysts in the 1700–1400 cm<sup>-1</sup> frequency range of ring-breathing ( $v_{CCN}$ ) modes of vibration. In both cases, the bands ascribable to liquid-like (physisorbed) py species are observed at 1592 (8a mode) and 1440 (shoulder) cm<sup>-1</sup>. In the case of the AuRO catalyst, a component was detected at about 1480 cm<sup>-1</sup>.

The intensities of the bands related to the py-Lewis species appear to be higher than those of the bands due to py-B species. In both cases, the peak located at  $1603-1605 \text{ cm}^{-1}$  can be assigned to the 8a mode of a stronger form of adsorbed py interacting with surface OH groups via H-bonding. No bands related to the formation of pyridinium surface species were detected at higher frequencies (~1630 cm<sup>-1</sup>), which indicates that strong Brønsted acid sites were absent on both supports. After evacuation at room temperature, the observed bands remain, though with decreased intensity, at 1603 (py coordinated to Lewis acid sites), 1576-7 (8b mode common to all adsorbed py species), 1492–1490, and 1445–1442 cm<sup>-1</sup>.

Water was then adsorbed on preadsorbed py to investigate the effect of the presence of  $H_2O$  on the availability of the acid sites of the supports. A further decrease in the intensity of the bands was observed upon the adsorption of 10 mbar  $H_2O$  on preadsorbed py at room temperature (blue lines in Fig. 3c and 3d) and further outgassing at increasing times (black fine lines) up to 30 min (cyan lines).

This behaviour (much more evident for AuZ) is a clear indication that water molecules compete with adsorbed pyridine for the same adsorption sites on the supports. It is worth noting that GVL hydrogenation to 1,4-PDO is strongly inhibited by the presence of water [56], which highlights the difficulty of performing this reaction in water.

#### 3.2.2. LA hydrogenation mechanism

LA catalytic hydrogenation has been reported to produce different products, depending on the catalyst and reaction conditions [57]. LA transformation into GVL and then 1,4-PDO is made up of consecutive hydrogenation/dehydration steps, which both occur via the formation of well-defined, but short-lived intermediates [58]. The proposed steps for LA reduction are shown in Scheme 1: the LA keto group is first reduced to 4-hydroxypentanoic acid (4-HPA) by H species that are formed upon the activation of molecular hydrogen on the metallic sites. This intermediate promptly dehydrates by undergoing intramolecular esterification to give GVL. It is known that Lewis and Brønsted acid sites promote catalytic dehydration [59]. This step therefore takes place on the Lewis sites of the titania and zirconia supports. The C=O bond is

Table 3

Effect of the reaction time and of the substrate in the microwave-assisted I	A hydrogenation carried out in	n the presence of H <sub>2</sub> over the A	AuRO catalyst.
--	--------------------------------	---	----------------

Catalyst	Substrate	t (h)	T (°C)	H <sub>2</sub> (bar)	Water (mL)	Conversion (%)	Yield, GVL (%)	Yield, 1,4-PDO (%)
AuRO	LA	4	200	50	solvent-free	100	0	100
		2	200	50	solvent-free	58	9.2	19.6
		4	200	50	2.5	100	4.6	18.3
AuRO	GVL	4	150	50	solvent-free	20	0	27.7
		4	200	50	solvent-free	88	0	3.7
		4	200	50	2.5	0	0	0

F. Bucciol et al./Journal of Catalysis xxx (xxxx) xxx



Scheme 1. Steps involved in LA hydrogenation to 1,4-PDO. Inset: proposed paths for hydrogen activation during LA hydrogenation on the AuRO (a) and AuZ (b) catalysts.

further hydrogenated to give the cyclic hemiacetal, which is in equilibrium with the open hydroxyl-aldehyde form (not shown), and the aldehydic carbonyl group is hydrogenated to obtain 1,4-PDO [60]. These steps are mostly reversible, which is an additional challenge for the control of selectivity.

LA hydrogenation can also proceed through the formation of  $\alpha$ -angelica lactone as an intermediate, but no experimental evidence was found to support this mechanism under the experimental conditions of this study. A patent on LA hydrogenation reported that the bifunctional PdRe/C catalyst that was used was able to hydrogenate angelica lactone to GVL and GVL to 1,4-PDO, at 200–250 °C and 100 bar of  $H_2$  with yields up to 90% [61]. Plausibly, more acidic conditions than those present when using the AuRO and AuZ catalysts are needed to obtain  $\alpha$ -angelica lactone, since it is known that this compound can be simply prepared by boiling levulinic acid in the presence of sulfuric or phosphoric acid and further removing the produced water by distillation [62]. In sequential LA conversion in particular, the similar surface acidity that was exhibited by the two Au catalysts (see Fig. 3) seemed inadequate to promote the conversion of LA to  $\alpha$ -angelica lactone, but appeared able to contribute to the transformation of 4-HPA into GVL. It has previously been reported that catalytic activity in the transformation of LA into  $\alpha$ -angelica lactone in the gas phase strongly depends on the amount and variety of acid sites [63,64].

Looking at Table 2, LA hydrogenation to 1,4-PDO is considerably more efficient when it is performed in the presence of AuRO rather than AuZ under the same experimental conditions. It is worth noting that (i) both catalysts expose the same metal sites, (ii) that the average size of the gold nanoparticles, and (iii) the particle-size distribution are very similar, and (iv) both supports expose Lewis sites.

When comparing the activity of AuRO and AuZ catalysts under MW irradiation in severe reducing conditions ( $200 \,^{\circ}$ C, 50 bar H<sub>2</sub>), it is worth noting that, in the case of reducible oxide supports, such as TiO<sub>2</sub>, the presence of oxygen vacancies generated by the loss of structural oxygen [65], alters reactant adsorption/activation and therefore affects catalytic performance [66]. These vacancies are able to fix oxygen from water [67] and alcohols [68]. Baker *et al.* have used DFT calculations to show that the active sites for -C = O reduction in furfural hydrogenation were the oxygen vacancies present at the surface of the Pd/TiO<sub>2</sub> catalyst [69]. However, oxygen vacancies can also display the opposing effect when strong interactions with oxygenated reactants occur [70].

LA continuous catalytic conversions (aqueous) to GVL in the gas phase over Au supported on  $Al_2O_3$ ,  $CeO_2$  and  $TiO_2$  have recently been compared [44]. A 100% GVL yield at a  $H_2/LA$  ratio = 1 was achieved, and it was shown that the use of reducible supports delivered a higher GVL production rate than  $Au/Al_2O_3$ , due to LA activation on the surface oxygen vacancies. It was also observed that pentanoic acid was generated in the presence of a higher  $H_2$ feed content ( $H_2/LA > 2$ ). In this study, a small amount of pentanoic acid was detected in the presence of AuZ (Table 2), i.e. over the non-reducible support, which may indicate that the absence of oxygen vacancies favoured the further dehydration of 4-HPA to pentanoic acid.

Another point that should be considered is the activation of hydrogen along with the occurrence of H-spillover phenomena. Indeed, more complete comprehension of the mechanisms of hydrogen activation would further the understanding of the whole reaction mechanism as well as of the role played by gold and the support. It was found that the H<sub>2</sub> molecule is dissociated at room temperature on the edge and corner sites of both Au nanoparticles and clusters, regardless of the nature of the support. Experimental evidence of the formation of Au-H and Au-OH species that are strongly bound to the metal sites and compete with the adsorption of the CO probe has been provided by FTIR spectroscopy [71]. In another study, the most active sites for H<sub>2</sub> dissociation were reported to be the free-step Au edges and other Au defect sites that are located away from the Au-O-Ti interface Au-OH species [72]. All these species can be formed on both AuRO and AuZ catalysts (inset in Scheme 1, a and b respectively) and strongly affect the activity and the selectivity in reactions involving hydrogen dissociation. However, the AuRO catalyst is much more efficient than the AuZ system.

It was shown that spillover phenomena involving dissociated H atoms occur at the surface of titania, where they were ionized to

8

H<sup>+</sup>, and that the released electrons occupied the shallow trapped states just below the conduction band of the oxide, which results in a semiconductor n-doping process [71,72]. These H<sup>+</sup> species can quickly diffuse into the TiO<sub>2</sub> bulk, possibly via long-range migration involving hopping between near-neighbour oxygen atoms in a helical path along the c-axis direction [73]. It can be proposed that the H<sup>+</sup> species are able to react with activated LA and GVL during the migration, which results in an improved LA-to-GVL process as well as 1,4-PDO hydrogenation, explaining the better catalytic performance of the AuRO catalyst.

# 3.3. Stability of the catalysts: Characterisation after MW-assisted reaction

In order to investigate catalyst stability, XRD analyses were performed on the AuRO system (Fig. 1a). They revealed that the peaks for the crystalline (anatase and rutile) phases of the support are unchanged after LA hydrogenation, as carried out under the various reaction conditions (reported in Fig. 1). In addition, as in the case of the as-prepared catalysts, no peaks were detected that could be related to the presence of crystalline Au (orange line as an eye guide in Fig. 1a), and the same was found for the used AuZ catalyst (orange line as an eye guide in Fig. 1b). However, although the crystallinity of the support is still maintained, a careful inspection of the XRD patterns indicates that the relative intensities of the peaks for the tetragonal and monocline crystalline phases of zirconia are slightly different, possibly indicating the occurrence of a phase transition from tetragonal to monoclinic zirconia under reaction conditions.

HR-TEM measurements were performed on selected used samples (Fig. 4), confirming the XRD findings, since the crystallinity of

the support is preserved, as demonstrated by the analysis of the observed diffraction fringes (a, b and c of Fig. 4).

Furthermore, according to the data summarised in Table 4, contained Au agglomeration was observed for both AuRO and AuZ catalysts, despite the severe reducing conditions achieved during the reactions under MW irradiation. In detail, as for the commercial AuRO catalyst (Fig. 4a, 4b and Table 4), a similar coalescence extent was observed regardless of the reaction conditions used. Gold nanoparticles with an average size of  $3.1 \pm 1.1$  nm were detected after 4 h of LA hydrogenation at 200 °C in the presence of 50 bar H<sub>2</sub> (d), whereas nanoparticles with an average size of  $3.2 \pm 1.2$  nm were present on the same catalyst after 4 h of reaction at 150 °C, using formic acid as the H-donor instead of molecular H<sub>2</sub> (e, the reaction was carried out in the presence of 50 bar N<sub>2</sub>).

Based on the particle-size distribution, slightly more pronounced Au coalescence was observed on AuZ after 4 h LA hydrogenation at 150 °C, using formic acid as the H-donor instead of molecular H<sub>2</sub> (Fig. 4f, the reaction was carried out in the presence of 50 bar N<sub>2</sub>). Indeed, the gold nanoparticles have an average size of 3.8 ± 1.0 nm. The corresponding metal Specific Surface areas (Au SSA, m<sup>2</sup>/g) were calculated for the used AuRO and AuZ catalysts (see Table 4) and compared with those of the as-prepared samples that were reported in Table 1.

Metal SSAs ranging from 37.5 to 36.7 m<sup>2</sup>/g were found for the used AuRO catalysts. The differences in metal surface area ( $\Delta$ % SSA) compared to the as-prepared catalyst suggest that coalescence is preserved in the presence of formic acid and of molecular hydrogen.

The used AuZ catalyst displays a metal SSA equal to  $35.3 \text{ m}^2/\text{g}$ , corresponding to an overall  $\Delta\%$  SSA of  $1.8 \text{ m}^2/\text{g}$ . These results appear to be in contrast with the literature, which has reported marked sintering of Au, Pd and Ru nanoparticles supported on tita-



**Fig. 4.** Representative HR-TEM images of the AuRO (a and) and AuZ (c) catalysts and corresponding Au particle-size distributions after LA hydrogenation in the presence of molecular  $H_2$  (b) and by H-transfer (AuRO, d and AuZ, e). Instrumental magnification:  $400,000 \times$  (a and b) and  $300,000 \times$  (c).

#### F. Bucciol et al./Journal of Catalysis xxx (xxxx) xxx

#### Table 4

Au mean diameter (nm)\* Reaction conditions Au SSA (m<sup>2</sup>/g)\* A% \$\$A\*\* Catalyst AuRO 200 °C, 4 h, 50 bar H<sub>2</sub>, LA 3.1 ± 1.1 37.5 +0.8 AuRO 150 °C, 4 h, 50 bar N2, LA + FA +0.5 $3.2 \pm 1.2$ 367 AuZ 150 °C, 4 h, 50 bar N2, LA + FA  $3.8 \pm 1.0$ 35.3 +1.8

Gold mean diameter, Specific Surface Area (Au SSA) and difference with that of the as-prepared catalyst ( $\Delta$ % SSA) of the AuRO and AuZ catalysts after microwave-assisted LA hydrogenation performed under different conditions.

\* Obtained by HR-TEM measurements.

\*\* SSA variation with respect to the value attained for the corresponding as-prepared catalyst.

nia after the first run of LA hydrogenation to GVL in dioxane at 200 °C and in the presence of 40 bar  $H_2$  [43].

#### 3.4. Recovery of the AuRO catalyst

The results of the XRD and HRTEM characterisation performed on the AuRO catalyst after MW-assisted reaction encouraged us to perform a further catalytic run over the used catalyst to explore the reusability of the material. Unexpectedly, only traces of 1,4-PDO were detected under the same reaction conditions (200 °C, 4 h, 50 bar H<sub>2</sub>).

TGA measurements were carried out on the AuRO catalyst before (as-prepared catalyst), and after the reaction (used catalyst) to investigate the reasons for this deactivation and the results are shown in Figure S-3.

Upon heating from 35 °C to 700 °C in a 80.0 mL/min N<sub>2</sub> flow (with a temperature ramp of 10.00 °C/min) the as-prepared AuRO catalyst showed a small weight loss, due to the desorption of water, and maintained 98.3% of its original weight. On the other hand, the used catalysts displayed several weight-loss values that depended on the reaction conditions, i.e. temperature and nature of the substrate (GVL or LA). Weight loss ranged between 2.8% and 13.7% and was more pronounced when the reaction was performed from LA rather than from GVL, and at 150 °C rather than 200 °C. These results confirm that the increase in temperature from 150 °C up to 200 °C promoted the reaction for both LA and GVL substrates and reveal that, by carrying out the reaction at 200 °C, lower amounts of unreacted species and/or products are able to remain adsorbed on the surface of the catalyst. The amount of these species appears to be slightly higher for LA (weight loss of 13.7% at 150 °C and 6.4% at 200 °C) than for GVL (6.8% at 150 °C and 2.8% at 150 °C). This trend can be reasonably explained when we consider that: (i) LA tends to form humins [74], whereas GVL is more stable; (ii) LA hydrogenation involves more steps than GVL hydrogenation; and (iii) the results of the catalytic tests revealed lower GVL conversions.

The presence of unreacted species and/or reaction products can poison the active sites of the support, such as the Lewis-acid sites and the oxygen vacancies. The AuRO catalyst was therefore submitted to different activation procedures and subsequently tested for MW-assisted LA hydrogenation to recover the catalytic activity. After each activation, the plasmon absorption band of gold was preliminary monitored by DR UV-Vis spectroscopy to check for possible nanoparticle agglomeration. (The spectrum of the used AuRO catalyst is reported as a reference, the position of the Au plasmonic band is the same as that of the as-prepared AuRO catalyst, see Figure S-1). The spectroscopic findings have been further confirmed by the results of the HR-TEM analyses performed on the used catalyst submitted to the same thermal treatments. In order to remove unreacted species and/or products without compromising Au dispersion, the catalyst was first calcined for 2 h at 400 °C, i.e. the temperature of the final calcination during its synthesis. The reactivated catalyst did not show any LA conversion, and an increase in the calcination time to 4 h failed to give positive results (data not shown). A comparison between the DR UV-Vis spectra of the reactivated catalysts and the used catalysts is reported in Fig. 5a. An increase in intensity and a red shift in the maximum of the plasmonic band of gold were observed, which can indicate that the Au nanoparticles agglomerated upon both calcination treatments. This hypothesis was validated by HR-TEM measurements carried out on the AuRO catalyst submitted to calcination for 4 h at 400 °C, that showed an increase of the size of the Au particles (Fig. 5b, indicated by arrows) up to  $7.0 \pm 2.1$  nm (Fig. 5c), hence explaining the loss of reactivity. Moreover, upon calcination at 400 °C, the colour of both reactivated samples unexpectedly changed from intense violet (a, downward) to light blueviolet (a, upward), which corroborated by the HRTEM findings on the used catalyst described in section 3.3, appear in contrast with



**Fig. 5.** (a): comparison of the DR UV–Vis spectra of the used (black curve) AuRO catalyst and of the same catalyst after calcination at 400 °C for 2 h (dashed light blue-violet curve), and for 4 h (light-blue-violet curve). The digital images taken on the powders of the catalyst after reaction and after calcination at 400 °C for 4 h are shown in (a), downward and upward, respectively. (b): representative HR-TEM image of the used AuRO catalyst submitted to calcination at 400 °C for 2 h, Fourier Transformed of the image (b, downward) and corresponding Au particle-size distribution (c). Instrumental magnification: 250,000×.



**Fig. 6.** (a): comparison of the DR UV–Vis spectra of the used AuRO catalyst (violet curve) and of the same catalyst submitted to MW-assisted calcination in 15 bar O<sub>2</sub> for 2 h (orange curve).(b): representative HR-TEM image of the used AuRO catalyst submitted to MW-assisted calcination in 15 bar O<sub>2</sub> for 2 h, Fourier Transformed of the image (b, upward) and corresponding Au particle-size distribution (c). Instrumental magnification: 300000X.

the occurrence of such agglomeration. It is worth noting that the distances measured on the Fourier Transform of the HR-TEM image (Fig. 5b, downward) were typical of defective titania phases, such as  $Ti_5O_9$  (JCPDS file number 00-011-0193) and  $Ti_3O_5$  (JCPDS file number 00-011-0217). It could be proposed that the reduced support contributes to the final colour of the used catalyst even after calcination.

Another attempt was performed by submitting the used AuRO catalyst to prolonged calcination at 500 °C for 24 h, with a gentle temperature ramp of 2 °C/min. Also in this case the catalytic activity was not restored despite these precautions. However, even if this strategy guaranteed the complete removal of the poisoning species, metal agglomeration was not avoided because a gold average size of 19.8  $\pm$  6.9 nm was obtained by HR-TEM analysis (Figures SI-4 a, SI-4b andSI-4c).

The above results indicate that conventional calcination treatment is not effective in reactivating the catalyst for MW-assisted LA hydrogenation regardless of the time and temperature chosen.

Another consideration that must be taken into account is that LA hydrogenation was performed under severe reducing conditions; 200 °C under 50 bar H<sub>2</sub> and MW-irradiation for 4 h. Classical reactive force field (ReaxFF) molecular-dynamics simulations have been used together with first-principles density functional theory (DFT) calculations to investigate the high-pressure hydrogenation of anatase TiO<sub>2</sub> nanoparticles [75]. The authors explored the behaviour of TiO<sub>2</sub> nanoparticles at 523 °C under vacuum conditions and showed that only a few oxygen vacancies were formed with crystal structure preservation, and relatively small numbers of surface atoms were displaced overall. Conversely, the reduction of the spherical nanoparticle to TiO<sub>1.9452</sub> was rapid (1 ns) when exposed to 200 bar H<sub>2</sub>, due to the large surface-to-volume ratio. Under these conditions, the atoms in the surface layer were displaced by 2–2.5 Å, on average, which is a larger distance than the typical Ti-O bond length. As a result, a disordered phase was created on the surface, whereas the crystal structure was preserved. The authors demonstrated that the oxygen vacancies reside longer on sites close to the {001} facets, and play a key role in the amorphisation of the surface. In addition, TiO<sub>2</sub> nanoparticles that had previously been treated with Al/H<sub>2</sub> were shown to undergo structural and optical property changes, and improved MW absorption. The high efficiency of MW absorption was linked to the disorderinduced property changes in the materials [76].

It can be therefore reasonably assumed that along with a retained growth of the Au particle size and with the presence of adsorbed organics attested by TGA, the AuRO catalyst underwent TiO<sub>2</sub> surface reduction/amorphisation under MW-assisted LA hydrogenation conditions and that the process is responsible for

catalyst deactivation. Indeed, the XRD analyses performed on the used catalysts (Fig. 2a) confirmed the crystallinity of the  $TiO_2$  nanoparticles after reaction.

To further investigate such hypothesis, the used catalyst was submitted to MW-assisted oxidation at 200 °C in 15 bar O<sub>2</sub> for 2 h. Upon this reactivation, the plasmonic band of Au was only slightly blue shifted to 18470 cm<sup>-1</sup> (orange curve in Fig. 6a) in agreement with the results of HR-TEM analysis which revealed contained agglomeration of the gold nanoparticles (average size of  $3.4 \pm 1.2$  nm, Fig. 6c) and possibly the partial reoxidation of the titania surface.

The presence of distances related to anatase (JCPDS file number 00-001-0562) and rutile (JCPDS file number 00-001-1292) phases seems to confirm such surface restoration. Moreover, the catalytic activity was partially regenerated; 25.5% GVL yield was achieved.

Although the MW-assisted oxidation treatment needs to be optimised, this result is of pivotal importance as it highlights the fact that MW-assisted reactivation in an oxygen atmosphere is needed to restore the surface of the catalyst, paving the way for catalyst recycling directly inside the MW reactor by simply purging with  $N_2$  and switching the feed from a  $H_2$  to an  $O_2$  atmosphere.

#### 4. Conclusions

MW-assisted LA hydrogenation over a commercial Au/TiO<sub>2</sub> (AuRO) catalyst and a lab-made Au/ZrO<sub>2</sub> (AuZ) catalyst has been investigated. The reaction was performed solvent-free and in the presence of H<sub>2</sub>O. Moreover, catalytic tests were carried out by H-transfer, and in the presence of molecular H<sub>2</sub>. Several parameters, including temperature, pressure and catalyst amount, were evaluated and complete LA reduction was obtained with 100% yield to 1,4-PDO at 200 °C without any solvent with 50 bar H<sub>2</sub> (4 h) over the AuRO catalyst. A reaction mechanism involving the cooperative effect of metal sites and the Lewis-acid sites of the support has been proposed. In this context, water prevents the formation of 1,4-PDO due to competition with the substrate for the Lewis sites of the support.

Both Au/TiO<sub>2</sub> and Au/ZrO<sub>2</sub> catalysts showed structural and morphological stability under MW-assisted LA hydrogenation, regardless the reaction conditions used. The results indicate that the AuRO catalyst can be reactivated by MW-assisted oxidation, paving the way for catalyst recycling directly inside the MW reactor.

#### **Declaration of Competing Interest**

There are no conflicts to declare.

#### Acknowledgements

M. M., S.T. and G.C. are grateful for financial support from the University of Turin (Ricerca Locale 2018).

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.09.041.

#### References

- [1] D.W. Rackemann, W.O.S. Doherty, Bioprod. Bioref. 5 (2011) 198-214.
- [2] J.M. Bermudez, J.A. Menendez, A.A. Romero, E. Serrano, J. Garcia-Martinez, R. Luque, Green Chem. 15 (2013) 2786–2792.
- D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Green Chem. 15 (2013) 584-595.
- [4] I.T. Horváth, H. Mehdi, V. Fábos, L. Boda, L.T. Mika, Green Chem. 10 (2008) 238-242
- [5] S. Tabasso, G. Grillo, D. Carnaroglio, E. Calcio Gaudino, G. Cravotto, Molecules 21 (2016) 413-429.
- [6] L. Xu, Z. Huo, J. Fu, F. Jin, Chem. Commun. 50 (2014) 6009–6012.
  [7] L. Li, D. Ren, J. Fu, Y. Liu, F. Jin, Z. Huo, J. Energy Chem. 25 (2016) 507–511.
- [8] J. Xiao, Z. Huo, D. Ren, S. Zhang, J. Luo, G. Yao, F. Jin, Process Biochem. 50 (2015) 793-798
- [9] K.H. Kang, U.G. Hong, Y. Bang, J.H. Choi, J.K. Kim, J.K. Lee, S.J. Han, I.K. Song, Appl. Catal. A 490 (2015) 153-162.
- [10] T.J. Korstanje, J.I. van der Vlugt, C.J. Elsevier, B. de Bruin, Science 350 (350) (2015) 298-302.
- [11] X. Liu, X. Wang, G. Xu, Q. Liu, X. Mu, H. Liu, J. Mater. Chem. A 3 (2015) 23560-23569
- [12] L. Yan, Q. Yao, Y. Fu, Green Chem. 19 (2017) 5527-5547.
- [13] L. Corbel-Demailly, B.K. Ly, D.P. Minh, B. Tapin, C. Especel, F. Epron, A. Cabiac, E. Guillon, M. Besson, C. Pinel, ChemSusChem 6 (2013) 2388-2395.
- [14] M. Li, G. Li, N. Li, A. Wang, W. Dong, X. Wang, Y. Cong, Chem. Commun. 50 (2014) 1414-1416.
- [15] Z. Wang, G. Li, X. Liu, Y. Huang, A. Wang, W. Chu, X. Wang, N. Li, Catal. Commun. 43 (2014) 38-41.
- [16] Q. Xu, X. Li, T. Pan, C. Yu, J. Deng, Q. Guo, Y. Fu, Green Chem. 18 (2016) 1287-1294
- D. Ren, X. Wan, F. Jin, Z. Song, Y. Liu, Z. Huo, Green Chem. 18 (2016) 5999-[17] 6002.
- [18] P.T. Anastas, J.C. Warner, Green chemistry: theory and practice, Oxford University Press, New York, 1998, p. 30.
- W. Luo, U. Deka, A.M. Beale, E.R.H. van Eck, P.C.A. Bruijnincx, B.M. [19] Weckhuysen, J. Catal. 301 (2013) 175-186.
- [20] J.C. Serrano-Ruiz, D. Wang, J.A. Dumesic, Green Chem. 12 (2010) 574–577.
- [21] C. Ortiz-Cervantes, J.J. Garcíia, Inorg. Chim. Acta 397 (2013) 124-128.
- [22] Y. Gong, L. Lin, Z. Yan, BioResources 6 (2011) 686-699.
- [23] M.G. Al-Shaal, W.R.H. Wright, R. Palkovits, Green Chem. 14 (2012) 1260-1263.
- [24] J.-P. Lange, R. Price, P.M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Angew. Chem. Int. Ed. 49 (2010) 4479-4483.
- [25] J.-P. Lange, R. Price, P.M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, Angew. Chem. 122 (2010) 4581-4585. [26] L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao, Q.-X.X. Guo, ChemSusChem 3 (2010) 1172-
- 1175.
- X.L. Du, Q.Y. Bi, Y.M. Liu, Y. Cao, K.N. Fan, ChemSusChem 4 (2011) 1838–1843. [27]
- [28] M. Chia, J.A. Dumesic, Chem. Commun. 47 (2011) 12233-12235.
- [29] I. Obregjn, I. Gandarias, M.G. Al-Shaal, C. Mevissen, P.L. Arias, R. Palkovits, ChemSusChem 9 (2016) 2488-2495.
- [30] G. Cravotto, D. Carnaroglio (Eds.), "Microwave Chemistry (De Gruyter Textbook)" De Gruyter, 2017.
- [31] Y. Tsukahara, A. Higashi, T. Yamauchi, T. Nakamura, M. Yasuda, A. Baba, Y. Wada, YJ. Phys. Chem. C 114 (2010) 8965-8970.
- [32] https://www.strem.com/catalog/family/Aurolite/
- [33] F. Menegazzo, M. Signoretto, M. Manzoli, F. Boccuzzi, G. Cruciani, F. Pinna, G. Strukul, J. Catal. 268 (2009) 122-130.
- [34] E. Kowalska, O.O. Prieto Mahaney, R. Abe, B. Ohtani, Phys. Chem. Chem. Phys. 12 (2010) 2344-2355.

- [35] J. Tiggesbaumker, L. Koller, H.O. Lutz, K.H. Meiwesbroer, Chem. Phys. Lett. 190 (1992) 42 - 47
- [36] A. Leibsch, Phys. Rev. B: Condens. Matter 48 (1993) 11317-11328.
- [37] A. Moores, F. Goettmann, New J. Chem. 30 (2006) 1121-1132.
- [38] G. Martra, Appl. Catal. A 200 (2000) 275-285.
- [39] F. Pinna, A. Olivo, V. Trevisan, F. Menegazzo, M. Signoretto, M. Manzoli, F. Boccuzzi, Catalysis Today 203 (2013) 196-201.
- [40] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal. 202 (2001) 256-267. [41] F. Menegazzo, M. Manzoli, A. Chiorino, F. Boccuzzi, T. Tabakova, M. Signoretto,
- F. Pinna, N. Pernicone, J. Catal. 237 (2006) 431-434.
- [42] M.G. Al-Shaal, M. Calin, I. Delidovich, R. Palkovits, Catal. Commun. 75 (2016) 65-68.
- [43] W. Luo, M. Sankar, A.M. Beale, Q. He, C.J. Kiely, P.C.A. Bruijnincx, B.M. Weckhuysen, Nat. Commun. 6 (2015) 6540, https://doi.org/10.1038/ ncomms7540.
- [44] F.K-. Mustafin, M.A. Cádenas-Lizana, J. Keane, Chem. Technol. Biotechnol. 92 (2017) 2221-2228.
- [45] S. Zhu, Y. Xue, J. Guo, Y. Cen, J. Wang, W. Fan, ACS Catal. 6 (2016) 2035–2042. [46] L. Landenna, A. Villa, R. Zanella, C. Evangelisti, L. Prati, Chinese, J. Catal. 37
- (2016) 1771-1775. [47] I. Obregjn, I. Gandarias, N. Miletić, A. Ocio, P.L. Arias, ChemSusChem 8 (2015)
- 3483-3488. [48] J. Deng, Y. Wang, T. Pan, Q. Xu, Q.-X. Guo, Y. Fu, ChemSusChem 6 (2013) 1163-
- 1167.
- [49] A.M. Ruppert, M. Jędrejczk, O. Sneka-Platek, N. Keller, A.S. Dumon, C. Michel, P. Sautet, J. Grams, Green Chem. 18 (2016) 2014-2028.
- [50] H. Knözinger, in: Fundamental Aspects of Heterogeneous Catalysis Studied by Particle Beams, Plenum Press, New York, 1991, pp. 167–189.
- [51] H.-P. Boehm, H. Knözinger, in: J.R. Anderson, M. Boudart (Eds.), Catal. Sci. and Technol, vol. 4, Springer, Berlin, 1983, pp. 40–189.
- [52] M.I. Zaki, M.A. Hasan, F.A. Al-Sagheer, L. Pasupulety, Colloids Surf. A: Physicochem. Eng. Aspects 190 (2001) 261-274.
- [53] C. Morterra, G. Cerrato, Langmuir 6 (1990) 1810-1812.
- [54] C. Morterra, G. Cerrato, F. Pinna, G. Meligrana, Top. Catal. 15 (2001) 53-61.
- [55] C. Morterra, G. Cerrato, G. Meligrana, Langmuir 17 (2001) 7053-7060.
- [56] M.G. Al-Shaal, A. Dzierbinski, R. Palkovits, Green Chem. 16 (2014) 1358-1364.
- [57] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502.
- [58] F.M.A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 49 (2010) 5510-5514.
- [59] R. Weingarten, G.A. Tompsett, W.C. Conner Jr., G.W. Huber, J. Catal. 279 (2011) 174-182
- [60] D. Licursi, C. Antonetti, S. Fulignati, M. Giannoni, A.M. Raspolli Galletti, Catalysts 8 (2018) 277-293.
- [61] D.C. Elliott, J.G. Frye, US Patent 5883266, 1998.
- [62] Y. Iwakura, K. Nagakubo, K. Hayashi, JP Patent 31007506, 1956.
- [63] P. Balla, V. Perupogu, P.K. Vanama, V.R.C. Komandur, J. Chem. Technol. Biotechnol. 91 (2016) 769-776.
- [64] V.V. Kumar, G. Naresh, M. Sudhakar, J. Tardio, S.K. Bhargava, A. Venugopal, Appl. Catal. A: General 505 (2015) 217–223.
- [65] M.V. Ganduglia-Pirovano, A. Hofmann, J. Sauer, Surf. Sci. Rep. 62 (2007) 219-270.
- [66] D.R. Mullins, Surf. Sci. Rep. 70 (2015) 42-85.
- [67] R.S. Smith, Z. Li, L. Chen, Dohnálek Zand, B.D. Kay, J. Phys. Chem. B 118 (2014) 8054-8061.
- [68] E. Farfan-Arribas, R.I. Madix, J. Phys. Chem. B 106 (2002) 10680-10692.
- [69] L.R. Baker, G. Kennedy, M.V. Spronsen, A. Hervier, X. Cai, S. Chen, L.-W. Wang, G.A. Somorjai, J. Am. Chem. Soc. 134 (2012) 14208-14216.
- [70] J. Paier, C. Penschke, J. Sauer, Chem. Rev. 113 (2013) 3949–3985.
- [71] M. Manzoli, A. Chiorino, F. Vindigni, F. Boccuzzi, Catal. Today 181 (2012) 62-67
- [72] D.A. Panayotov, S.P. Burrows, J.T. Yates, J.R. Morris, J. Phys. Chem. C 115 (2011) 22400-22408
- [73] E.J. Spahr, L. Wen, M. Stavola, L.A. Boatner, L.C. Feldman, N.H. Tolk, G. Lüpke, Phys. Rev. Lett. 104 (2010) 205901.
- [74] B. Velaga, R.P. Parde, J. Soni, N.R. Peela, Micropor. Mesopor. Mat. 287 (2019) 18 - 28
- [75] S. Selcuk, X. Zhao, A. Selloni, Nat. Mater. 17 (2018) 923-928.
- [76] M. Green, P. Xiang, Z. Liu, J. Murowchick, X. Tan, F. Huang, X. Chen, J. Materiomics 5 (2019) 133-146.