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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.9b02139 • Publication Date (Web): 16 Sep 2019

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Pt/ZrO₂ Prepared by Atomic Trapping: an Efficient Catalyst for the Conversion of Glycerol to Lactic Acid with Concomitant Transfer Hydrogenation of Cyclohexene

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ABSTRACT: A series of heterogeneous catalysts consisting of highly dispersed Pt nanoparticles supported on nanosized ZrO_2 (20 to 60 nm) was synthesized and investigated for the one-pot transfer hydrogenation between glycerol and cyclohexene to produce lactic acid and cyclohexane, without any additional H_2 . Different preparation methods were screened, by varying the calcination and reduction procedures with the purpose of optimizing the dispersion of Pt species (i.e. as single-atom sites or extra-fine Pt nanoparticles) on the ZrO_2 support. The Pt/ ZrO_2 catalysts were characterized by means of transmission electron microscopy techniques (HAADF-STEM, TEM), N_2 -physisorption, H_2 temperature-programmed-reduction (H_2 -TPR), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Based on this combination of techniques it was possible to correlate the temperature of the calcination and reduction treatments with the nature of the Pt species. The best catalyst consisted of sub-nanometer Pt clusters (< 1 nm) and atomically-dispersed Pt (as Pt^{2+} and Pt^{4+}) on the ZrO_2 support, which were converted into extra-fine Pt nanoparticles (average size = 1.4 nm) upon reduction. These nanoparticles acted as catalytic species for the transfer hydrogenation of glycerol with cyclohexene, which gave an unsurpassed 96% yield of lactic acid salt at 96% glycerol conversion (aqueous glycerol solution, NaOH as promoter, 160 °C, 4.5 h at 20 bar N_2). This is the highest yield and selectivity of lactic acid (salt) reported in the literature so far. Reusability experiments showed a partial and gradual loss of activity of the Pt/ ZrO_2 catalyst, which was attributed to the experimentally observed aggregation of Pt nanoparticles.

KEYWORDS: glycerol, lactic acid, Pt catalyst, transfer hydrogenation, cyclohexene

Introduction

Biomass is a renewable and, therefore, sustainable alternative to fossil resources like oil, gas and coal for the production of bulk and fine chemicals.¹⁻³ Glycerol is one of the most attractive bio-based platform molecules due to the broad scope of chemical products that can be derived from it (e.g. lactic acid, acrolein, acrylic acid, 1,2- and 1,3-propanediol) and for its availability, which is a consequence of being the main side product of the manufacturing of biodiesel through transesterification of triglycerides from vegetable oils with methanol.⁴⁻⁵ Therefore, the production of valuable fine and bulk chemicals from glycerol has attracted a lot of interest from both academia and industry.⁶⁻⁸ Among the products that can be obtained from glycerol, lactic acid (LA) and alkyl lactates are attractive bio-based platform molecules with several applications, ranging from the synthesis of the biodegradable poly-lactic acid to the use as green solvents.⁹ Lactic acid and lactates can be produced from glycerol through a dehydrogenation-rearrangement pathway (Scheme 1), which would provide a viable alternative to the current production of lactic acid by fermentation of carbohydrates.^{4, 9-12} The dehydrogenation-rearrangement of glycerol implies the nominal formation of H₂ (Scheme 1) and in this sense can be correlated to the use of glycerol as feedstock for the sustainable production of H₂ through a aqueous phase reforming (APR).^{8, 13-14} Hydrogen is widely used in the chemical industry (e.g. ammonia synthesis, Fischer-Tropsch process, steel industry and various hydrogenation reactions) and in the fuel cell systems as a clean power source.^{2, 8, 15} Clearly, routes that allow producing H₂ from a renewable source such as biomass represent a sustainable alternative to the current production from fossil fuels through methane steam reforming, which requires extremely harsh conditions.^{2, 16}

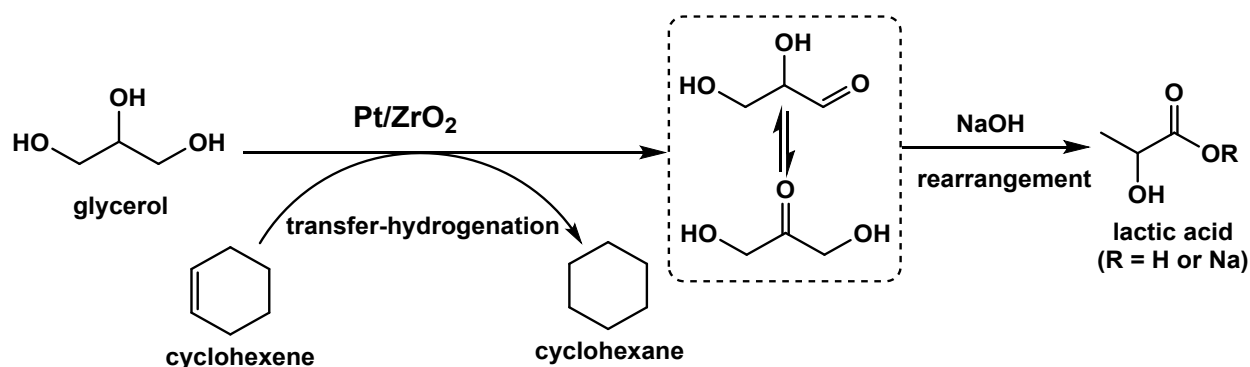
The first reports on the conversion of aqueous glycerol into a lactic acid salt employed strongly basic solutions (NaOH and KOH in stoichiometric excess relative to glycerol) at high

temperature (300 °C).¹⁷⁻¹⁹ The combination of an excess of base and high temperature promoted the rate of dehydrogenation in the first step of the reaction network, and the rate of the rearrangement in the second step by neutralizing the formed lactic acid. However, these conditions are not desirable for practical application nor from the point of view of green chemistry. The reaction temperature can be lowered to 180 °C under a He atmosphere by using a noble metal catalyst (Pt/C or Ir/C) in combination with a homogeneous base, reaching 95% conversion of glycerol and 55% selectivity towards lactic acid.²⁰⁻²¹ The oxidative dehydrogenation of glycerol can also be carried out in the presence of O₂, in which case water is the side-product. In this context, supported Au and its alloy catalysts (AuPt/TiO₂) in combination with NaOH gave 30% glycerol conversion and 86% selectivity to lactic acid at 90 °C.¹⁷ More recent reports proved that the presence of a base is not essential under this oxidative atmosphere, with a bifunctional catalyst consisting of Pt supported on a zeolite (Sn-MFI) achieving an excellent 81% selectivity towards lactic acid at 90% conversion of glycerol under O₂ (6 bar) at a relatively mild temperature (90 °C).¹⁰ Between the employed approaches, the path in the absence of O₂ allows generating valuable H₂ but requires relatively high temperature and a base to promote the dehydrogenation, whereas the reactions conducted under O₂ do not require a base (though at the cost of the turnover frequency per metal site) but the hydrogen atoms removed from glycerol react with oxygen to form a low-value product as water.¹⁰

A third approach that provides an attractive alternative to those described above consists in combining the dehydrogenation of glycerol with the hydrogenation of another compound. Few reports described the hydrogenation of cyclohexene or nitrobenzene using glycerol as hydrogen source, but focusing only on the efficiency of the hydrogenation step and not on that of the conversion of glycerol.²²⁻²⁵ Here, we report a catalytic system that combines the dehydrogenation

of glycerol and hydrogenation of cyclohexene over a Pt/ZrO₂ heterogeneous catalyst in a one-pot batch reaction under N₂ atmosphere (Scheme 1). We show that the careful design of the catalyst enables the efficient conversion of glycerol to lactic acid with much higher selectivity and under significantly milder conditions compared to those previously reported for the dehydrogenation of glycerol in the absence of O₂. Additionally, by performing the reaction in the presence of a model hydrogen acceptor as cyclohexene, we combined a very high lactic acid yield with the production of cyclohexane. In our catalyst design we selected Pt as active species, since this metal is highly active and, thus, widely used in hydrogenation and dehydrogenation reactions.²⁶ Since Pt is a very expensive element, it is of crucial importance to maximize the activity per gram of metal (and thus the TON). For this purpose, several preparation methods have been developed to obtain highly and uniformly dispersed Pt nanoparticles, such as wet-impregnation, sol-immobilization and deposition-precipitation.²⁷⁻³⁰ Very recently, a method based on atomic trapping was developed for the preparation of highly dispersed Pt, even at atomic level.³¹⁻³³ It was reported that the oxidized Pt species can disperse as single atoms on a CeO_{2-x} support upon calcination at 800 °C under air. The obtained catalyst showed excellent catalytic performance in the low-temperature oxidation of CO and in the conversion of methane into C₂ hydrocarbons.³⁴⁻³⁵ Only a few kinds of supports (i.e., CeO_{2-x}, TiO₂ and nitrogen doped carbon) were found to promote such dispersion of Pt species at atomic level.^{31, 35-36} Here, these concepts have been extended to the preparation of highly dispersed Pt species (as Pt²⁺ and Pt⁴⁺) on a nanosized ZrO₂ (particle size between 20 and 60 nm; average size: 32 nm). This oxide was chosen because of the similarity of its coordination geometry (zirconium is coordinated to 7 oxygens) to that found in CeO_{2-x} (with 0 < x < 0.5 as a consequence of the presence of Ce(III) along Ce(IV) species),³⁷ but its potential as support for atomically dispersed Pt species has not been explored yet.³⁸ The Pt species were

converted into extra-fine Pt nanoparticles upon reduction by H_2 , and this system was studied for the first of time for the combined dehydrogenation of glycerol and hydrogenation of cyclohexene, achieving unsurpassed yield and selectivity of lactic acid.



Scheme 1. Catalytic route from glycerol to lactic acid using cyclohexene as hydrogen acceptor.

Experimental

Materials

Glycerol (99%), 1,3-dihydroxyacetone dimer (97%), glyceraldehyde (90%), glycolic acid (99%), lactic acid (98%), pyruvic aldehyde (40 wt% in H_2O), cyclohexene (99%), cyclohexane (99.5%), sodium hydroxide (98%), benzene (99.9%), hydro platinumic acid ($H_2PtCl_4 \cdot xH_2O$, 99.9%), zirconium oxide (nanopowder, <100 nm), cerium oxide (nanopowder), titanium oxide (P25) were purchased from Sigma Aldrich. Glyceric acid (20 wt% in H_2O) was purchased from TCI Chemicals. The H_2O used in this work was always of MilliQ grade. All chemicals were used without further purification.

Catalyst synthesis

A wet-impregnation method was used for the preparation of the Pt/ZrO₂ catalysts. Typically, ZrO₂ (2.0 g) was mixed with an aqueous solution of H₂PtCl₄ (4.5 g Pt per L), with the volume of the latter being tuned to the target loading of Pt, and the slurry was stirred at room temperature until the water was evaporated. The solid mixture was then dried at 100 °C in air overnight in an oven. The resulting solid was milled into a fine powder and then calcined in air (400, 550 or 800 °C, heating rate 3 °C/min). The calcined catalysts were reduced in a tubular oven under H₂ flow (99.9%; 200 mL/min) at a selected temperature (100, 250 or 400 °C, heating rate 3 °C/min) for 2 h. The gas flow was switched to N₂ for 1 h to remove adsorbed H₂ from the catalyst surface. A typical catalyst prepared by this method was named as aPt/ZrO₂-b-Rc, in which a, b and c stand for the wt% loading of Pt (a), the calcination temperature (b) and the reduction temperature (c). In addition, the catalyst prepared with 2 wt% of Pt was also reduced directly at 250 °C under a H₂ flow for 2 h after overnight drying (without calcination). This catalyst was named 2Pt/ZrO₂-DR250.

Characterization of the catalysts

Transmission electron microscopy (TEM) images were obtained using a CM12 (Philips) electron microscope operating at 120 keV. The samples were prepared by ultra-sonication in ethanol, after which a droplet of the suspension was added to a carbon coated 400 mesh copper grid. The images were taken with a slow scanning CCD camera.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and EDX mapping were collected using an aberration-corrected cubed FEI Titan microscope operating at an acceleration voltage of 300 kV. The samples were prepared by

suspending the material in ethanol and depositing drops of the suspension on a copper grid covered with a holey carbon film.

Nitrogen physisorption isotherms were measured at -196 °C using a Micromeritics ASAP 2420 apparatus. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area. The Barrett-Joyner-Halenda (BJH) method was used to calculate the pore volume.

Elemental analysis by inductively-coupled plasma optical emission spectrometry (ICP-OES) was performed using a Perkin Elmer Optima 7000 DV instrument to determine the actual Pt loadings in the catalysts.

X-ray Photoelectron Spectroscopy (XPS) analysis was carried out by mounting the catalysts on a conductive tape adhered to the XPS sample holder. No further treatment was carried out prior to the XPS measurement. The sample was loaded into the device and the pressure was reduced below $1 \cdot 10^{-7}$ mbar. The XPS measurements were performed using a Surface Science SSX-100 ESCA instrument equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). During the measurement, the pressure was kept below $2 \cdot 10^{-9}$ mbar in the analysis chamber. For acquiring the data, a spot diameter of 600 μm was used. The neutralizer was turned on, to avoid charging effects. All XPS spectra were analyzed using the Winspec software package developed by LISE laboratory, University of Namur, Belgium including Shirley background subtraction and peak deconvolution.

Hydrogen-temperature programmed reduction (H_2 -TPR) measurements were performed on an Autochem II 2920 from Micromeritics. In a typical experiment, 80 mg of sample was pre-treated at 500 °C (heating rate 10 °C/min) for 1 h in a flow of He (30 mL/min). Subsequently, the sample was cooled to 50 °C under the same flow of He. The reduction analysis was performed from 50 to 900 °C (10 °C/min) in a 30 mL/min flow of 5 vol.% H_2 in He.

X-ray diffraction (XRD) measurements were performed on a D8 Advance Bruker diffractometer with a Cu K α_1 radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns were collected under 40 kV and 40 mA in the range of 10°-80°.

Catalytic tests

The catalytic tests were carried out in a 100 mL Parr stainless steel autoclave reactor equipped with a Teflon liner and an overhead stirrer. In a typical test, a predetermined amount of the Pt/ZrO₂ catalyst was loaded into the reactor together with an aqueous solution of glycerol (0.5 M in 20 ml), NaOH (0.015 mol) and cyclohexene (0.02 mol, as organic phase). The reaction was performed under N₂ (20 bar) for 4.5 h at 160 °C (heating time 0.5 h not counted) at a stirring speed of 800 rpm. Then, the reactor was depressurized and the biphasic liquid was separated into an aqueous and an organic phase, which were filtered to remove the catalyst. The organic phase was analyzed by gas chromatography using a Thermo Trace GC equipped with a Restek Stabilwax-DA column (30 m \times 0.32 mm \times 1 μ m) and a FID detector. The aqueous phase was first neutralized and diluted by aqueous H₂SO₄ (1 M), then analyzed by high performance liquid chromatography [HPLC, Agilent Technologies 1200 series, Bio-Rad Aminex HPX-87H 300 \times 7.8 mm column, T = 60 °C, with 0.5 mM aqueous H₂SO₄ as eluent (flow rate: 0.55 mL/min) using a combination of refractive index detector and UV detector]. Each component was calibrated using solutions of the individual component at 4 different concentrations. Selected catalytic tests were performed on three different batches of 2Pt/ZrO₂-550-R250, showing good reproducibility of the results (deviation in the lactic acid yield value within $\pm 4\%$). For these experiments, the average value of the yield is reported.

For the catalyst recycling test, a small amount of the reaction mixture was collected for analysis and the remaining mixture was filtered to recover the catalyst. The catalyst was washed first with

H₂O (20 mL), then with ethanol (20 mL), and this procedure was repeated 3 times, after which the solid was dried overnight at 100 °C. The obtained solid was used for the next run in the recycling test.

Definitions

The glycerol conversion (Conv./%) is defined by equation 1:

$$\text{Conv.} = \frac{C_{(g,0)} - C_{(g)}}{C_{(g,0)}} \times 100\% \quad (1)$$

in which $C_{(g)}$ is the molar concentration of glycerol after a certain reaction time and $C_{(g,0)}$ is the initial glycerol concentration.

The yield of lactic acid (Y_{LA}) is defined by equation 2:

$$Y_{\text{LA}} = \frac{C_{(\text{LA})}}{C_{(g,0)}} \times 100\% \quad (2)$$

in which $C_{(\text{LA})}$ is the molar concentration of lactic acid after a certain reaction time and $C_{(g,0)}$ is the initial molar concentration of glycerol.

The product selectivity for a compound P is defined by equation 3:

$$S_{\text{p}} = \frac{C_{(\text{p})}}{C_{(g,0)} - C_{(g)}} \times 100\% \quad (3)$$

in which $C_{(\text{p})}$ is the molar concentration of a product after a certain reaction time.

The selectivity towards the transfer hydrogenation is defined by equation 4:

$$S_{\text{transfer-H}} = n * \frac{y(\text{cyclohexane}) - 2 * y(\text{benzene})}{\sum_i x * y(p_i)} \times 100\% \quad (4)$$

in which n is the molar ratio between cyclohexene and glycerol in the reaction mixture, $y(\text{cyclohexane})$ is the yield of cyclohexane, $y(\text{benzene})$ is the yield of benzene - which is obtained from the dehydrogenation of cyclohexene, which most likely occurs as a disproportionation with formation of two cyclohexane molecules per benzene molecule; $y(p_i)$ is the yield of each product that is obtained from the dehydrogenative oxidation of glycerol, e.g. lactic acid, glyceric acid or

glycolic acid, and x is the number of H_2 that can be removed from glycerol by dehydrogenation to each possible product (i.e. $x = 1$ for lactic acid; $x = 2$ for glyceric acid; $x = 3$ for glycolic acid).

The term “lactic acid” is used in this article to describe the product obtained from the reaction mixture, which actually is sodium lactate (mixed with small portion of lactic acid from hydrolysis).

Results and Discussion

Synthesis and characterization of the Pt/ZrO₂ catalysts

With the aim of developing an active and selective heterogeneous catalyst for the dehydrogenation of glycerol combined with the hydrogenation of cyclohexene at relatively mild temperature, we designed a system in which the Pt actives species would be highly dispersed on nanosized ZrO₂ as support, possibly even as single atoms.^{31-32, 35} A series of Pt/ZrO₂ catalysts with different loading of the noble metal was prepared by wet-impregnation, calcination and then reduced by H₂ in a tubular oven. The actual loadings of Pt determined by ICP-OES measurement (Table 1) was very similar to the theoretical ones, and ranged between 0.6% and 8.4%. The BET surface area decreased only slightly after loading the ZrO₂ support with 2 wt% Pt (~10%, from 32 to 29 m²/g), which indicates that the presence of Pt did not affect significantly the textural properties of ZrO₂.

Table 1. Pt loading on the Pt/ZrO₂ catalysts and surface area before and after supporting Pt on ZrO₂.^a

Entry	Material	Pt loading/wt%	Surface area/(m ² /g)	Pt particle size/nm
1	ZrO ₂	0	32	n.a.
2	0.5Pt/ZrO ₂ -550-R250	0.6	n.d.	0.8
3	1Pt/ZrO ₂ -550-R250	1.1	n.d.	1.2
4	2Pt/ZrO ₂ -550-R250	2.1	29	1.4
5	5Pt/ZrO ₂ -550-R250	4.8	n.d.	2.0
6	9Pt/ZrO ₂ -550-R250	8.4	n.d.	2.6

^a n.d. = not determined; n.a. = not applicable.

HAADF-STEM and TEM were used to characterize the presence and size of Pt particle on ZrO₂ (Figure 1 and 2). Remarkably, clusters at the sub-nanometer scale and single atomic Pt were observed on the ZrO₂ support after calcination at 550 °C in air (2Pt/ZrO₂-550, Figure 1.A, Figure 2.A, B and Figure S1). This demonstrates that the Pt species were highly and even atomically dispersed on ZrO₂ after calcination in air.^{31, 34} Upon subsequent reduction of this catalyst in H₂ (250 °C, 1 h), very small, well-dispersed Pt nanoparticles with an average particle size of 1.4 nm formed on the ZrO₂ surface (2Pt/ZrO₂-550-R250, Figure 1.C and Figure 2.C). On this sample, the size of Pt ranges from sub-nanometer clusters (from 0.35 nm) to nanoparticles (up to 2.5 nm). The dispersion behavior of Pt on ZrO₂ is very similar to that reported for Pt/CeO_{2-x}, Pt/CN (nitrogen doped carbon) and Rh/ZrO₂ systems characterized by atomically dispersed Pt or Rh species.^{31-32, 39-40} The presence of atomically dispersed cationic Pt species in the material obtained by calcination but prior to reduction (2Pt/ZrO₂-550) is further supported by XPS analysis (Figure 3.A), which evidenced that all Pt in this material was in oxidized state, mainly as Pt²⁺ (at 72.7 eV, 84% peak area) and to a lesser extent as Pt⁴⁺ (75.0 eV, 16% peak area). No Pt⁰ species were observed, confirming the absence of metallic nanoparticles. The oxidized Pt species existing as highly dispersed single atoms and very small clusters are probably coordinated to ZrO₂ through

Pt-O-Zr bonds.^{31, 33, 35, 39, 41-43} After reduction at 250 °C, the majority of the oxidized Pt species were reduced to Pt⁰ (at 71.2 eV, 62% peak area, Figure 3.B), in agreement with the formation of metallic Pt nanoparticles observed in 2Pt/ZrO₂-550-R250. However, Pt²⁺ (at 72.7 eV, 33% peak area) and Pt⁴⁺ (at 75.0 eV, 5% peak area) species were still present in this catalyst.^{31, 43}

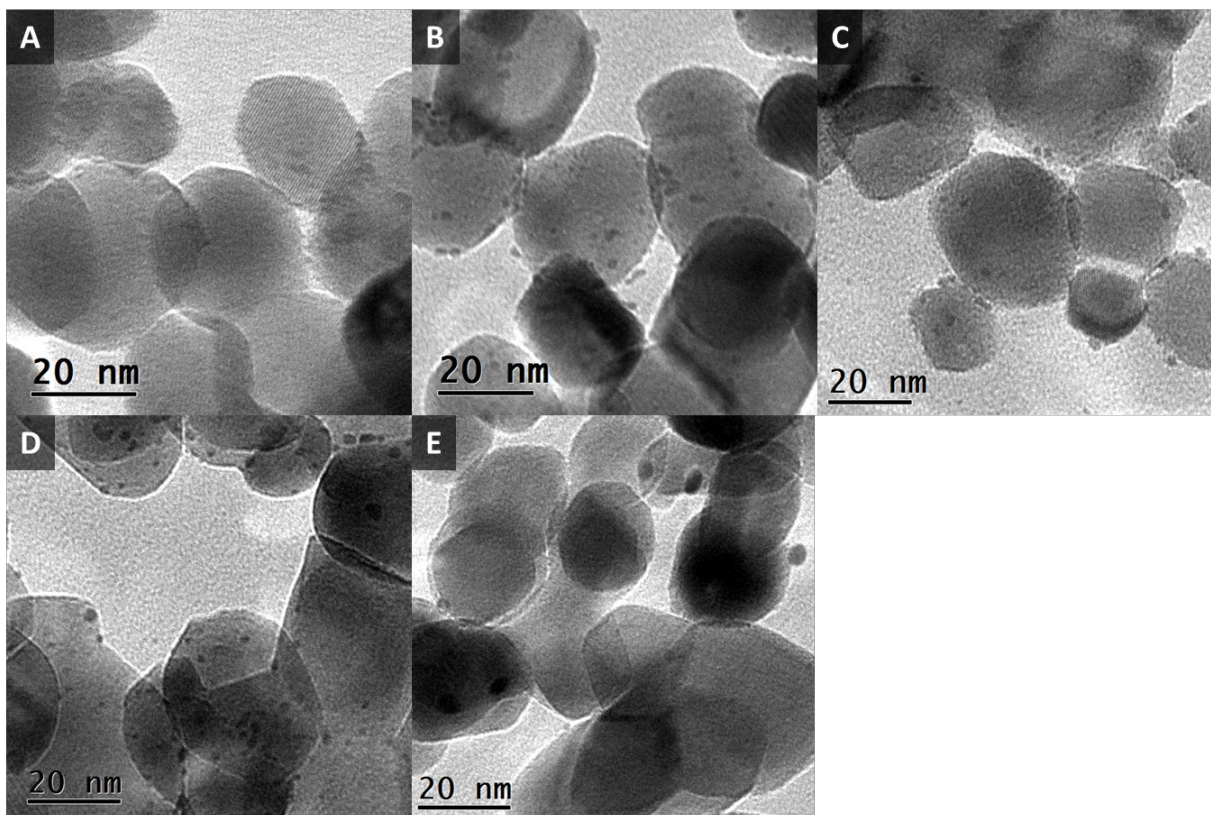


Figure 1. TEM images of 2Pt/ZrO₂ catalysts prepared by different calcination and reduction procedures. (A) 2Pt/ZrO₂-550; (B) 2Pt/ZrO₂-550-R100, average particle size of Pt: 1.4 nm; (C) 2Pt/ZrO₂-550-R250, average particle size of Pt: 1.4 nm; (D) 2Pt/ZrO₂-550-R400, average particle size of Pt: 1.8 nm; (E) 2Pt/ZrO₂-DR250, average particle size of Pt: 3.7 nm. Note: the resolution of these TEM images does not allow identification of nanoparticles < 0.5 nm.

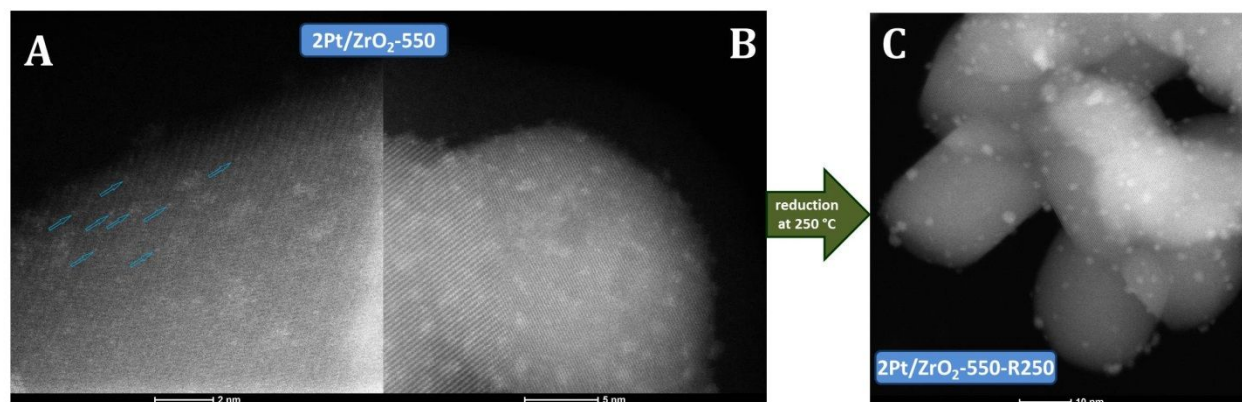


Figure 2. HAADF-STEM images of : (A, B) the 2Pt/ZrO₂ catalyst calcined at 550 °C (2Pt/ZrO₂-550); and (C) the same material after reduction at 250 °C (2Pt/ZrO₂-550-R250). In image (B), the arrows point to the single atom Pt species.

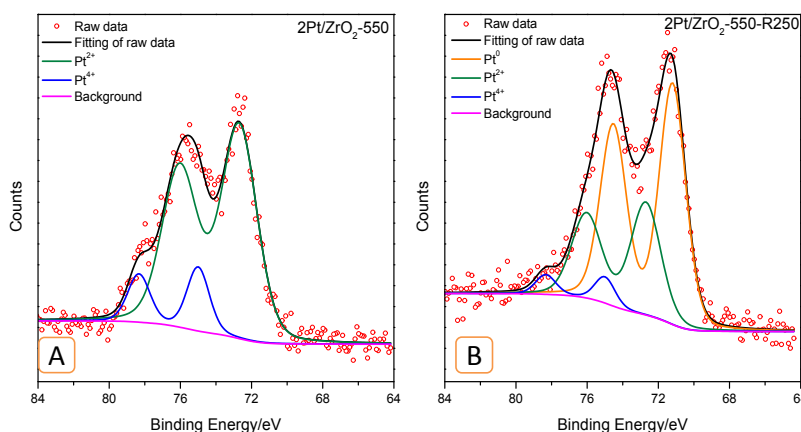


Figure 3. Pt 4f XPS spectra of various Pt/ZrO₂ catalysts. (A) 2Pt/ZrO₂-550, area of Pt²⁺ peak, 84%; area of Pt⁴⁺ peak, 16%; (B) 2Pt/ZrO₂-550-R250, area of Pt⁰ peak, 62%; area of Pt²⁺ peak, 33%; area of Pt⁴⁺ peak, 5%.

To investigate in more detail the effect of the temperature of the reduction step, 2Pt/ZrO₂-550 was also reduced at 100 and 400 °C under H₂ flow (Figure 1.B and D). By increasing the temperature of the reduction process from 100 to 400 °C, the average size of Pt nanoparticles

increased from 1.4 nm (100 °C) to 1.8 nm (400 °C). This result can be explained considering that a higher reduction temperature leads to a reduction of a larger fraction of the oxidized Pt species to metallic Pt, though it also promotes the growth of larger Pt nanoparticles. In the Pt/ZrO₂ catalyst that was reduced directly at 250 °C by H₂ without previous calcination step, only few Pt particles were observed on the surface of ZrO₂ (Figure 1.E), and these display a significantly larger average size (3.7 nm) compared to those in 2Pt/ZrO₂-550-R250 (1.4 nm). This suggests that the calcination process strongly enhances the chemical interaction between oxidized Pt species and ZrO₂, which is critical for the subsequent formation of extra-fine Pt nanoparticles upon reduction.

Considering the crucial role exerted by the calcination step on the state and size of the Pt species on the catalyst, we decided to study the effect of different calcination temperatures (400 and 800 °C, compared to 550 °C discussed above) on the dispersion of Pt species on ZrO₂. In all cases, the catalysts were reduced at 250 °C in a H₂ flow after the calcination. The TEM images of 2Pt/ZrO₂ calcined at 400 °C did not show any particles before reduction, while Pt nanoparticles with an average size of 2.0 nm were observed after reduction (2Pt/ZrO₂-400-R250, Figure S2.A), which is slightly larger than the size of the nanoparticles in 2Pt/ZrO₂-550-R250 (Figure 1.C and 2.B). On the other hand, when the calcination was carried out at 800 °C, only very large Pt particles (around 50 nm, determined by EDX-mapping) were observed before reduction (2Pt/ZrO₂-800, Figure 4.A). Though not detected, a small fraction of Pt as single atoms might also be present, as suggested by the fact that after reduction at 400 °C a small amount of very fine Pt nanoparticles (~ 1 nm) was observed alongside the large Pt nanoparticles (2Pt/ZrO₂-800-R400, Figure 4.C). These results are in agreement with previous reports, which showed that the calcination temperature can largely affect the interaction between Pt atoms and the oxide used as

support.^{33, 36, 40, 44} The effect of decreasing the Pt loading to 0.5% on the nature of the Pt species was investigated by HAADF-STEM for the materials calcined at 550 or 800 °C (Figure S3). In 0.5Pt/ZrO₂-550, sub-nanometer Pt clusters and even single atoms similar to those in 2Pt/ZrO₂-550 were observed, though obviously in a lower amount. On the other hand, no Pt species could be detected in 0.5Pt/ZrO₂-800 (Figure S3 and S4), which indicates that the lower Pt loading prevents the formation of the large Pt nanoparticles observed in the case of 2Pt/ZrO₂-800 and that Pt most likely exists only as single atoms in this material.

The reducibility of 2Pt/ZrO₂ as a function of the calcination temperature was investigated further by H₂-TPR from 50 to 800 °C (Figure 5). The intense peak in the 50-220 °C range and centered at 110 °C, which is visible in the TPR profiles of the materials calcined at 400 and 550 °C but is absent in that of the parent ZrO₂, is attributed to the reduction of oxidized Pt species.^{40-41, 45-48} The area of this peak becomes smaller when the calcination temperature increases. In the material calcined at 800 °C, the intensity of this peak is further decreased and its position is shifted to higher temperature (150 °C). This much lower tendency of 2Pt/ZrO₂-800 to be reduced below 250 °C is in agreement with what observed by TEM and HAADF-STEM (see Figure S2.B and 4). This supports the hypothesis that the calcination at 800 °C promotes more efficiently the formation of highly dispersed and fully anchored oxidized Pt species in ZrO₂.^{36, 39} All H₂-TPR profiles present a broad signal ranging from 250 to 450 °C, which stems from two overlapping peaks centered at 325 and 380 °C (Figure 5). The peak at 325 °C can be ascribed to the reduction of remaining, oxidized Pt species (Pt²⁺ and Pt⁴⁺), which based on the XPS data (*vide supra*) account for 38% of the Pt atoms in 2Pt/ZrO₂-550-R250, i.e. after reduction at 250 °C.^{41, 48-49} The peak at 380 °C is ascribed to the reduction peaks of coordinatively unsaturated Zr⁴⁺ species at the surface of ZrO₂.⁴¹ This peak is slightly shifted to lower temperature compared to the

corresponding peak of the parent ZrO_2 (at 410 °C), which suggests that the presence of Pt species promotes the reduction of ZrO_2 , possibly by hydrogen spillover.^{41, 50-52} The peak at 600 °C, which appeared in the profiles of all the samples, is ascribed to the reduction of (nearly) coordinatively saturated Zr^{4+} at surface terraces or in the bulk of ZrO_2 .^{41, 52-53}

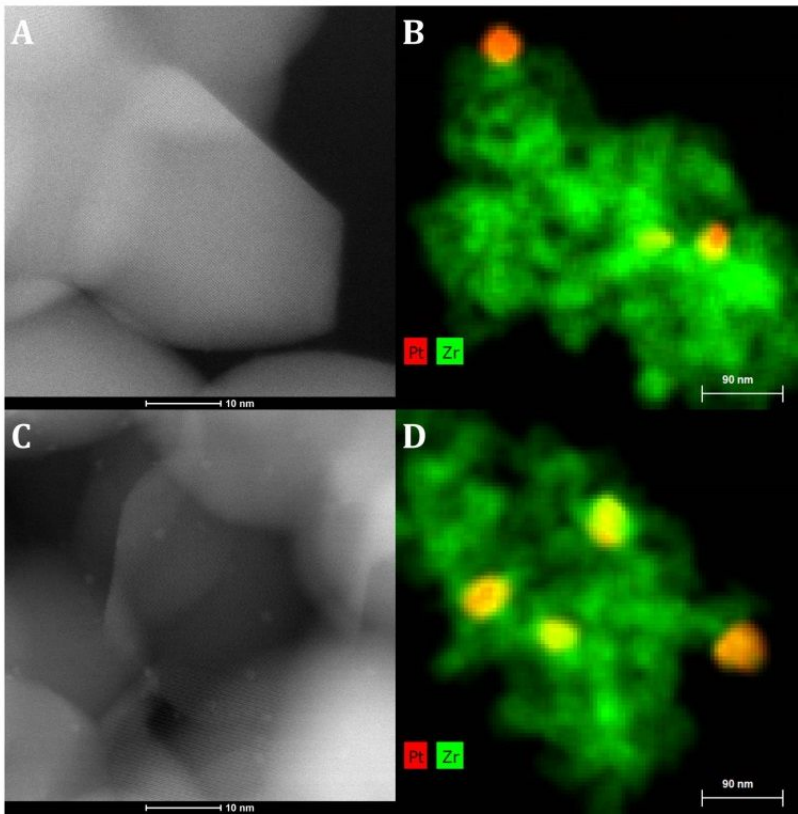


Figure 4. HAADF-STEM images (left) and EDX-mapping (right) of 2Pt/ ZrO_2 calcined at 800 °C (A and B, 2Pt/ ZrO_2 -800); and the same material after reduction at 400 °C (C and D, 2Pt/ ZrO_2 -800-R400). EDX-mapping: Zr: green; Pt: red.

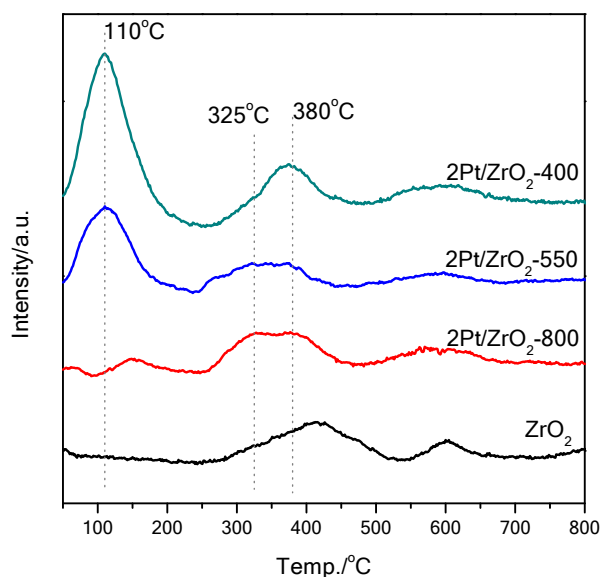


Figure 5. TPR profile of 2Pt/ZrO₂ catalysts calcined at different temperature (400, 550 and 800 °C) and the support ZrO₂.

Next, we monitored the effect of the Pt loading on the features of the final catalyst, while keeping the temperature of the calcination (550 °C) and that of the reduction (250 °C) constant. Before reduction, Pt is present in the form of highly dispersed species with sub-nanometer size for Pt loading between 0.5 and 2% (Figure 2.A,B and Figure S5.A, B). With higher loadings (5% and 9%), small Pt nanoparticles with average size of 1.3 and 1.5 nm, respectively, were detected by TEM (Figure S5.C and D). This suggests that a Pt loading $\geq 5\%$ exceeds the maximum capacity of ZrO₂ surface of hosting highly dispersed Pt species. The Pt atoms that cannot interact strongly with ZrO₂, aggregate as small nanoparticles.^{40, 54} After reduction at 250 °C under H₂ flow, Pt nanoparticles were observed for all samples (0.5-9Pt/ZrO₂-550-R250, Figure S6), and the average particle size gradually increased from 0.8 nm to 2.6 nm. This series of materials with different loading of Pt on ZrO₂ (0.5-9Pt/ZrO₂) was further characterized by XRD (Figure S7). All

XRD patterns display the characteristic peaks of monoclinic ZrO_2 . No diffraction peaks due to Pt were observed on the Pt/ ZrO_2 catalysts (before or after reduction) when the Pt loading was ≤ 5 wt%, whereas the characteristic peaks of metallic Pt (face centered cubic crystal) are observed for 9Pt/ ZrO_2 . This is due both to the small size and low loading of the Pt nanoparticles, which implies that the diffraction peaks of Pt are too broad and have too low intensity to be detected.

In summary, by systematically studying the effect of the Pt loading, the calcination temperature and the reduction temperature, we can conclude that the formation of atomically dispersed Pt species on ZrO_2 is promoted by lower Pt loadings and by higher calcination temperatures. These conditions also lead to the formation of smaller nanoparticles upon reduction with H_2 , with a smaller size being also favored by lower reduction temperature.

Catalytic Performance of the Pt/ ZrO_2 Catalysts

The prepared Pt/ ZrO_2 catalysts were tested for the conversion of glycerol to lactic acid using cyclohexene as the hydrogen acceptor (Scheme 1 and Table 2). Initially, 2Pt/ ZrO_2 -550 (without reduction) was tested as catalyst for this reaction and showed 57% conversion of glycerol with 55% yield of lactic acid. The selectivity of the transfer hydrogenation ($S_{(\text{Transfer-H})}$ in Table 2) was 31%, which means 31% of the hydrogen generated from the oxidation of glycerol was employed to reduce cyclohexene to cyclohexane (Entry 1 in Table 2). When the catalyst was reduced at 100 °C in H_2 flow, the catalytic results were very similar to the “unreduced” one (Entry 2, Table 2). The TEM analysis showed a clear difference between the two catalysts (Figure 1), with no Pt nanoparticle being visible on the unreduced sample and very small, well-dispersed Pt nanoparticles appearing upon reduction at 100 °C in H_2 flow. Combining this with the catalytic results, we infer that the 2Pt/ ZrO_2 -550 catalyst is reduced during the reaction. The catalyst

prepared by reduction at 250 °C, 2Pt/ZrO₂-550-R250, showed significantly higher conversion of glycerol (96%) and yield of lactic acid (96%), which is the highest yield of lactic acid from glycerol in the state of art (Entry 3, Table 2).^{9-10, 17, 55} The selectivity in the transfer hydrogenation also increased, reaching 36%. When the reduction temperature of the catalyst was increased to 400 °C, the activity slightly decreased, with 88% glycerol conversion and 86% lactic acid yield (Entry 4, Table 2). All reactions produced minor amounts (< 2%) of glyceric acid, glycolic acid and propanediol as side products. For what concerns the conversion of cyclohexene, very high selectivity towards the hydrogenation to cyclohexane was observed, with no or minor dehydrogenation to benzene (Table 2). Combining the catalytic performance with the characterization results, it can be concluded that the highly dispersed oxidized Pt species, Pt²⁺ and Pt⁴⁺ (as determined by XPS and TPR), which are most abundant on the unreduced catalyst 2Pt/ZrO₂-550, are probably not the active sites for the dehydrogenation of glycerol. These oxidized species are easily reduced to metallic Pt nanoparticles (Pt⁰), which are highly active in catalyzing the dehydrogenation of glycerol, in line with several literature reports proving the hydrogenation/dehydrogenation activity of these species with a variety of substrates.^{32-33, 35, 49-50, 56-57} On the other hand, when the catalyst was directly reduced at 250 °C after wet-impregnation without prior calcination (2Pt/ZrO₂ DR250, Entry 5, Table 2), it showed much lower catalytic performance compared to the 2Pt/ZrO₂ 550-R250. Combining these catalytic results with the TEM characterization, the activity trend can be correlated to much larger and fewer Pt nanoparticles present on the surface of 2Pt/ZrO₂-DR250. This underlines the importance of the calcination step in the preparation of highly dispersed, very small and thus highly active Pt nanoparticles supported on ZrO₂.

The suitability of ZrO₂ as support for Pt active species was further demonstrated by comparing the activity of 2Pt/ZrO₂ 550-R250 to that of analogous Pt-based catalysts prepared using TiO₂ or CeO₂ as support. Particularly, CeO₂ has been reported to promote the formation of atomically-dispersed Pt species.^{32-33, 35} Our results indicate that the catalyst prepared using TiO₂ has significantly lower activity than its counterpart on ZrO₂, whereas the Pt catalyst supported on CeO₂ has slightly lower activity than the one on ZrO₂ (Table S1). Therefore, we focused the rest of our study on Pt/ZrO₂ catalysts.

Table 2. Catalytic conversion of glycerol to lactic acid using a Pt/ZrO₂ prepared with different reduction methods.^a

Entry	Catalyst	Conv. _{GLY} (%)	Y _{LA} (%)	S _(transfer-H) (%)	Selectivity in the conversion of glycerol (%)				Yield in the conversion of cyclohexene (%) ^b	
					Lactic acid	Glyceric acid	Glycolic acid	Propane-diol	Cyclohexane	Benzene
1	2Pt/ZrO ₂ -550	57	55	35	97	0.9	0.5	1.8	8.9	0.5
2	2Pt/ZrO ₂ -550-R100	56	54	27	97	1.2	0.6	1.0	7.7	0
3	2Pt/ZrO ₂ -550-R250	96	95	36	99	0.5	0.2	0.7	17	0
4	2Pt/ZrO ₂ -550-R400	88	85	41	97	0.9	0.5	1.4	18	0
5	2Pt/ZrO ₂ -DR250	71	69	15	97	1.0	0.0	1.6	5.1	0

^a Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N₂ pressure: 20 bar. ^b Under the employed reaction conditions (mol_{glycerol} : mol_{cyclohexene} = 1 : 2) the maximum theoretical yield of cyclohexane is 50%.

The calcination temperature of Pt/ZrO₂ was found to affect significantly the size and dispersion of Pt species on the support (*vide supra*). These differences have a clear effect on the catalytic performance (Table 3). The Pt/ZrO₂ prepared by calcination at 400 °C and reduction at 250 °C

(2Pt/ZrO₂-400-R250), showed 46% conversion of glycerol and 46% yield of lactic acid (Entry 1, Table 3), while 2Pt/ZrO₂-550-R250 showed significant higher conversion of glycerol (96%) and yield of lactic acid (95%) (Entry 2, Table 3). The improved activity is ascribed to the smaller size of the Pt nanoparticles in the latter catalyst (compare Figure 1.C and Figure S2.A). Further increase in the calcination temperature to 800 °C (2Pt/ZrO₂-800-R250) caused a drastic drop in activity (24% glycerol conversion, Entry 3, Table 3). Keeping the calcination temperature at 800°C but increasing the reduction temperature to 400 °C (2Pt/ZrO₂-800-R400), which was used to further reduce the Pt species, led to even worse activity (12% glycerol conversion, Entry 4, Table 3). It should be noted that for the two catalysts prepared by calcination at 800 °C, the efficiency of transfer hydrogenation was just around 1%, which means that almost none of the hydrogen from glycerol was transferred to cyclohexene. The low activity of these two catalysts can be correlated to the observed large Pt nanoparticles present in the material already prior to reduction (see Figure 4), which implies that a low fraction of the Pt atoms are exposed on the surface and thus available for catalyzing the reaction. Based on these results, it can be concluded that a calcination temperature of 550 °C leads to an intermediate interaction between oxidized Pt species and ZrO₂, which then allows their reduction leading to the formation of very small Pt nanoparticles that are highly dispersed on the surface of the support and that thus display high catalytic activity.

Table 3. Catalytic conversion of glycerol to lactic acid using Pt/ZrO₂ catalysts calcined at different temperatures. ^a

Entry	Catalyst	Conv.-GLY (%)	Y _{LA} (%)	S _(transfer-H) (%)	Selectivity in the conversion of glycerol (%)				Yield in the conversion of cyclohexene (%) ^a	
					Lactic acid	Glyceric acid	Glycolic acid	Propane-diol	Cyclohexane	Benzene
1	2Pt/ZrO ₂ 400-R250	46	46	35	99	0.3	0.0	0.8	8.1	0
2	2Pt/ZrO ₂ 550-R250	96	95	36	99	0.5	0.2	0.7	17	0
3	2Pt/ZrO ₂ 800-R250	24	23	0.9	98	0.3	0.0	1.9	0.1	0
4	2Pt/ZrO ₂ 800-R400	12	10	0	87	0.7	0.7	11	0	0

^a Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N₂ pressure: 20 bar. ^a Under the employed reaction conditions (mol_{glycerol} : mol_{cyclohexene} = 1 : 2) the maximum theoretical yield of cyclohexane is 50%.

Optimization of Pt loading, NaOH Amount and Reaction Temperature

Catalysts with different loading of Pt on ZrO₂ were also tested to investigate the effects of this parameter on the catalytic performance. The same nominal molar ratio Pt/glycerol (1/1950) was used in all reactions, i.e. different weights of Pt/ZrO₂ catalyst were employed. The conversion of glycerol and the yield of lactic acid improved upon an increase in the loading of Pt from 0.5 to 2%, whereas further increase of the loading to 5 and 9% caused a drop of activity (Figure 6). In all these tests, the selectivity towards lactic acid was higher than 97%, with very minor yields (≤ 0.2%) of side products, i.e. glyceric acid, glycolic acid and propanediol. The yield of cyclohexane from the transfer hydrogenation reaction was in the same range with all catalyst (between 16 and 20%). The results can be rationalized considering that at lower loading of Pt (0.5 and 1%), the larger total mass of support employed might hinder the accessibility of the Pt nanoparticles,¹¹

whereas at higher loading of Pt (5 and 9%) the larger size and worse dispersion of the Pt nanoparticles on the ZrO_2 surface (Figure S6) account for the lower activity of the catalysts. The intermediate loading of Pt (2%) provided the best balance between these two factors, leading to the observed highest activity with 2Pt/ ZrO_2 550-R250. An alternative or additional explanation for the better performance of the 2% catalyst compared to those with lower loading is that the 2% Pt catalyst (with Pt particle size of 1.4 nm) displays the largest fraction of suitable metallic sites for the dehydrogenation of glycerol.

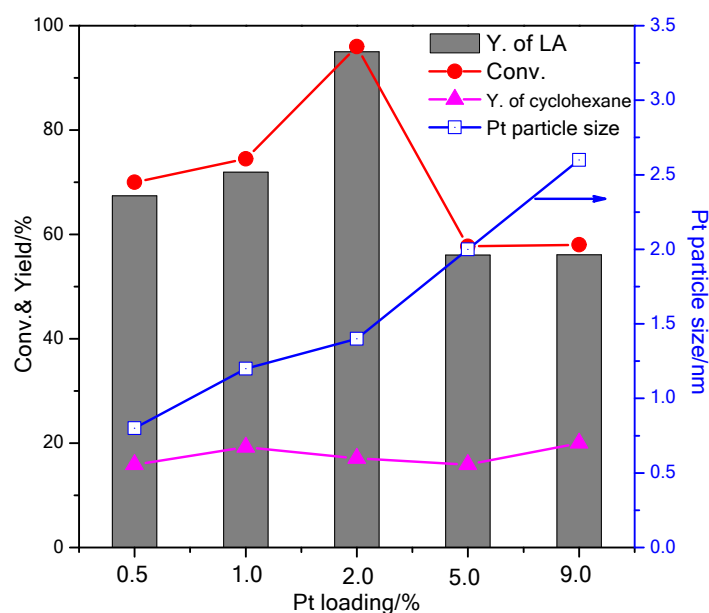


Figure 6. Catalytic performance of Pt/ ZrO_2 550-R250 catalysts with different Pt loading (0.5-9%). Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N_2 pressure: 20 bar.

All the catalytic tests were conducted in the presence of NaOH. The role of this strong base was studied by varying the molar ratio between NaOH and glycerol (from 0 to 2) in the reaction

mixture (Figure S8). Without addition of NaOH, both the conversion of glycerol and the selectivity to lactic acid were very low (conversion of glycerol, 1.3%). When increasing the molar ratio between NaOH and glycerol, the conversion of glycerol gradually increased reaching 96% with 99% selectivity towards lactic acid at NaOH/glycerol = 1.5. However, a further increase in the NaOH/glycerol molar ratio to 2 caused a decrease in the conversion of glycerol to 73%, suggesting that excess NaOH can inhibit the activity of the catalyst. These results confirm that the presence of a NaOH in the reaction mixture is critical to promote the deprotonation of one of the hydroxyl groups of glycerol, thus promoting the dehydrogenation of glycerol on the surface of the Pt nanoparticles.^{9, 17, 58-59} Moreover, NaOH can catalyze the isomerization of glyceraldehyde and dihydroxyacetone, and reacts with the formed lactic acid to yield sodium lactate (which is very stable in the reaction system) thus shifting the equilibrium concentrations towards the products (Scheme 1) and granting very high selectivity towards the lactic acid.^{9, 17-18, 21} A reference reaction with only NaOH and no Pt catalyst gave very low conversion of glycerol (7.3%), which is significantly lower compared to the conversion achieved in the presence of the 2Pt/ZrO₂-550-R250 catalyst (96%). This demonstrates the crucial role played by the Pt/ZrO₂ catalyst under the relatively mild reaction conditions employed here.¹⁷⁻²¹

The 2Pt/ZrO₂-550-R250 catalyst was further tested at different temperatures (from 120 to 180 °C). By increasing the reaction temperature, the expected trend of increasing glycerol conversion was observed, going from 25% at 120 °C to full conversion at 180 °C. The selectivity to lactic acid was nearly constant and always > 95% with very similar side products distribution in all cases (Table S2). Also the conversion of cyclohexene and the yield of cyclohexane increased with the temperature. On the other hand, the selectivity of transfer hydrogenation did not show a

clear trend as a function of the reaction temperature, reaching the highest efficiency in the reaction carried out at 140 °C.

Detailed Study of Trans-hydrogenation Process

The catalytic results presented in Table 2 and 3 show that the only a fraction of the hydrogen atoms removed from glycerol are employed in the transfer hydrogenation of cyclohexene. This is probably due to the intrinsic low reactivity of the double bond in cyclohexene but also to the hydrophilicity of the Pt/ZrO₂ catalysts, which causes them to be preferentially located in the aqueous phase of the reaction mixture (consisting of water and glycerol), thus limiting the contact with cyclohexene (which together with cyclohexane constitutes the organic phase). As a consequence, the rate of the hydrogenation step is lower than that of the dehydrogenation. Though combining the conversion of glycerol to the transfer hydrogenation of cyclohexene is attractive, it is also interesting to evaluate the catalytic performance of the best catalyst identified in this work (2Pt/ZrO₂ 550-R250) in the absence of cyclohexene. The test was carried out under conditions (reaction at 140 °C) at which the conversion of glycerol would be far from being complete. The results demonstrate that the presence of cyclohexene as hydrogen acceptor does not affect the catalytic performance, as both reactions showed nearly the same conversion of glycerol and yield of lactic acid (Table S3). To further investigate the formation of free H₂ in our system, we conducted an additional experiment with no hydrogen acceptor, higher amount of glycerol and lower N₂ pressure (3 bar) (Table S4). Under these conditions, the reaction generated 10 bar free H₂ after reaction, which correspond to 98% yield relative to the glycerol conversion. This experiment demonstrated that the dehydrogenation of glycerol did lead to the formation of free H₂.

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3 Additionally, a linear alkene and a linear alkyne were also studied as hydrogen acceptors,
4 instead of cyclohexene (Table S5). When 1-decene was used as hydrogen acceptor, the 2Pt/ZrO₂
5 550-R250 catalyst exhibited very high activity (glycerol conversion 97%) and selectivity towards
6 the lactic acid salt (99%). Moreover, the selectivity of the transfer-hydrogenation (92%) was
7 much higher than with cyclohexene as hydrogen acceptor. This is probably due to the better
8 accessibility of the C-C double bond in the linear 1-decene. On the other hand, when 1-decyne
9 was used as the hydrogen acceptor, the catalytic activity of 2Pt/ZrO₂ 550-R250 was almost fully
10 inhibited (1.3% glycerol conversion). This indicates that 1-decyne cannot be used as hydrogen
11 acceptor in this system (i.e. under basic hydrothermal conditions), possibly due to poisoning of
12 the Pt catalyst.
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28 Kinetic Test

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30 The reaction was monitored as a function of reaction time with catalyst 2Pt/ZrO₂-550-R250.
31 This test showed that under the employed conditions the reaction behaves as being first order
32 with respect to glycerol (Figure 7). The turnover frequency for the conversion of glycerol based
33 on the amount of Pt and calculated from the linear part of the kinetic curve (i.e. the first 1.5 h)
34 was 995 h⁻¹. The selectivity towards lactic acid was > 95% at all stages, which can be related to
35 the rapid conversion of the dihydroxyacetone and/or glyceraldehyde formed from the
36 dehydrogenation of glycerol into the lactic acid salt (see Scheme 1). The yield of cyclohexane via
37 the transfer hydrogenation reaction increased within the first 1.5 h, after which it remained nearly
38 constant.
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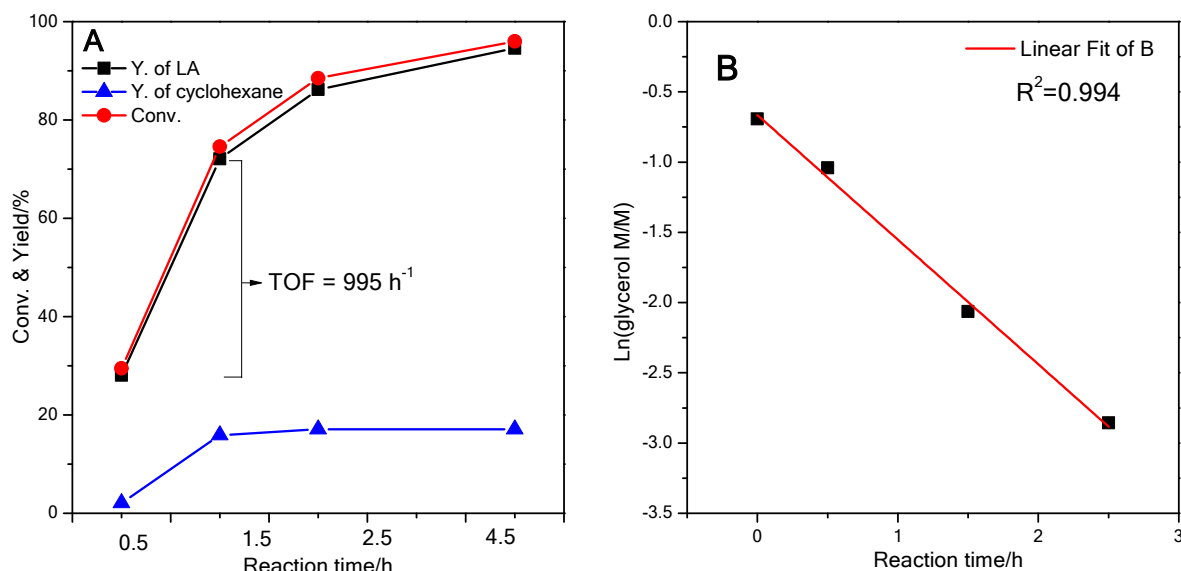


Figure 7. Conversion of glycerol and transfer hydrogenation over the 2Pt/ZrO₂ 550-R250 catalyst as a function of reaction time (A); and linear fitting of the natural logarithm of the concentration of glycerol as a function of the reaction time (B). Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; N₂ pressure: 20 bar.

Reusability

The best catalyst identified in this work, 2Pt/ZrO₂-550-R250, was selected for a reusability test (Figure 8A). The catalyst was reused in 5 consecutive runs, displaying a partial and gradual loss of activity, corresponding to a decrease in glycerol conversion from 96% in the first run to 54% in the fifth run. The selectivity towards the lactic acid remained very high (> 97%) in all runs. In addition, the yield of cyclohexane from transfer hydrogenation was about constant for the 5 runs. The observed decrease in activity in the conversion of glycerol is attributed to an increase in the size of the Pt nanoparticles from 1.4 nm in the fresh catalyst to 4.6 nm after the fifth run, as

evidenced by TEM analysis (Figure 8B). Such aggregation of Pt nanoparticles led to lower exposed Pt surface and thus to the observed decrease in activity.

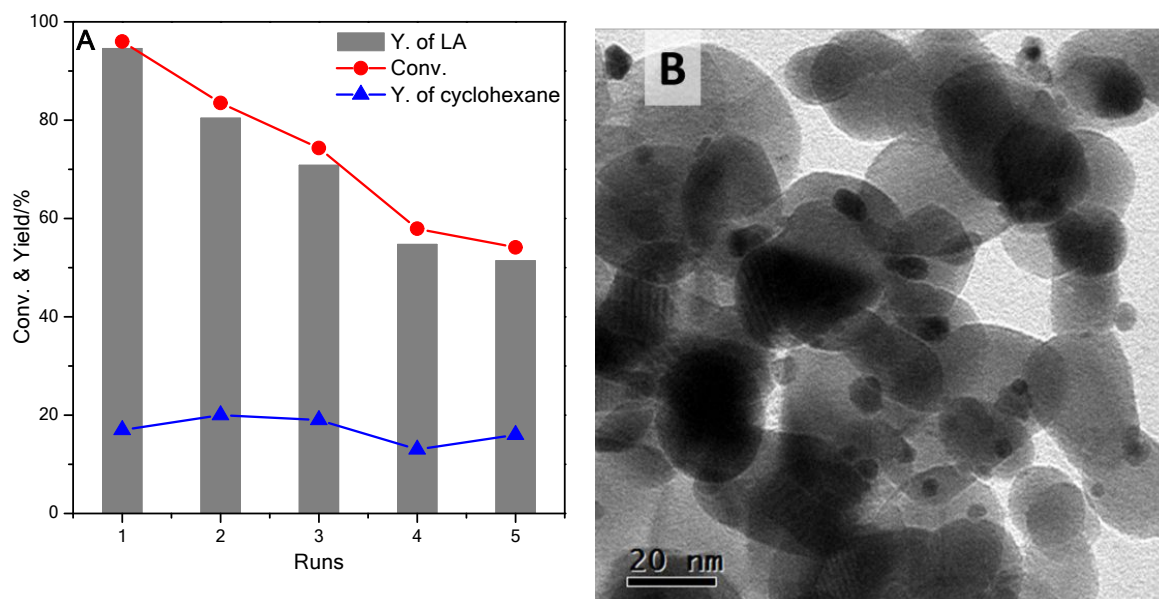


Figure 8. Reusability test of the 2Pt/ZrO₂ 550-R250 catalyst for the conversion of glycerol and transfer hydrogenation: (A) Catalytic performance upon recycling; the solid catalyst was recovered by filtration, washed with water and ethanol and dried at 100 °C after each run. (B) TEM picture of the catalyst after 5 recycles; average particle size of Pt: 4.6 nm. Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; nominal Pt/glycerol ratio = 1/1950; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N₂ pressure: 20 bar.

Conclusions

We developed a novel catalytic system based on highly dispersed Pt species supported on nanosized ZrO₂ with high activity and selectivity for the one-pot conversion of glycerol into lactic acid (salt), with concomitant transfer hydrogenation of cyclohexene to cyclohexane. Careful tuning of the synthesis method through optimization of the calcination temperature, the

reduction temperature and the loading of Pt allowed to prepare sub-nanometer Pt clusters and atomically dispersed Pt species (as Pt^{2+} and Pt^{4+}), which were converted into extra-fine Pt nanoparticles upon reduction. The most active catalyst (prepared by calcination at 550 °C and reduction at 250 °C) was not the material with the smallest size of the Pt domains but the one that combined a high dispersion of nanoparticles with a narrow size distribution centered at 1.4 nm with a relatively large loading of Pt (2 wt%) on the nanosized ZrO_2 support. This 2Pt/ ZrO_2 -550-R250 catalyst exhibited very high activity (96% glycerol conversion) and selectivity towards lactic acid salt (99%) at 160 °C, 4.5 h under N_2 atmosphere and in the presence of NaOH. This reaction also gave a 36% selectivity in the transfer-hydrogenation from glycerol to cyclohexene. The transfer hydrogenation concept could also be employed with 1-decene, achieving similarly high glycerol conversion (97%) and selectivity towards sodium lactate (99%) but significantly higher selectivity in the transfer-hydrogenation (92%). Aggregation of the very fine Pt nanoparticles into larger ones (ca. 5 nm) caused a partial deactivation of the catalyst upon reuse.

In perspective, the straightforward method introduced here allows producing catalysts with highly dispersed Pt nanoparticles with tunable size between 0.8 nm (at 0.5 wt% Pt) and 2.6 nm (at 9 wt% Pt) that are expected to display enhanced activity in several hydrogenation or dehydrogenation reactions.^{33, 60}

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ASSOCIATED CONTENT

Supporting Information

Figure S1. Supplementary STEM images for 2Pt/ZrO₂-550. **Figure S2.** TEM images of 2Pt/ZrO₂ catalysts calcined and reduced with different procedures. **Figure S3.** STEM images of 0.5Pt/ZrO₂ catalysts calcined at different temperatures. **Figure S4.** STEM images coupling with EDX-mapping of 0.5Pt/ ZrO₂-800. **Figure S5.** TEM images of Pt/ZrO₂ catalysts with different loading after calcination at 550 °C. **Figure S6.** TEM images of Pt/ZrO₂ catalysts with different loading after calcination at 550 °C and reduction at 250 °C. **Figure S7.** XRD patterns of calcined ZrO₂ and Pt/ZrO₂ catalysts with various Pt loadings. **Figure S8.** Effect of the amount of NaOH on the catalytic performance of 2Pt/ZrO₂-550-R250. **Table S1.** Catalytic conversion of glycerol to lactic acid using Pt catalysts supported on different oxides. **Table S2.** Catalytic conversion of glycerol to lactic acid using a Pt/ZrO₂ catalyst at different reaction temperature. **Table S3.** Catalytic conversion of glycerol to lactic acid using a Pt/ZrO₂ catalyst, as a function of the presence of cyclohexene. **Table S4.** Catalytic conversion of glycerol to lactic acid using 2Pt/ZrO₂ 550-R250. **Table S5.** Catalytic conversion of glycerol over 2Pt/ZrO₂ 550-R250 in the presence of 1-decene or 1-decyne as hydrogen acceptor.

ACKNOWLEDGMENT

Zhenchen Tang thank the financial support from China Scholarship Council for his PhD grant. All the authors thank the technical support from Erwin Wilbers, Anne Appeldoorn and Marcel de Vries, the TEM support from Dr. Marc Stuart and the ICP-OES support from Johannes van der Velde. Pei Liu and Sara Bals acknowledge financial support from the European Commission under the Horizon 2020 Programme by means of the grant agreement No. 731019 EUSMI.

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