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HAL Id: hal-03412726
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Submitted on 4 Nov 2021

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Tuning the selectivity of phenol hydrogenation using Pd, Rh and Ru nanoparticles supported on ceria- and titania-modified silicas

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Graphical abstract

Highlights

- Pd-based catalysts showed higher selectivity toward cyclohexanone.
- Rh and Ru-based catalysts showed higher selectivity towards cyclohexanol.
- Titania-based support enhanced selectivity towards cyclohexanol for all metals.

Abstract

The large-scale production of biomass-derived fuels generates large amounts of lignocellulosic residues that may further be converted into bio-derived value-added chemicals. Here, we investigate the selective hydrogenation of phenol as a model compound for lignocellulosic derivatives. Pre-formed PVP-stabilized nanoparticles (NPs) of Pd, Ru and Rh prepared using an organometallic approach were immobilized on different magnetic silica-based supports modified with TiO\textsubscript{2} or CeO\textsubscript{2}. In phenol hydrogenation studies, the Pd NP catalysts show high selectivity towards
cyclohexanone, while Ru and Rh NP catalysts primarily afford cyclohexanol. Titania-containing supports increase the selectivity towards cyclohexanol for both Pd- and Rh-based catalysts. Interestingly, the combination of Ru NPs and titania-modified silica results in 100 % selectivity of cyclohexanol. After removal of the PVP-stabilizer by thermal treatment, the catalyst combining Pd NPs and titania-modified silica leads to 100 % selectivity towards cyclohexanone. Despite the difficulties associated with the de-polymerization of biomass residues, the development of new catalyst materials for highly selective transformations of biomass-derived platform molecules contributes to a sustainable production of various value-added chemicals for manifold applications.

Keywords: metal nanoparticles; hydrogenation; selectivity; phenol; magnetic support

1. Introduction

The use of renewable resources is one of the most often discussed topics today, especially when considering the mitigation of fossil fuel consumption and emission of greenhouse gases [1]. The production of ethanol from sugar cane is an illustrative example [2]. However, its production generates organic residues that are typically burnt to generate energy. A transformation of these residues into value-added chemicals is highly desirable in terms of ecological sustainability and economics. A rapid pyrolysis process has been shown to afford a highly oxygenated bio-oil containing a substantial amount of phenolic compounds. Unfortunately, the high oxygen content has some disadvantages [3]. Therefore, a reduction of the oxygen content either via hydrodeoxygenation (HDO) reactions or the production of value-added hydrogenated products has to be performed, sometimes referred to as upgrading of the bio-oil. Owing to the complexity of the bio-oil matrix, low molecular weight compounds such as phenol are used as lignocellulosic-derivative models for representative experimental studies. In general, the hydrogenation of phenol leads to a mixture of cyclohexanone, cyclohexanol, and also deoxygenated products from HDO reactions (scheme 1) [4].

Scheme 1. Products of phenol hydrogenation and hydrodeoxygenation.

Cyclohexanone and cyclohexanol are important intermediates for the synthesis of industrially relevant ε-caprolactam and adipic acid that are used in the production of nylon-6, nylon-6,6 and polyamide resins, for instance. Large-scale production are mainly based on the hydrogenation of phenol or the oxidation of cyclohexene [5]. Thereby, the hydrogenation of phenol is a less energy-consuming process than the oxidation of cyclohexene. Importantly, for a highly selective production of cyclohexanone, further hydrogenation reactions to cyclohexanol and other HDO products have to be efficiently inhibited [6]. Supported metal catalysts, such as Pd [6–
12], Pt [13,14], Rh [14–18] and Ru[19–22] were reported to provide high selectivities of phenol transformation into cyclohexanone and cyclohexanol. Supported Pd catalysts range amongst the best performing catalysts for a liquid phase phenol hydrogenation [12,23–26]. A promoting effect of the supporting material on the catalytic properties of Pd-based catalysts has been observed, e. g. on Pd/SiO₂ [6], Pd/TiO₂ [10], Pd/ CeO₂ [25,27] or Pd/Al₂O₃ systems [6,7]. The hydrodeoxygenation of cyclohexanol affords cyclohexane. Thus the selective hydrogenation of phenol to cyclohexanol, i.e. the tandem phenol hydrogenation/HDO process, is an attractive strategy towards the formation of (cyclo-)alkanes. This strategy demonstrates the possibility of fuel production from lignocellulosic bio-feedstocks [4,28].

Taking the multiple reactions pathways into account, the necessity for rationally designed highly selective catalysts becomes evident. In general, colloidally dispersed metallic NPs as catalysts can be advantageous, as they show high surface-to-volume ratios and provide a high number of catalytically active reaction sites. In this context, a separation of nanoscale catalysts from reaction intermediates or products and the stability of the NPs represent major challenges. These issues can be addressed by an immobilization of the NPs on solid supports, especially magnetic supports, which promotes NPs stabilization and also facilitates catalyst recovery and reusability [29]. Here, it has to be noted that the catalyst support must be carefully selected because metal-support and support-substrate interactions might affect the catalytic activity of the supported metal NPs. In the case of phenol hydrogenation, the support is particularly important regarding the possible adsorption of the substrate on acidic and basic sites of the latter. The adsorption of phenol on acidic sites occurs in a co-planar orientation and promotes cyclohexanol formation. On the other hand, the adsorption at basic sites occurs in a non-planar orientation and the step-wise addition of hydrogen favors the formation of cyclohexanone [6].

Herein, we investigate a series of new catalyst systems for the selective hydrogenation of phenol. They were prepared by the immobilization of preformed PVP-stabilized Pd, Ru and Rh NPs on magnetic silica supports modified with ceria and titania [30]. Pd, Ru, and Rh NPs were prepared via an organometallic approach, which allows high reproducibility and size control. The influence of different parameters such as metal, H₂/phenol ratio, contact time, and solvent on the catalytic performance was investigated systematically. The facile separation of the magnetic Fe₃O₄-SiO₂ support is an important advantage of the liquid phase catalysis studies discussed in the following.

2. Experimental Section

Chemicals were reagent grade and used as received, unless otherwise stated. Deionized water was used in the preparation of aqueous solutions. Furnished by Carlo-Erba, Tetrahydrofuran (TH) and pentane were purified by filtration on adequate column in a purification apparatus (MBraun) and degassed before use via a freeze–pump–thaw process. Hydrogen was purchased from Air Liquide (Alphagaz). Pd/C (3 wt%) was purchased from Aldrich. Concerning metal precursors, [Ru(COD)(COT)] was purchased from Nanomeps and [Pd₂(dba)₃] from Aldrich. [Rh(η⁵-C₅H₅)₃] organometallic complex was prepared according to a slightly improved method from the literature starting from rhodium trichloride RhCl₃.xH₂O and allylmagnesiumchloride [CH₂=CHCH₂MgCl] [30]. Initially, 1.5 g of RhCl₃.xH₂O was added to a Schlenk flask
and the atmosphere was changed to Ar using a vacuum/Ar line. The rhodium salt was solubilized in 140 mL THF (dry and without stabilizer), that was transferred from a Schlenk flask under Ar through a cannula. The addition of 36 mL allylmagnesium chloride solution (2 mol L\(^{-1}\) in THF) was made under vigorous magnetic stirring and a cold bath (ethanol with liquid N\(_2\)). The reaction mixture was kept under magnetic stirring for 20 h. The solution color changed to yellow and the THF was slowly removed under vacuum. In order to enhance the extraction of the product, the solid was removed from the Schlenk wall using a spatula under a constant flow of argon. The product was extracted by the addition of small portions of dry pentane under argon atmosphere. The suspension was transferred by cannula to a celite column. The pentane was removed under vacuum and the product transferred to a sublimation apparatus inside a glove box (MBRAUN, Germany. Water and O\(_2\) lower than 1 ppm). The sublimation was done under vacuum and 50 °C. The purified Rh(C\(_3\)H\(_5\))\(_3\) (0.7 g) was stored at -3 ºC in a freezer inside the glove box.

Transmission electron microscopy observations (TEM) were performed at the “Centre de microcaractérisation Raymond Castaing” in Toulouse (UMS-CNRS 3623). TEM grids were prepared by drop-casting of the crude colloidal solution in THF onto a holey carbon-coated copper grid under argon atmosphere in a glove box. TEM analyses were performed on a JEOL 1400 electron microscope operating at 120 kV with resolution point of 2 Å. Statistical size distributions were built by counting non-touching particles and nanoparticle mean diameters were determined, by analyzing the TEM images with Image J tool software. The analyses were performed by assuming that the nanoparticles are spherical. Size distributions are given as the mean diameter ± the standard deviation.

Metal content of the catalysts was determined by flame atomic absorption spectroscopy (FAA S, Shimadzu AA6300). The calibration curve was built using a 1000 ppm standard solution (Specesol®), which was diluted to prepare solutions containing 1, 4, 12 and 20 ppm of Rh, with R\(^2\) = 0.997. The samples were refluxed in a mixture of aqua-regia for 3 h and then diluted in water before analysis.

The acid properties of the supports were determined by temperature programmed desorption of ammonia (NH\(_3\)–TPD). About 100 mg of each support was pretreated under He flow (60 mL/min) at 250 °C (10 °C/min) for 1 h. Ammonia (4 % NH\(_3\)/He, 60 mL/min flow) was adsorbed at r.t. and degassed with He flow to remove weakly adsorbed molecules. Desorption was performed under He flow (60 mL/min) by varying the temperature from r. t. to 500 °C (10 °C/min). The experiments were performed in a TPD set up connected to a UHV chamber with a mass spectrometer (Balzers QMS 200).

2.1. Synthesis of polyvinylpirrolidone (PVP) stabilized Ruthenium, Rhodium and Palladium nanoparticles (M@PVP NPs)

All metal nanoparticles were prepared by a modification of a previously reported method in a glove box and vacuum-line techniques [31]. Accordingly, Rh, Ru and Pd@PVP NPs were prepared by hydrogen treatment of the corresponding organometallic complexes dissolved in THF and in the presence of PVP. Typically, inside a glove box (MBRAUN, Water and O\(_2\) contents< 1 ppm), 42 mg [Ru(COD)\((\text{COT})\)], 30 mg [Rh(η\(^3\)-C\(_3\)H\(_5\))\(_3\)] or 61 mg [Pd\(_2\)(dba)\(_3\)] were introduced into a 300 mL Fischer-Porter glass reactor. Then, 30 mL of a PVP solution in THF (136 mg in anhydrous, stabilizer free and degassed THF) were added under argon flow in a cold
bath (ethanol and liquid N\textsubscript{2}) without stirring. The reactor was pressurized with 3 bar H\textsubscript{2} and the stirring initiated. The cold bath was then removed and the reactor kept under static pressure and magnetic stirring for 24 h at room temperature (r. t.). Thereafter, black colloidal solutions were formed. Excess H\textsubscript{2} was eliminated and THF evaporated under reduced pressure. The obtained solid materials were then washed with pentane (2 x 15 mL) to remove formed by-products resulting from the decomposition of the metal precursors, i. e. the ligands, and finally dried in vacuo. Black solids denoted as Ru@PVP, Rh@PVP, and Pd@PVP were afforded. Batches of metal NPs were all stored inside a glove box prior to use. TEM samples were prepared by placing a drop of the as-prepared metal NPs onto a carbon-coated copper grid under argon atmosphere.

2.2. Preparation of supported metal catalysts

The magnetic supports used to immobilize the NPs are based on silica-coated magnetite and prepared following a previously described procedure [30]. To tune the surface properties of this silica-coated magnetite, ceria and titania were deposited onto the surface, according to reference [30]. The supports are denoted as FFSi, FFSiCe, and FFSiTiti for silica-coated magnetite, ceria- and titania-modified silicas, respectively. Immobilization of the metal NPs (nominal 1.5 wt%) was performed by dispersing 200 mg of magnetic support and 40 mg of metal NPs in 80 mL THF under stirring for 48 h. Then, the obtained solids were recovered under the assistance of magnetic fields and washed twice with 40 mL THF. The obtained solids were finally dried under vacuum. The metal contents were analyzed by FAAS.

2.4. Phenol hydrogenation

The hydrogenation of phenol was performed inside a 100 mL Fischer-Porter glass reactor as following: 3 mL of phenol solution (25 mmol L\textsuperscript{-1} in hexane) were mixed with 36 mg of each catalyst (1.25 mmol Ru, Rh or Pd; substrate to metal ratio of 20) and exposed to 6 bar H\textsubscript{2} (constant pressure) at 75 °C. The reactor was purged twice with 1 bar H\textsubscript{2} before setting the working pressure to a constant value of 6 bar. Additional reactions were performed under different conditions as specified in table footnotes. Aliquots were collected after 0.08, 0.25, 0.42, 0.58, 1, 2, 3, 4 and 20 h. For this purpose, the reactor was cooled to r.t. and depressurized prior to sample collection with a syringe under a N\textsubscript{2} flow. Phenol conversion and product selectivity were determined by GC using a Shimadzu GC 2010 chromatographer equipped with a Rtx5 capillary column (30 m, I.D. 0.25 mm, Restek, United States). The injector and detector temperatures were 200 °C and a temperature program was applied (40 °C for 5 min, heating to 135 °C at 5 °C min\textsuperscript{-1} and then to 150 °C at 20 °C min\textsuperscript{-1}, static temperature at 150 °C for 5 min). For GC analysis, the samples were prepared in n-hexane and biphenyl was added as an internal standard. All steps for the GC analysis were performed at similar conditions for all catalytic reactions to limit any bias.

3. Results and Discussion

3.1. Catalysts preparation and characterization
Rh, Pd, and Ru NPs were synthesized according to Pan et al. by the decomposition of organometallic precursors in the presence of H₂ and polyvinylpyrrolidone (PVP) as stabilizing agent [31]. This method is highly reproducible and affords very small and well-controlled metal NPs with narrow particle size distribution and uniform morphology. Despite requiring the use of organic solvents and stabilizers, the surface of the synthesized NPs is free of contaminants, as the olefinic metal precursors lead to volatile decomposition products. Using PVP as a stabilizer leads to a steric stabilization, which makes the metal surface largely accessible for substrate adsorption. The organometallic complexes used as metal sources in this study are [Rh(η³-C₃H₅)₃], [Ru(COD)(COT)] and [Pd₂(dba)₃] (Fig. 1). The three different batches of metal NPs, namely PVP-stabilized Rh, Pd and Ru NPs, were prepared using identical metal-to-polymer ratios and reaction conditions. The NP mean sizes of 1.9 ± 0.3, 2.0 ± 0.4 and 1.3 ± 0.3 nm for Rh@PVP, Pd@PVP, and Ru@PVP were determined by analysis of TEM micrographs (Fig. 2).

**Fig. 1.** Structure of the organometallic complexes used as metal sources: (a) [Rh(η³-C₃H₅)₃], (b) [Ru(COD)(COT)] and (c) [Pd₂(dba)₃]

**Fig. 2.** TEM micrographs of (A) Rh@PVP, (B) Pd@PVP and (C) Ru@PVP NPs. with corresponding size distributions fitted to Gaussian function (A’, B’ and C’). Scale bar = 50 nm.

All synthesized colloidal NPs were subsequently immobilized onto three different supports: 1) silica-coated magnetite (FFSi), 2) ceria-modified silica-coated magnetite
(FFSiCe) and 3) titania-modified silica-coated magnetite (FFSiTi) [30]. Catalysts were prepared by mixing the support with the colloidal NPs at r. t. under vigorous stirring. The weak interaction of PVP and the metal surface does not limit the immobilization of metal NPs onto the supports. Considering the targeted application of the materials in catalysis, the high solubility of PVP in polar solvents is expected to result in pronounced metal leaching. This issue was circumvented by using apolar n-hexane as solvent in the first experiments. TEM analysis of the materials after NP immobilization revealed that the metal NPs are well-dispersed on the different supports without apparent changes in morphology or size (see Fig. S1). The metal loading amounts to 1.3 to 1.5 % wt. according to FAAS.

3.2. Phenol Hydrogenation

3.2.1. Impact of metal and support

Table 1 summarizes the results from the catalytic test reaction regarding phenol conversion and product selectivity (cyclohexanone, cyclohexanol, and cyclohexane) by using Rh, Ru, and Pd PVP-stabilized NPs supported on the three different magnetic supports studied (FFSi, FFSiCe, and FFSiTi) after reaction times of 2 and 20 h under 6 bar H2 and 75 °C. Blank tests, i. e. three supports without metal NPs, showed no conversion of phenol (Table 1, entry 1 and 2). For comparison (Table 1, entry 3), a catalytic reaction was performed under the same conditions using a commercially available Pd/C catalyst. Pd/C showed a high activity in the phenol hydrogenation after both 2 and 20 h, but it lacked selectivity and afforded a mixture of cyclohexanone and cyclohexanol. The hydrodeoxygenation product, cyclohexane, was not observed under the mild reaction conditions.

**Table 1. Hydrogenation of phenol using supported Rh, Ru, and Pd NPs.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>Cyclohexanone</th>
<th>Cyclohexanol</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 h/20 h</td>
<td>2 h/20 h</td>
<td>2 h/20 h</td>
<td>2 h/20 h</td>
</tr>
<tr>
<td>1</td>
<td>Blankc</td>
<td>0/0</td>
<td>0/0</td>
<td>0/0</td>
<td>0/0</td>
</tr>
<tr>
<td>2</td>
<td>Blanked</td>
<td>0/0</td>
<td>0/0</td>
<td>0/0</td>
<td>0/0</td>
</tr>
<tr>
<td>3</td>
<td>Pd/C</td>
<td>99/100</td>
<td>47/39</td>
<td>53/61</td>
<td>0/0</td>
</tr>
<tr>
<td>4</td>
<td>FFSiPd</td>
<td>94/100</td>
<td>90/82</td>
<td>6/12</td>
<td>4/6</td>
</tr>
<tr>
<td>5</td>
<td>FFSiCePd</td>
<td>86/99</td>
<td>86/80</td>
<td>12/17</td>
<td>2/3</td>
</tr>
<tr>
<td>6</td>
<td>FFSiTiPd</td>
<td>91/99</td>
<td>82/78</td>
<td>16/19</td>
<td>2/3</td>
</tr>
<tr>
<td>7</td>
<td>FFSiRh</td>
<td>100/100</td>
<td>26/1</td>
<td>71/87</td>
<td>3/12</td>
</tr>
<tr>
<td>8</td>
<td>FFSiCeRh</td>
<td>100/100</td>
<td>39/5</td>
<td>61/94</td>
<td>0/1</td>
</tr>
<tr>
<td>9</td>
<td>FFSiTiRh</td>
<td>100/100</td>
<td>12/0</td>
<td>88/99</td>
<td>0/1</td>
</tr>
<tr>
<td>10</td>
<td>FFSiRu</td>
<td>93/100</td>
<td>24/1</td>
<td>73/92</td>
<td>3/7</td>
</tr>
<tr>
<td>11</td>
<td>FFSiCeRu</td>
<td>99/100</td>
<td>17/0</td>
<td>83/100</td>
<td>0/0</td>
</tr>
<tr>
<td>12</td>
<td>FFSiTiRu</td>
<td>100/100</td>
<td>0/0</td>
<td>100/100</td>
<td>0/0</td>
</tr>
<tr>
<td>13</td>
<td>FFSiRh^e</td>
<td>100/100</td>
<td>48/47</td>
<td>52/53</td>
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<tr>
<td>14</td>
<td>FFSiCeRh^e</td>
<td>100/100</td>
<td>47/39</td>
<td>53/61</td>
<td>0/0</td>
</tr>
<tr>
<td>15</td>
<td>FFSiTiRh^e</td>
<td>100/100</td>
<td>56/43</td>
<td>44/57</td>
<td>0/0</td>
</tr>
</tbody>
</table>
Comparing our supported Pd NP catalysts with commercial Pd/C, the conversion at 2 h was slightly lower, reaching values in the range of 86-94 % (Table 1, entries 4-6). However, the lowest cyclohexanone selectivity was as high as 82% observed after 2 h for the FFSiTiPd catalyst (Table 1, entry 6). This is roughly twice as high as the reference catalyst’s selectivity. After 20 h, the conversion reached 99-100 % and cyclohexanone selectivity was reasonably constant for all prepared Pd catalysts (> 78%, Table 1, entries 4-6). A reduction of the cyclohexanone selectivity can be expected due to a further hydrogenation yielding cyclohexanol. After 2 and 20 h of reaction time, the catalysts containing Rh and Ru NPs show higher phenol conversion than those with Pd, but the selectivity shifts towards cyclohexanol after only 2 h of reaction time (Table 1, entry 7-12). These results indicate that Rh and Ru catalysts are more efficient in the hydrogenation of cyclohexanone into cyclohexanol. The Ru catalysts supported on ceria and titania were highly selective towards cyclohexanol, with a 100 % selectivity after 20 h reaction time (Table 1, entries 11 and 12). These results show that the metal plays a key role in the product selectivity during hydrogenation of phenol, clearly overweighing effects from the support material.

Nevertheless, the role of the latter cannot be totally neglected. To gain insights into the impact of the support on selectivity, a quantification of acid sites on each support used was performed by temperature-programmed desorption of ammonia (NH₃-TPD; Fig. S2, Table S1). The results indicate that FFSiTi has more and stronger acidic sites compared to the FFSi and FFSiCe supports. The catalysts prepared with titania-modified magnetic silica afforded higher amounts of cyclohexanol (Fig. 3, blue circles). This behavior can be correlated to the presence of more acidic sites. A stronger interaction between the aromatic ring and the support is expected, leading to a co-planar adsorption of phenol. This, in turn, favors the formation of cyclohexanol [6]. The NH₃-TPD results show that the FFSi support has less acidic sites than its titania- and ceria-modified counterparts (Table S1) with the desorption peak at an intermediate position. Accordingly, the interaction of phenol with the support is weaker, which increases the selectivity towards cyclohexanone. This is especially relevant in the case of the Pd catalysts (Fig. 3, black triangles). Interestingly, the formation of the HDO product, i.e. cyclohexane (< 10 %), was observed for all metal NPs supported on FFSi (Fig. 3, black squares), which is remarkable. Indeed, the conversion of phenol into cyclohexane is typically observed in more harsh reaction conditions. For example, Zhao et al. [28] reported the hydrodeoxygenation of phenol using a Pd/C catalyst at 150 °C, 50 bar H₂, substrate/catalyst ratio ca. 500 in diluted H₃PO₄ aqueous solution. The formation of cyclohexane observed in our study is very interesting and will be further investigated in the future.

Pd NP catalysts show a preferred formation of cyclohexanone, whereas Ru and Rh NP catalysts are more selective towards cyclohexanol. Contrary to the nature of the catalytically active metal, the product selectivity seems largely independent of the support material. For the Rh NP catalysts an increase in selectivity over time can be observed. Moreover, the influence of the support is more pronounced compared to Pd-
and Ru-based catalysts. In the beginning of the catalytic reactions, Rh NP catalysts, although very active to phenol hydrogenation, are less selective than the Ru ones. Moreover, FFSiCeRu and FFSiTiRu were the only ones to reach 100% selectivity towards cyclohexanol after 4 and 2 h, respectively. At similar reaction times, the FFSiCeRh and FFSiTiRh materials show lower selectivities of 71 and 88%, respectively. The Rh NP catalysts are the most active, achieving a quantitative conversion already after 5 min reaction duration. The Ru NP catalysts show lower degrees of conversion compared to Pd and Rh catalysts, but after 30 min the conversion suddenly increased with time. This might suggest that the Ru NPs initially were - at least - partly oxidized, which can be rationalized by the fact that the catalysts were exposed to air before catalytic testing. During catalysis, the material undergoes reduction processes, as shown before in the case of RuO₂ NPs [32]. For Pd and, especially, Rh such an effect seems to be less relevant, presumably due to a lower degree of surface oxidation of the metal species.
Fig. 3. Phenol hydrogenation/hydrodeoxygenation using PVP-stabilized (A) Pd, (B) Ru, and (C) Rh NPs supported onto FFSi (black), FFSiCe (red) and FFSiTi (blue). Conversion of phenol (empty squares) and selectivity to cyclohexanol (circles), cyclohexanone (triangles), and cyclohexane (squares).

For a more detailed investigation of the catalytic behavior of Rh NP catalysts at initial low conversions, the reaction conditions were altered by a ten-fold increase of the substrate-to-metal ratio from 20 to 200. The obtained results show very pronounced changes in selectivity. In fact, the selectivity towards cyclohexanol decreases for all Rh catalysts, when compared to a S/C ratio of only 20. At initial reaction times, the reaction selectivity was directed towards cyclohexanone for all Rh NP catalysts (Fig. 4). For longer reaction times, the selectivity towards cyclohexanone and cyclohexanol tends to be similar. For the FFSiTiRh catalyst, the selectivity towards cyclohexanone is higher.
up to 4 h of reaction duration, which indicates that the titania catalyst is stronger affected by the lower molar ratio of catalyst. This new set of results confirms that Ru NP catalysts are more selective towards cyclohexanol than Rh ones, while the Pd NP catalysts are the only able to efficiently prevent a further hydrogenation of cyclohexanone to cyclohexanol.

![Graph showing conversion and selectivity over time](image)

**Fig. 4.** Phenol hydrogenation/hydrodeoxygenation using FFSiRh (A), FFSiCeRh (A) and FFSiTiRh (C) with substrate/metal molar ratio = 20 (black) and 200 (blue). Conversion of phenol (empty squares) and selectivity to cyclohexanol (circles), cyclohexanone (triangles) and cyclohexane (squares).

### 3.2.2 Study of pressure influence
The performance of the FFSiPd catalyst was investigated at 55 °C under varying H₂ pressure (Fig. 5). Expectedly, the degrees of conversion decrease with decreasing H₂ pressure, yet the predominant selectivity towards cyclohexanone was essentially unaffected. The samples collected after 4 h reaction time show similar phenol conversion, as well as product selectivity, indicating the reaction can be catalyzed efficiently at H₂ pressures down to 1 bar.

![Fig. 5. Phenol hydrogenation/hydrodeoxygenation using FFSiPd at H₂ pressure of 6 bar (black), 3 (red) and 1 bar (blue). Conversion of phenol (empty squares) and selectivity to cyclohexanol (circles), cyclohexanone (triangles) and cyclohexane (squares).](image)

### 3.2.3 Removing the stabilizer by thermal treatment

The stabilizing role of the PVP polymer surrounding the metal NPs has already been described in the previous sections. Due to its location at the surface of the catalytically active NPs, effects on catalytic activity and selectivity are likely. Usually, the presence of PVP as stabilizer leads to strong metal leaching when the catalysts are dispersed in water, but the removal of the PVP stabilizer also has the advantage of performing the reaction in aqueous environments without any leaching. Therefore, we investigated the catalytic activity of Pd NP catalysts after a calcination at 300 °C for 2 h, obtaining the catalysts denoted as FFSiPd, FFSiCePd, and FFSiTiPd. The phenol hydrogenation reaction was studied using the calcined PVP-free catalysts in water and n-hexane using similar reaction conditions (Table 2). The selectivity towards cyclohexanone achieved using the calcined Pd NP catalysts was even higher, reaching 95% in n-hexane and 100% in water. In water, the conversion and selectivity reached 100% for the calcined FFSiTiPd catalyst. Cyclohexanol was not observed and cyclohexane was observed only for FFSiCePd in water, although this catalyst showed the lowest degrees of conversion in both solvents. In n-hexane, the catalyst showed a small improvement in the catalytic performance, except for FFSiCePd that suffered from severe deactivation. The improvement of the catalysts selectivity towards cyclohexanone in aqueous solvent is very interesting. It has to be noted that the catalysts could not be fully recovered using a magnet. An additional centrifugation step was necessary for a complete recovery of the catalysts.
Table 2. Hydrogenation of phenol with calcined Pd catalysts using water and \textit{n}-hexane as solvent.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv (%)\textsuperscript{b}</th>
<th>Selectivity (%)\textsuperscript{b}</th>
<th>cyclohexanone</th>
<th>cyclohexanol</th>
<th>cyclohexane</th>
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<tr>
<td>1</td>
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\textsuperscript{a}Reactions conditions: phenol (75 \textmu mol, in 3 mL \textit{c} water or \textit{d} \textit{n}-hexane), catalyst (36 mg, 3.7 \textmu mol), substrate/catalyst = 20, 75°C, 6 bar H\textsubscript{2}. \textsuperscript{b}Conversion and selectivity determined by GC after 2 h of reaction.

4. Conclusions

In this work, we have prepared a series of supported catalysts comprising nanosized metal NPs of Pd, Ru and Rh deposited onto either pure magnetic silica support or on modified supports by the addition of ceria or titania. This series of similarly prepared catalyst materials allowed us to systematically study the effect of different metals and different supports in the hydrogenation/hydrodeoxygenation of phenol. The main conclusions drawn by the obtained results are as follows. First, Pd-based catalysts show higher selectivity towards cyclohexanone (~90 \%). Second, Rh- and Ru-based catalysts show higher selectivity towards cyclohexanol (100 \%). Furthermore, the modification of the magnetic silica support by the addition of titania leads to an enhanced selectivity towards cyclohexanol for all metal species. In addition, thermal removal of the polymeric stabilizer enables the use of the catalyst in aqueous solvent and further increases the selectivity of Pd-based catalyst towards cyclohexanone (100 \%). Despite the difficulties associated with the de-polymerization of biomass residues, we believe that the development of selective transformations of biomass-derived platform molecules may help to select value-added target products. Our findings clearly indicate that it is possible to produce cyclohexanone and cyclohexanol under mild reaction conditions with high selectivity from phenol as a model substrate compound. Synergistic effects between catalytically active metal species and a modified support material provide excellent degrees of conversions and high selectivities. Advantageously, no time-consuming separation steps for the recovery of the catalysts are necessary, paving the way towards a large-scale production.

AppendixA. Supplementary data

Supplementary data associated with this article can be found, in the online version at

Acknowledgments
This work was supported by CAPES-COFECUB (project N°695/10), CNPq, INCT-Catalise, FAPESP (2016/16738-7, 2018/26253-6), CNRS and UPS-Université de Toulouse. L. R. Vono thanks FAPESP (grant # 2010/11102-0) for his PhD fellowship.
We also thank Prof. Martin Schmal and Marcos Anacleto NUCAT/COPPE/UFRJ for NH$_3$-TPD analysis. We also thank Dr. Marvin Frisch (TUB, Germany) for the revision the final draft of the manuscript.

CRediT author statement

**LLR Vono**: Conceptualization, Methodology, Investigation, Writing- Original draft preparation, Review & Editing. **C Broicher**: Investigation, Writing- Original draft preparation, Review & Editing. **L Philippot**: Supervision, Conceptualization, Methodology, Writing- Reviewing and Editing. Funding Acquisition: **LM Rossi**: Supervision, Conceptualization, Methodology, Writing- Reviewing and Editing, Funding Acquisition.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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