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Transfer hydrogenation from glycerol over a Ni-Co/CeO$_2$ catalyst: a highly efficient and sustainable route to produce lactic acid

Zhenchen Tang, Huatang Cao, Yehan Tao, Hero J. Heeres and Paolo P. Pescarmona

Chemical Engineering Group, Engineering and Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

School of Materials, University of Manchester, Manchester M139PL, United Kingdom

Graphical Abstract

Highlights
- Efficient conversion of glycerol to lactate with concomitant transfer to various H$_2$ acceptors.
A bimetallic NiCo/CeO₂ catalyst showed much higher activity than the monometallic counterparts.

The NiCo/CeO₂ catalyst achieved very high yield of lactic acid salt (93%) at 97% glycerol conversion.

The NiCo/CeO₂ catalyst also gave high activity and selectivity in the transfer hydrogenation.

**ABSTRACT:** Bimetallic Ni-Co catalysts supported on nanosized CeO₂ were prepared and investigated as heterogeneous catalysts for the transfer hydrogenation between glycerol and various H₂ acceptors (levulinic acid, benzene, nitrobenzene, 1-decene, cyclohexene) to selectively produce lactic acid (salt) and the target hydrogenated compound. The bimetallic NiCo/CeO₂ catalyst showed much higher activity than the monometallic Ni or Co counterparts (with equal total metal mass), thus indicating strong synergetic effects. The interaction between the metallic sites and the CeO₂ support was thoroughly characterised by means of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDX) mapping, X-ray photoelectron spectroscopy (XPS), hydrogen-temperature programmed reduction (H₂-TPR) and X-ray diffraction (XRD). Combining characterisation and catalytic results proved that the Ni species are intrinsically more active than Co species, but that incorporating Co into the catalyst formulation prevented the formation of large Ni particles and led to highly dispersed metal nanoparticles on CeO₂, thus leading to the observed enhanced activity for the bimetallic system. The highest yield of lactic acid (salt) achieved in this work was 93% at 97% glycerol conversion (160 °C, 6.5 h at 20 bar N₂, NaOH: glycerol = 1.5). The NiCo/CeO₂ catalyst also exhibited high activity and selectivity towards the target hydrogenated products in the transfer hydrogenation reactions between glycerol and various H₂ acceptors. Batch recycle experiments showed good reusability, with retention of 80% of the original activity after 5 runs.

**KEYWORDS:** glycerol, lactic acid, Ni catalyst, Co catalyst, alloy effects, transfer hydrogenation
1. Introduction

Biomass represents a sustainable alternative carbon source compared to the use of fossil resources like oil, gas and coal.\textsuperscript{1-3} Considering the limited reserves of the fossil fuel, growing research efforts are being devoted to the development of efficient catalytic systems for biomass valorisation into biofuels and biobased chemicals.\textsuperscript{1, 3, 4} For the upgrading of biobased compounds into valuable chemicals, metallic catalysts are often required for one or more step(s) in a multi-step reaction that may involve hydrogenation, oxidation and/or hydrogenolysis.\textsuperscript{3, 4} On one hand, the noble metal catalysts, such as Au, Pt, Pd and Ru, often exhibit excellent catalytic performance in some specific reactions;\textsuperscript{3} on the other hand, their high cost limits the extension of their application from lab-scale to the industry. Moreover, these catalysts often suffer from stability issues since the nanoparticles tend to aggregate and thus decrease their activity under hydrothermal reaction conditions.\textsuperscript{4, 5} As such, there is a strong need for developing noble-metal-free catalysts, which ideally should have comparable performance and better stability compared to those noble metal catalysts.\textsuperscript{3} Among the biobased compounds that typically require the use of noble metal catalysts for its oxidation, glycerol is an attractive platform molecule.\textsuperscript{6, 7} It is produced in large amounts (above 1 million tons crude glycerol in 2016) as the major side product from the biodiesel industry by transesterification of vegetable oils with methanol.\textsuperscript{4, 8} This led to an oversupply of glycerol and, therefore, has prompted both academia and industry to develop efficient catalytic routes to convert it into several valuable chemical products.\textsuperscript{9-11} Lactic acid and alkyl lactates can be produced from glycerol through a dehydrogenation-rearrangement pathway (Scheme 1).\textsuperscript{8, 12-14} Lactic acid has a wide range of applications, including that as monomer of poly-lactic acid, a biodegradable bio-polymer with various applications in the food, pharmaceutical and packaging industry.\textsuperscript{12} Currently, lactic acid is produced by fermentation of carbohydrates, which generates large amounts of salts in the product work-up section and has a relatively low volumetric production rate.\textsuperscript{15, 16} The chemocatalytic route involving the dehydrogenation of glycerol and consecutive rearrangement of the triose intermediates (Scheme 1) is considered a viable, sustainable alternative to the fermentation process.\textsuperscript{12} This chemocatalytic route implies a nominal formation of H\textsubscript{2} and in this sense can be correlated to the use of glycerol as feedstock for the sustainable production of H\textsubscript{2} through aqueous-phase reforming (APR).\textsuperscript{7, 11, 17} Hydrogen is widely used in current chemical industry (e.g. ammonia synthesis, Fischer-Tropsch process, steel industry and various hydrogenation reactions) and in the power fuel cell systems as a clean power source.\textsuperscript{2, 11, 18} Clearly, routes that allow producing H\textsubscript{2} from a renewable source such as biomass represent a sustainable alternative to the current production
through methane steam reforming, which is based on a fossil resource and requires extremely harsh conditions.\textsuperscript{2,19}

\begin{center}
\begin{tikzpicture}

\node[align=center] (A) {glycerol};
\node[align=center, right of=A, xshift=2cm] (B) {\(\text{NiCo/\text{CeO}_2}\)};
\node[align=center, right of=B, xshift=2cm] (C) {glyceric acid};
\node[align=center, right of=C, xshift=2cm] (D) {H\textsubscript{2}O};
\node[align=center, right of=D, xshift=2cm] (E) {\(\text{NaOH}\)};
\node[align=center, right of=E, xshift=2cm] (F) {lactic acid (salt)};

\draw[->, green, very thick] (A) -- (B) node[midway, above, green] {\text{hydrogen acceptors}};
\draw[->, green, very thick] (B) -- (C) node[midway, above, green] {\text{hydrogenated products}};
\draw[->, green, very thick] (C) -- (D) node[midway, above, green] {\text{transfer-hydrogenation}};
\draw[->, green, very thick] (D) -- (E) node[midway, above, green] {\text{NaOH}};
\draw[->, green, very thick] (E) -- (F) node[midway, above, green] {\text{NaOH}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.} Catalytic route from glycerol to lactic acid and from a hydrogen acceptor (cyclohexene, levulinic acid, benzene, nitrobenzene or 1-decene) to the corresponding hydrogenated product with inter-molecular transfer hydrogenation.

The conversion of glycerol into lactic acid requires metallic sites for the first step, i.e. the dehydrogenative oxidation, and a base or a combination of Brønsted and Lewis acid sites for the second step (Scheme 1). Most studies used noble metal catalysts for the first step, such as Pt, Pd, Au and their alloys.\textsuperscript{12,20-22} Pt/C was used for the hydrogenolysis of glycerol under He atmosphere and gave 55\% selectivity to lactic acid at 95\% conversion of glycerol.\textsuperscript{23,24} Supported Au and its alloy catalysts (AuPt/TiO\textsubscript{2}) were firstly used with O\textsubscript{2} as the oxidant, reaching 30\% glycerol conversion and 86\% selectivity to lactic acid at 90 °C.\textsuperscript{21} The first report of a bifunctional catalyst for the conversion of glycerol into lactic acid without adding a base employed Pt supported on a zeolite (Sn-MFI) and achieved an excellent 81\% selectivity towards lactic acid at 90\% conversion of glycerol under O\textsubscript{2} (6 bar) at a relatively mild temperature (90 °C).\textsuperscript{14} Catalysts based on non-noble transition metals, such as Ni, Co and Cu, were also found to be active in converting glycerol to lactic acid under inert atmosphere in the presence of a base.\textsuperscript{20,25-29} A Ni/graphite catalyst tested at 250 °C for 2 h yielded 89\% lactic acid at full glycerol conversion.\textsuperscript{20} A series of 30\%CuO/ZrO\textsubscript{2} catalysts were also
developed and reached 95% yield of lactic acid at 200 °C.\textsuperscript{29} A recent study reported a 20\%Co\(_2\)O\(_4\)/CeO\(_2\) catalyst that achieved 80\% selectivity to lactic acid with 85\% glycerol conversion at 250 °C for 8 h.\textsuperscript{27} All these non-noble metal catalysts were employed in the presence of a homogeneous base (NaOH) and at relatively high reaction temperatures (200-250 °C), under which conditions the base alone would display a significant activity in the conversion of glycerol to lactic acid.\textsuperscript{30,31} An additional drawback of the Ni, Cu and Co-based systems is the high metal-to-glycerol ratio that was needed to achieve acceptable reaction rates. Moreover, the Cu and Co-based catalysts suffered remarkable loss of activity upon reuse, probably due to leaching of metal species in the hydrothermal conditions.\textsuperscript{27,29} If the conversion of glycerol to lactic acid (salt) is carried out under inert atmosphere, the initial dehydrogenative oxidation step (Scheme 1) nominally liberates one molecule of H\(_2\) per molecule of glycerol.\textsuperscript{14,25} However, the hydrogen generated in such system is highly diluted by N\(_2\) in most cases and is thus difficult to collect. In this context, it is more attractive to utilise \textit{in situ} the hydrogen removed from glycerol in the reduction of relevant target compounds. Here, we report a bimetallic Ni-Co catalyst supported on CeO\(_2\) with remarkably high activity in the transfer hydrogenation between glycerol and several H\(_2\) acceptors, under relatively mild hydrothermal conditions (160 °C) and in the presence of NaOH as promotor. The choice of investigating a Ni-based catalyst was inspired by the above-mentioned activity of this metal in converting glycerol to lactic acid, combined with its well-known activity in catalysing hydrogenation reactions as significantly cheaper alternative to noble metals (e.g. Pt and Pd).\textsuperscript{3,32} The idea of using Ni in a bimetallic system was justified by previous reports that showed that the catalytic performance of Ni could be enhanced by incorporating another component, such as Co or Cu, which led to stronger metal-support interaction with consequent smaller metal particle size.\textsuperscript{3,4,33,33} Namely, bimetallic Ni-based catalysts supported on ZrO\(_2\) showed much better performance in the dry reforming of methane (Ni-Co) or in the oxidative steam reforming of methanol (Ni-Cu) compared to their monometallic counterparts.\textsuperscript{34-36} In this work, different oxides were tested as support for the Ni-based catalysts, with CeO\(_2\) leading to the highest activity in glycerol conversion. Our bimetallic Ni-Co catalytic system was also compared to its monometallic counterparts, showing higher activity and allowing to reach very high conversion of glycerol with excellent selectivity towards lactic acid, and to combine this reaction with the efficient hydrogenation of several unsaturated compounds in a one-pot process.

\textbf{Experimental section}

\textbf{Reactants and materials}
Glycerol (99%), 1,3-dihydroxyacetone dimer (97%), glyceraldehyde (90%), glycolic acid (99%), lactic acid (98%), pyruvic aldehyde (40 wt% in H2O), cyclohexene (99%), cyclohexane (99.5%), sodium hydroxide (98%), benzene (99.9%), levulinic acid (99%), 4-hydroxypentanoic acid, γ-valerolactone (99%), nickel(II) nitrate hexahydrate (98.5%), cobalt(II) nitrate hexahydrate (98%), copper(II) nitrate hemi(pentahydrate) (98%), titanium oxide (P25), magnesium oxide (99%), cerium oxide (nanopowder, nominally <25 nm, though some large particles were observed by TEM; this compound is denoted as CeO2 for the sake of simplicity, though it contains both CeIV and CeIII and it is thus actually CeO2-x), zirconium oxide (nanopowder, <100 nm) were purchased from Sigma Aldrich. Glyceric acid (20 wt% in H2O), nitrobenzene (99.5%), aniline (98%), azobenzene (98%), azoxybenzene (98%) was purchased from TCI Chemicals. Active carbon Norit SX1G was purchased from Cabot. The H2O used in this work was always of MilliQ grade. All chemicals were used without further purification.

Catalyst synthesis

Wet impregnation method was used for the preparation of catalysts based on Ni, Co, Cu, NiCo, NiCu supported on CeO2 and ZrO2. Typically, CeO2 (2 g) was mixed with an aqueous solution of Ni(NO3)2 or Co(NO3)2 or Cu(NO3)2 or the combination of two of them (2 M, certain volume for the designed loading of Ni, Co and Cu). The slurry was stirred at room temperature until the water evaporated. The solid mixture was then dried at 100 °C overnight. The resulting solids were milled to fine powder and then calcined at 550 °C in the oven under static air (heating rate 3 °C/min). The calcined catalysts were further reduced in a tube oven under H2 flow (99.9% and 200 mL/min) at 400 °C (heating rate 3 °C/min) for 2 h. The gas flow was switched to N2 for 1 h to wipe away the adsorbed H2 on the catalyst surface before taking the catalyst out from the tube oven. A typical reduced catalyst prepared by this method was named as 10NiCo/CeO2, in which 9 stand for the total loading of Ni and Co, in which the weight ratio between Ni and Co is always kept as 1:1. In addition, as a reference, the catalyst was also used directly after calcination at 550 °C without further reduction in H2, which was named as 10NiCo/CeO2-C.

Catalytic tests

The catalytic experiments were carried out in a 100 mL Parr stainless steel autoclave reactor equipped with a Teflon liner and an overhead stirrer. In a typical experiment test, a predetermined amount of the NiCo/ZrO2 catalyst together with a mixture of aqueous solution of glycerol (0.5 M in 20 ml), NaOH (015 mol) and cyclohexene (02 mol, as organic phase) were loaded into the reactor.
The reaction was performed under N\(_2\) (20 bar) for 4.5 h at 160 °C (extra heating time 0.5 h) at a stirring speed of 800 rpm. The reactor was depressurised and the reaction content (in two phases) was taken separately and filtered to remove the catalyst. The organic phase was analysed by gas chromatography using a Thermo Trace GC equipped with a Restek Stabilwax-DA column (30 m × 0.32 mm × 1 μm) and a FID detector. And the aqueous phase was first neutralised and diluted by H\(_2\)SO\(_4\) (1 M), then analysed by high performance liquid chromatography (HPLC, Agilent Technologies 1200 series, a Bio-Rad AminexHPX-87H 300 × 7.8 mm column, T = 60 °C, with 0.5 mM H\(_2\)SO\(_4\) as an eluent (flow rate: 0.55 mL/min) using a combination of refractive index detector and ultra-violet detector. For the analysis of nitrobenzene and its products, conversion and selectivity were determined by GC analysis using an Agilent Technologies 7980B GC equipped with an Agilent DB-5#6 (5%-Phenyl)-methylpolysiloxane column (15 m, 320 μm ID). The identification of the products was performed by GC-mass spectrometry (GC-MS) on an HP 6890 Series GC equipped with a Restek Rxi-5Si MS fused silica column (30 m, 250 μm ID) coupled to an HP 5973 Mass Selective Detector. Each component was calibrated using solutions of the individual components at 4 different concentrations.

For the catalyst recycle tests, a small amount of the reaction mixture was collected for analysis and the remaining mixture was filtered and the catalysts were recovered. The catalysts were washed first with H\(_2\)O (20 mL), then with ethanol (20 mL), and this procedure was repeated 3 times, after which the solid was dried overnight at 100 °C. This solid was used for another batch experiment.

**Characterisation of the catalysts**

Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX) mapping measurements were performed on a FEI Tecnai T20 electron microscope operating at 200 keV with an Oxford Xmax 80T detector. The samples were prepared by ultra-sonication in ethanol followed by drop-casting of the material on a copper grid.

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.

Inductively-coupled plasma optical emission spectrometry (ICP-OES) was performed using a Perkin Elmer Optima 7000 DV instrument in order to obtain the actual Pt loadings on the supports.

X-ray Photoelectron Spectroscopy (XPS) was measured by mounting the catalysts on a conductive tape adhered to the XPS sample holder. No further treatment was carried out prior XPS
measurement. Then, the sample was loaded into the load lock and the pressure were 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 Kα 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 size of 600 µm diameter was used. The neutralizer was on to avoid charging effects. All XPS spectra were analysed using the Winspec software package developed by LISE laboratory, University of Namur, Belgium including Shirley background subtraction and peak deconvolution.

Hydrogen-temperature programmed reduction (H₂-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 down 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.% H₂ in He.

X-ray diffraction (XRD) measurements were performed on a D8 Advance Bruker diffractometer with a CuKα 1 radiation ($\lambda=1.5418$ Å). The XRD patterns were collected under 40 kV and 40 mA in the range of 10°-80°.

**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.

Product selectivity for a compound $P$ is defined by equation 2:

$$S_p = \frac{C(p)}{C(g,0) - C(g)} \times 100% \quad (2)$$

in which $C(p)$ is the molar concentration of a product after a certain reaction time.

The yield of transfer hydrogenation is defined by equation 3:

$$Y_{\text{trans-H}} = \frac{\sum(x \cdot n(p))}{n(g,0) - n(g)} \times 100% \quad (3)$$

in which $x$ is the number of hydrogen atoms needed for the reduction of product 1, $n(p)$ is the molar amount of product 1, $n(g)$ is the molar amount of glycerol after a certain reaction time and $n(g,0)$ is the initial molar amount of glycerol.

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).
3. Results and Discussion

Preliminary screen of supports and metals

Our study of the conversion of glycerol into lactic acid coupled with the transfer hydrogenation to an unsaturated compound started with the investigation of the catalytic behaviour of Ni catalysts (10 wt%) as a function of the type of the material (activated carbon (AC) and various metal oxides) on which the metal particles were supported by wet impregnation. The five catalysts were tested at 160 °C in the presence of NaOH as promoter and using a model compound as cyclohexene as the H₂ acceptor (Table 1). Ni supported on AC, MgO and TiO₂ showed relatively low activity (entries 1-3, Table 1), whereas the activity was significantly higher when nanosized CeO₂ and nanosized ZrO₂ were used as support for Ni (glycerol conversion 53% and 63%, respectively; entry 4-5, Table 1), in line with previous reports on other (de)hydrogenation reactions.²⁴⁻³³ In all cases, high selectivity towards lactic acid (>91%) was observed. This is attributed to the presence of NaOH, which effectively promotes the deprotonation of glycerol and catalyses the successive isomerisation of the intermediates (glyceraldehyde and dihydroxyacetone) into the lactic acid salt (Scheme 1), thus granting very high selectivity towards the desired product.²¹⁻²²,²⁸⁻³⁷ Small amounts of glyceric acid, glycolic acid and propanediol were detected as side products (Table 1). Glyceric acid is formed through the further dehydrogenation of glyceraldehyde and glycolic acid probably originates from oxidative C-C bond cleavage of glyceric acid.¹³ Propanediol (as a mixture of 1,2- and 1,3-isomers) probably forms via the hydrogenolysis of glycerol.³⁸⁻⁴⁰ In addition, for all reactions, very minor amounts of glyceraldehyde and propanoic acid were observed as side products, with selectivity below 0.2% for each of them.

Table 1. Catalytic performance of Ni catalysts supported on activated carbon and various metal oxides.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. GLY (%)</th>
<th>YLA (%)</th>
<th>S (transfer-H) (%)</th>
<th>Selectivity in the conversion of glycerol (%)</th>
<th>Yield in the conversion of cyclohexene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lactic acid</td>
<td>Glyceric acid</td>
</tr>
<tr>
<td>1</td>
<td>10Ni/AC</td>
<td>22</td>
<td>21</td>
<td>42</td>
<td>97</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10Ni/MgO</td>
<td>6.2</td>
<td>5.7</td>
<td>42</td>
<td>91</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>10Ni/TiO₂</td>
<td>14</td>
<td>13</td>
<td>29</td>
<td>98</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>10Ni/ZrO₂</td>
<td>63</td>
<td>60</td>
<td>33</td>
<td>95</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>10Ni/CeO₂</td>
<td>53</td>
<td>52</td>
<td>20</td>
<td>98</td>
<td>0</td>
</tr>
</tbody>
</table>
Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; Ni catalyst: 0.1 g; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N\textsubscript{2} pressure: 20 bar. *Under the employed reaction conditions (mol\textsubscript{glycerol} : mol\textsubscript{cyclohexene} = 1 : 2) the maximum theoretical yield of cyclohexane is 50%.

Based on this preliminary study, CeO\textsubscript{2} and ZrO\textsubscript{2} were selected as supports for further study of Ni-based catalysts. Then, we aimed at improving the catalytic performance by incorporating another metallic component, i.e. Co or Cu.\textsuperscript{3,4,33} The activity of the bimetallic catalysts was compared to the monometallic counterparts (Table 2), while keeping the total loading of metal at 10 wt% (and with 1:1 mass ratio for the bimetallic systems). The incorporation of Co into the catalyst formulation was highly beneficial when CeO\textsubscript{2} was used as support (10NiCo/CeO\textsubscript{2}), leading to 91% glycerol conversion (entry 1, Table 2) compared to 53% conversion obtained over 10NiCo/CeO\textsubscript{2} and 46% conversion over 10Co/CeO\textsubscript{2} (entry 5, Table 2). Also the incorporation of Cu enhanced the activity compared to the monometallic counterparts, though the effect was less marked (compare entry 2 in Table 2 to entry 5 in Table 1 and entry 6 in Table 2). On the other hand, the 10NiCo/ZrO\textsubscript{2} catalyst showed almost the same activity as the monometallic 10Ni/ZrO\textsubscript{2}, (compare entry 3 in Table 2 with entry 4 in Table 1), whereas the incorporation of Co proved more beneficial when ZrO\textsubscript{2} was the support, reaching 80% glycerol conversion (entry 4, Table 2). These results indicate a complex interplay between the type of metals and the support. The benefit brought about by the bimetallic formulation will be elucidated further in the case of the optimum catalyst, i.e. 10NiCo/CeO\textsubscript{2} (vide infra). In all these tests, the selectivity towards lactic acid remained very high (94-96%). Glyceric acid, glycolic acid and propanediol were detected as the main side products, with selectivity <6% in total. Though the incorporation of Cu enhanced the activity of the Ni-based catalysts, leaching of metal species was observed in the basic medium under hydrothermal conditions, with significant amount of brown Cu-containing precipitate deposition on the stirring bar and reactor walls.\textsuperscript{28,33,41-43} Therefore, 10NiCo/CeO\textsubscript{2} was selected for further investigation aimed both at a deeper evaluation of the catalytic performance and at understanding the relationship between structure and catalytic behaviour.

Table 2. Catalytic performance of Ni, Co, Cu and bimetallic Ni catalysts supported on CeO\textsubscript{2} and ZrO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv\textsubscript{GLY} (%)</th>
<th>Y\textsubscript{LA} (%)</th>
<th>S\textsubscript{(transfer-H)} (%)</th>
<th>Selectivity in the conversion of glycerol (%)</th>
<th>Yield in the conversion of cyclohexene (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10NiCo/CeO\textsubscript{2}</td>
<td>91</td>
<td>85</td>
<td>24</td>
<td>94</td>
<td>0.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Yields based on the conversion of glycerol; all results were the average of two parallel experiments.
Under the employed reaction conditions (mol glycerol : mol cyclohexene = 1 : 2) the maximum theoretical yield of cyclohexane is 50%. The weight ratio between Ni and (Co or Cu) in the bimetallic catalysts is 1/1.

**Characterisation of the NiCo/CeO₂ catalysts**

The catalysts presented in this work were prepared by wet impregnation, followed by calcination and finally reduction by H₂. The actual loading of Ni and/or Co determined by ICP-OES (Table 3) was, found to be very close to the nominal 10 wt% loading. In the bimetallic Ni-Co catalyst, the actual loading of Ni and Co is 5.6 wt% for both metals, which is slightly higher than the theoretical 5 wt%. The BET surface area was measured before and after loading Ni and Co, showing only a slight decrease (from 32 to 28 m²/g) compared to the fresh CeO₂ support.

**Table 3.** Elemental composition and specific surface area of CeO₂ and Ni, Co, Ni-Co catalysts supported on CeO₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ni loading/%</th>
<th>Co loading/%</th>
<th>Surface area/[m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CeO₂</td>
<td>n.d.</td>
<td>n.d.</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>10Ni/CeO₂</td>
<td>9.9</td>
<td>n.a.</td>
<td>n.d.</td>
</tr>
<tr>
<td>3</td>
<td>10Co/CeO₂</td>
<td>n.a.</td>
<td>9.5</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>10NiCo/CeO₂</td>
<td>5.6</td>
<td>5.6</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>10NiCo/CeO₂</td>
<td>4.4</td>
<td>4.4</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* the sample was measured after 5 runs; n.a.: not applicable; n.d.: not determined.
To investigate the possible organisation of Ni, Co and Ni-Co species in crystalline phases on the CeO$_2$ support, the catalysts were further characterised by XRD before and after reduction (Figure 1). The materials before reduction (Figure 1A) display the characteristic peaks of the CeO$_2$ support together with the typical peaks of NiO (in 10Ni/CeO$_2$-C) or Co$_3$O$_4$ (in 10Co/CeO$_2$-C). The bimetallic 10NiCo/CeO$_2$-C shows a broad peak at 36.7°, which is slightly shifted compared to the Co$_3$O$_4$ peak (37°) and has been attributed to the mixed oxide NiCo$_2$O$_4$. After reduction at 400 °C in H$_2$ flow, besides the peaks of the CeO$_2$ support, only one peak at 44.7° belonging to metallic Ni can be seen in the pattern of 10Ni/CeO$_2$ (Figure 1B). On the other hand, no signals stemming from Co and/or Ni phases were observed in 10Co/CeO$_2$ and 10NiCo/CeO$_2$. These results suggest that relatively large crystalline Ni particles formed upon reduction in 10Ni/CeO$_2$, while the Co or Ni-Co species obtained after reduction were highly dispersed in the other two catalysts.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of calcined CeO$_2$ and Ni, Co and Ni-Co catalysts supported on CeO$_2$ before (A) and after reduction (B).

To achieve deeper insight on the dispersion status of Ni, Co and bimetallic Ni-Co catalysts supported on nanosized CeO$_2$, TEM and STEM-EDX-mapping were used to investigate the average size of these metallic domains (Figure S1, 2 and 3). Since the atomic mass of cerium is much higher than that of nickel or cobalt, it is hard to determine the particle size of Ni, Co or Ni-Co alloy on the CeO$_2$ support based on TEM pictures (Figure S1), as the darker zones are not necessarily corresponding to Ni or Co domains.

Analysis by STEM coupled with EDX mapping was more informative as it allows identifying the elemental composition within the image (Figure 2). The large green domains in Figure 2A and 3B...
indicate the presence of Ni-containing nanoparticles on CeO₂. Based on the XRD data (Figure 1A), these domains are identified as large NiO nanoparticles (mainly around 100 nm, with some smaller particles, see Figure 2A) in the sample before reduction (10Ni/CeO₂-C), and to large domains of metallic Ni (around 75 nm, Figure 2B) after the sample was reduced (10Ni/CeO₂). For the monometallic material prepared by supporting Co on CeO₂ and prior to reduction (10Co/CeO₂-C), the Co₃O₄ identified by XRD (Figure 1A) was found to be better dispersed on the CeO₂ support (Figure 2C) compared to NiO on CeO₂. The 10Co/CeO₂ material obtained upon reduction showed nearly homogeneously dispersed Co species (Figure 2D), which indicates that the particle size of Co is lower than the detection limit of EDX-mapping (around 30 nm). The relatively small size of the Co nanoparticles is also in agreement with the absence of any signal due to metallic Co in the XRD pattern of 10Co/CeO₂ (Figure 1B), which suggests a strong metal-support interaction between Co and CeO₂.⁴, 33, 35, 45, 46, 48

**Figure 2.** EDX-mapping coupled with STEM (dark field) pictures of monometallic Ni and Co catalysts supported on CeO₂ before and after reduction. (A) 10Ni/CeO₂ C, (B) 10Ni/CeO₂, (C) 10Co/CeO₂ C, (D) 10Co/CeO₂. The green, red and blue dots represent Ni, Co and Ce, respectively.

STEM and EDX-mapping of the Ni-Co bimetallic material prior to reduction (10NiCo/CeO₂-C), showed that both Ni and Co are nearly homogeneously dispersed on the CeO₂ surface (Fig 4 A-D). This demonstrates that the presence of Co prevents the aggregation of Ni species, in contrast to the
large domains observed in 10Ni/CeO₂-C. After reduction at 400 °C under H₂, Ni and Co still preserve very good dispersion, with no large metal particles (i.e. > 30 nm) being visible (Figure 3H). The strong interaction between Co and the CeO₂ support, which promotes the observed high dispersion of both Co and Ni on the surface, has been shown to be related to the formation of a thin layer of reduced CeO₂ at the interface with the metallic Co.³⁵ Based on our results, we infer that this feature prevents Ni from forming large particles in the process of calcination and reduction.³³, ³⁵, ⁴⁶

Figure 3. EDX-mapping coupled with STEM (dark field) pictures of bimetallic Ni-Co catalysts supported on CeO₂ before and after reduction. (A-D) 10NiCo/CeO₂-C, (E-H) 10NiCo/CeO₂. The green, red and blue dots represent Ni, Co and Ce, respectively.

The reducibility of Ni, Co and Ni-Co supported on CeO₂ was further investigated by H₂-TPR (Figure 4). The support, CeO₂, exhibited two dominant peaks centred at 490 °C (from 300 to 550 °C) and 880 °C (from 700 to above 900 °C), which are attributed to the reduction of surface ceria and bulk ceria, respectively.³⁵, ⁴⁹ Besides the reduction peaks of CeO₂ at 420 and 815 °C, which are slightly shifted to lower temperature, the monometallic 10Ni/CeO₂-C displays two peaks at 213 °C (minor) and 320 °C (dominant), which are attributed to the reduction of adsorbed oxygen and NiO, respectively.³⁵, ⁵⁰ The monometallic 10Co/CeO₂-C showed two main peaks at 260 and 315 °C, which are attributed to the two-step reduction Co₃O₄→CoO→Co.⁵¹, ⁵² The large and broad shoulder extending from 350 to 500 °C, which is probably due the reduction of surface CeO₂. Compared to the monometallic Ni catalyst, the significant increase of the intensity of the reduction peak of surface CeO₂ in the monometallic Co catalyst supports the existence of a strong metal-support interaction between Co
and CeO₂, which is in agreement with the formation of a thin layer of reduced support on the metallic Co surface reported in the literature. The 10NiCo/CeO₂-C material showed almost identical profile as the one of 10Co/CeO₂-C, with all the peaks shifted by ca. 5 °C to lower temperature. This suggests that, in the bimetallic Ni-Co catalyst, the reduction behaviour is mainly dictated by the presence of Co, including the strong metal-support interaction indicated by the broad shoulder between 350 to 500 °C. This result explains the observed much better dispersion of the metal species in the bimetallic Ni-Co catalyst compared to the monometallic Ni catalyst (Figure 2 and 4).

![Graph showing H₂-TPR profile of calcined CeO₂ and Ni, Co and Ni-Co catalysts supported on CeO₂.](image)

**Figure 4.** H₂-TPR profile of calcined CeO₂ and Ni, Co and Ni-Co catalysts supported on CeO₂.

The characterisation by EDX-mapping and H₂-TPR indicates a geometrical effect of the presence of Co on the dispersion of Ni on the CeO₂ support. To investigate further the interaction between Co, Ni and the support, selected catalysts were analysed by XPS (Figure S2-4). The XPS signal of the Ni 2p₃/₂ core level region of the unreduced 5Ni/CeO₂-C catalyst was deconvoluted into 3 main peaks: at 853.6 eV, assigned to NiO; at 855.6 eV, attributed to Ni(OH)₂ and/or NiO(OH); and a satellite peak at 860.6 eV. Similar peaks were identified by deconvoluting the Ni 2p₃/₂ signal of the unreduced 10NiCo/CeO₂-C catalyst (Figure S2.A and B). After reduction (Figure S2.C and D), in addition to the 3 peaks mentioned above, the deconvolution allowed identifying a peak ascribed to Ni⁰ (at 852.3 eV) in catalysts 5Ni/CeO₂ and 10 NiCo/CeO₂. These data confirm the successful reduction to metallic Ni. The fact that the majority of the XPS signal stems from oxidised Ni species can be explained considering that XPS is a surface technique (information from the top 1-10 nm of the
material) and that the surface of the particles is expected to tend to oxidise in contact with air and moisture.\textsuperscript{58,59} The XPS signal of the Co 2p\textsubscript{3/2} core level region of the unreduced 5Co/CeO\textsubscript{2}-C catalysts was deconvoluted into 3 main peaks: at 779.5 eV, assigned to cobalt oxides (CoO and/or Co\textsubscript{3}O\textsubscript{4}); at 781.5 eV, ascribed to Co(OH)\textsubscript{2}; and a satellite peak at 785.5 eV.\textsuperscript{55,60,61} Analogous peaks were identified by deconvoluting the Co 2p\textsubscript{3/2} signal of the unreduced 10NiCo/CeO\textsubscript{2}-C catalyst (Figure S3.A and B). After reduction (Figure S3.C and D), in addition to the 3 peaks mentioned above, the deconvolution showed a peak assigned to Co\textsuperscript{0} (at 778.0 eV) in the catalysts 5Co/CeO\textsubscript{2} and 10 NiCo/CeO\textsubscript{2}.\textsuperscript{55,62} Similarly to what discussed in the case of the supported Ni particles, the presence of oxidised Co species in the reduced samples is attributed to the formation of a layer of oxides and hydroxides at the surface of the particles, formed by contact with air and moisture. The features of the XPS signal of the Ce 3d core level region support the anticipated strong interaction between Co and CeO\textsubscript{2} (Figure S4). This is indicated by surface reduction of Ce\textsuperscript{4+} and the increase in Ce\textsuperscript{3+} observed in the XPS spectra of the Co-containing catalysts (whereas this effect is absent in the spectra of the catalysts containing Ni but no Co). This matches well with the literature and with our H\textsubscript{2}-TPR results.\textsuperscript{35,52,54} The XPS data are not conclusive on possible synergistic electronic effects between Ni and Co. Therefore, we infer that the main reason for the improved catalytic performance of bimetallic 10NiCo/CeO\textsubscript{2} is the smaller size and better dispersion of the Ni-containing particles.

**Optimisation of the performance of catalyst 10NiCo/CeO\textsubscript{2}**

Based on this characterisation study, the optimum activity observed with the bimetallic 10NiCo/CeO\textsubscript{2} catalyst is attribute to presence of the more active Ni compared to the monometallic 10Co/CeO\textsubscript{2}, and to the better dispersion of the active metallic species compared to the monometallic 10Ni/CeO\textsubscript{2} catalyst. To further confirm the nature of the active sites, unreduced Ni, Co and bimetallic Ni-Co catalysts were tested under the same conditions employed for the reduced catalysts (Table S1). In the unreduced materials, the metal oxides (NiO, Co\textsubscript{3}O\textsubscript{4} and NiCo\textsubscript{2}O\textsubscript{4}) would be the catalytic sites rather than the metallic sites. However, all the unreduced catalysts had significantly lower activity compared to reduced ones (Table 1 and 2), with the conversion of glycerol being < 16% in all cases. These results confirm that the metallic sites are the active site in this transfer hydrogenation reaction between glycerol and cyclohexene, in agreement with what shown in the literature.\textsuperscript{27-29}

The Ni, Co and Ni-Co catalysts with different loading (2, 5 and 10 wt%) supported on CeO\textsubscript{2} were tested to gain better understanding on the effect of the Ni and Co composition (Figure 5). With the Ni/CeO\textsubscript{2} catalysts, the conversion of glycerol increased with the metal loading up to 5 wt% Ni, at
which it reached 55%, whereas it remained nearly constant upon further increase to 10 wt % of Ni. This trend is completely different from the one observed with the Co/CeO$_2$ and NiCo/CeO$_2$ catalysts, for which the glycerol conversion and the lactic acid yield exhibited an increasing trend with the increase in metal loading (Figure 5A). The performance of these catalysts can be analysed also in terms of TON (Figure 5B). These data show that the turnover number is nearly constant as a function of metal loading for the monometallic Co-catalysts, whereas an increasing loading of Ni causes a gradual decrease in TON, which is more marked for the monometallic Ni-catalysts compared to the bimetallic Ni-Co materials. These trends are in agreement with the tendency of Ni to form large particles at high loading (see Figure 3.A-B), which implies that a smaller fraction of the metal is available to act as active site, thus leading to the observed lower TON. On the other hand, Co maintain small metallic domains on the CeO$_2$ surface also at 10 wt% metal loading (Figure 2.C-D), thus enabling to have a nearly constant TON as a function of metal loading. The highest TON was observed for 2Ni/CeO$_2$ and 2NiCo/CeO$_2$, whereas among the catalysts with 10 wt% metal loading, the highest TON was found for 10NiCo/CeO$_2$, despite the decrease compared to the 2 wt% material. This confirms the higher intrinsic activity of Ni compared to Co in catalysing the dehydrogenative oxidation of glycerol. Non-noble metal catalysts are generally used with high loading to give high productivity. Indeed, when the catalytic performance is compared in terms of productivity (Figure 5C) the highest value among the tested catalysts is obtained with the material with the highest TON among those with 10 wt% metal loading, i.e. 10NiCo/CeO$_2$. This underlines the benefit of the presence of Co in combination with Ni on the catalytic performance.$^{33-35, 44, 48}$

![Figure 5](image_url)

**Figure 5.** Catalytic performance of Ni, Co and bimetallic Ni-Co catalysts as a function of the metal loading supported on CeO$_2$: (A) Glycerol conversion and lactic acid yield; (B) TON: turnover number, defined as the total number of glycerol molecules converted per each metal atom; (C) Productivity, defined as the total mass of lactic acid produced per gram of heterogeneous catalyst per hour.
Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; catalyst: 0.1 g; NaOH: 15 mmol; temperature: 160°C; reaction time: 4.5 h; N₂ pressure: 20 bar.

The 5NiCo/CeO₂ catalyst, which achieved intermediate glycerol conversion at 160 °C, was selected for investigating the effect of the reaction temperature (in the range 140 to 200 °C, Figure S2). The conversion of glycerol increased with higher reaction temperature, from 11% (at 140 °C) to 99% (at 200 °C) while the selectivity to lactic acid remained > 98%. The selectivity towards the transfer hydrogenation was steady at around 25% in all range of temperatures. It should be noted that, when only NaOH was used in the reaction system, the conversion of glycerol was rather low, though it increased from 1.6 to 16% (from 140 to 200 °C, Figure S5). This demonstrates the need for a heterogeneous catalyst to carry out the dehydrogenation reaction in this range of relatively mild temperatures.\(^{30, 31}\)

To further investigate the effects of the catalyst amount on this reaction, different weights of catalyst (from 0.025 to 0.15 g) were used, while all other parameters were kept constant. The results show a gradual increase in the conversion of glycerol from 29% to >99.9% upon increase of the loading of the 10NiCo/CeO₂ catalyst (Figure S6).

The role of NaOH was studied in more detail by varying the molar ratio between NaOH and glycerol (from 0 to 2, Figure S7). Without the addition of NaOH, both the conversion of glycerol and the selectivity to lactic acid were very low (conversion of glycerol = 3.5%). If the molar ratio between NaOH and glycerol was increased, the conversion of glycerol gradually increased reaching 91% with 85% yield of lactic acid salt 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 81%, thus indicating that the employed ratio (1.5) is the optimum value. These results confirm that the presence of a NaOH in the reaction mixture is critical to induce the deprotonation of one of the hydroxyl groups of glycerol, thus promoting the dehydrogenation of glycerol.\(^{21, 28}\) Moreover, NaOH can catalyse the isomerisation of glyceraldehyde and dihydroxyacetone and lead to the formation of sodium lactate with very high selectivity.

The reaction profile as a function of the reaction time was studied with the 10NiCo/CeO₂ catalyst (Figure S8). The conversion of glycerol increased almost linearly within the first 4.5 h, corresponding to a productivity of lactic acid 17.4 g\(_{(\text{LA})}/(\text{g(\text{metal})h})\). The selectivity towards lactic acid stayed always above 90% and the total selectivity towards by-products (glyceric acid, glycolic acid and propanediol) was around 4%. The selectivity towards the transfer hydrogenation slightly decreased with the reaction time, from 31% to 26%. These results suggest that under the employed
reaction conditions the dehydrogenation of glycerol is the rate-determining step, and that once the dihydroxyacetone and/or glyceraldehyde formed, they would be transformed into lactic acid (salt) in a very fast and selective way.

Catalyst 10NiCo/CeO$_2$ was also selected for a reusability test (Figure 6). The fresh catalyst showed 91% conversion of glycerol and 85% yield to lactic acid, while recycling after straightforward washing and drying led to a slight, gradual decrease in activity. After 5 runs, the conversion of glycerol decreased was 73%, while the selectivity towards lactic acid remained unaltered (> 94%). Meanwhile, the selectivity in transfer hydrogenation gradually increased from 24 to 28% between the first and the fifth run. The gradual loss of activity is probably caused by the leaching of a small fraction of the active components in the alkaline hydrothermal reaction system, since the loading of Ni and Co decreased from 5.6 wt% (each) in the fresh catalyst to 4.4 wt% (each) after 5 runs (entry 5, Table 3).

![Figure 6](image)

**Figure 6.** Reusability test of the 10NiCo/CeO$_2$ catalyst for the conversion of glycerol and transfer hydrogenation. Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); cyclohexene: 20 mmol; catalyst: 0.1 g; NaOH: 15 mmol; temperature: 160°C; N$_2$ pressure: 20 bar.

*Substrate scope for the transfer hydrogenation reaction from glycerol*
During the optimisation of the Ni-based catalyst presented above, cyclohexene was employed as hydrogen acceptor in the transfer hydrogenation reaction from glycerol. To expand the scope of applicability of the transfer hydrogenation, we tested a set of H₂ acceptors with different features (a biobased compound as levulinic acid, an aromatic compound as benzene, a compound containing both an aromatic ring and another reducible group as nitrobenzene and a linear, terminal alkene as 1-decene). While cyclohexene and 1-decene were selected as model compounds, the hydrogenation of benzene, nitrobenzene and levulinic acid is of potential industrial relevance. The tests were carried out with a 1:1 molar ratio between glycerol and the hydrogen acceptor, at 160 °C under N₂ atmosphere (Scheme 2 and Table 4).

When levulinic acid was employed as the H₂ acceptor, two main products were observed: 4-hydroxypentanoic acid (27% yield), obtained by hydrogenation of the carbonyl group of levulinic acid, and γ-valerolactone (48% yield), obtained by further dehydration (Scheme 2 and entry 1 in Table 4). γ-valerolactone can be used as food additive, solvent and precursor for polymers. This reaction also gave an 86% yield of lactic acid at 87% glycerol conversion with a very good 88% selectivity in the transfer hydrogenation.

When benzene was tested as H₂ acceptor, a very high selectivity (97%) in the transfer hydrogenation from glycerol was observed, with cyclohexane being the only product (corresponding to complete reduction of benzene). The reduction of benzene is the industrial route for the production of cyclohexane, which is employed as precursor in the synthesis of adipic acid used in the manufacturing of nylon. The yield achieved here (25%) is promising considering that under the employed reaction conditions (1:1 molar ratio between glycerol and benzene), the maximum theoretical yield of cyclohexane is 33%. These results were coupled with 79% conversion of glycerol and 77% yield of lactic acid (entry 2, Table 4).

When nitrobenzene was employed as hydrogen acceptor, the reduction of the nitro group is expected to be favoured over the reaction of the aromatic ring. Indeed, the observed products (azoxybenzene with 59% yield, azobenzene with 18% yield and aniline with 7.5% yield) all originate from the reduction of the nitro group (Scheme 2). These are all industrially valuable products, with azoxybenzene being utilized in dyes, reducing agents and polymerisation inhibitors; azobenzene being used as dyes, indicators and additives in polymer; and aniline finding application in producing pesticides, dyes and as the precursors to polyurethane. For this reaction, the selectivity in the transfer hydrogenation from glycerol was > 100%. This can be explained considering the strong oxidative ability of nitrobenzene, which led to the further oxidation of the triose intermediates to glyceric acid and glycolic acid (entry 3, Table 4), similarly to what is
generally observed in the oxidation of glycerol in the presence of O$_2$.$^{25, 80-82}$ Therefore, glyceric acid (52% yield) becomes the major product under these conditions, with lactic acid being obtained in much lower yield (23%).

When 1-decene was selected as a linear H$_2$ acceptor with a primary C=C bond, 92% conversion of glycerol and 91% yield of lactic acid was achieved after reaction, while 85% of decene was hydrogenated to decane, corresponding to a remarkably high 94% selectivity in the transfer hydrogenation (entry 4, Table 4). This is much higher than what was found when using cyclohexene as the H$_2$ acceptor (entry 5, Table 4). This result is probably due to the higher accessibility of the C=C bond in a linear alkene with a terminal double bond as 1-decene compared to the more sterically-hindered cyclohexene.

The study of substrate scope for the transfer hydrogenation reaction from glycerol demonstrated that our catalytic system based on 10NiCo/CeO$_2$ is able to efficiently promote the conversion glycerol to lactic acid while exploiting the liberated hydrogen in the reduction of different unsaturated compounds to achieve the synthesis of useful target products without requiring an external H$_2$ source.
Scheme 2. Reduction routes of various H$_2$ acceptors.

Table 4. Catalytic performance of 10NiCo/CeO$_2$ catalysts with different H$_2$ acceptors.

<table>
<thead>
<tr>
<th>Entry</th>
<th>H$_2$ acceptor</th>
<th>Conv. Gly (%)</th>
<th>$S_{\text{transfer-H}}$ (%)</th>
<th>Yields of products from glycerol (%)</th>
<th>Yields of products from H$_2$ acceptor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>lactic acid</td>
<td>glyceric acid</td>
</tr>
<tr>
<td>1</td>
<td>levulinic acid</td>
<td>87</td>
<td>88</td>
<td>86</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>benzene</td>
<td>79</td>
<td>97</td>
<td>77</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Reaction conditions: aqueous glycerol solution: 10 mmol (0.5 M, 20 mL); H₂ acceptor: 10 mmol; catalyst: 0.1 g; NaOH: 15 mmol; temperature: 160°C; N₂ pressure: 20 bar. a: 25 mmol NaOH was used in the reaction, due to the extra 10 mmol consumption by levulinic acid. b: 20 mmol cyclohexene was used in the reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-hydroxy pentanoic acid</td>
<td>γ-valerolactone</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>cyclohexane (the maximum theoretical yield of cyclohexane is 33.3%).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>azoxybenzene; P2: azobenzene; P3: aniline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>decane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>cyclohexane (the maximum theoretical yield of cyclohexane is 50%).</td>
<td></td>
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</tr>
</tbody>
</table>

Conclusions

Bimetallic Ni-Co catalysts supported on CeO₂ were prepared and tested for the transfer hydrogenation from glycerol to various unsaturated compounds, in which lactic acid and the corresponding hydrogenated products were obtained in a one-pot batch reaction. Introducing Co into the formulation of the Ni-based catalysts was crucial to prevent the aggregation of Ni into large particles. This was proven by the higher activity of the bimetallic 10NiCo/CeO₂ catalyst compared to the Ni- or Co-based counterparts, and by characterisation of the catalytic materials by EDX-mapping and H₂-TPR, which demonstrated the high dispersion of Ni-Co sites on the CeO₂ support. The bimetallic 10NiCo/CeO₂ catalyst exhibited very high activity (91% glycerol conversion) and selectivity to lactic acid (94%) at 160 °C, 4.5 h under N₂ atmosphere in the presence of NaOH as promoter. This result demonstrates that excellent conversion and selectivity can be achieved with a catalyst with a relatively low loading of Ni and Co and that operates at milder reaction conditions compared to other non-noble metal catalysts for glycerol dehydrogenation reactions. Moreover, various H₂ acceptors (levulinic acid, benzene, nitrobenzene, 1-decene, cyclohexene) were tested in the transfer hydrogenation from glycerol, exploiting in-situ the hydrogen liberated in the dehydrogenative oxidation of glycerol to generate several useful products.

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Reference

33. S. De, J. Zhang, R. Luque and N. Yan, Energ Environ Sci, 2016, 9, 3314-3347.