Selective Hydrogenation of Glycolic Acid to Renewable Ethylene Glycol over Supported Ruthenium Catalysts

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The production of industrially demanded polymer precursor ethylene glycol (EG) from biomass-accessible aqueous glycolic acid (GA) was investigated in this study. The systematic investigation of different active metals as well as, for the first time, various support materials revealed Ru/TiO$_2$ and Ru/ZrO$_2$ to be the most active catalysts in the heterogeneously catalyzed reduction of GA with molecular H$_2$. Catalytic activity is enhanced by facilitated reduction of the active Ru species due to metal-support interactions. An assessment of several other catalyst properties (metal surface area, acid properties, porosity) revealed that high metal dispersion is also beneficial. Up to 94% GA conversion and 95% selectivity for EG were obtained under optimized and mild reaction conditions (105 °C, 60 bar H$_2$ pressure, 23 h, Ru/TiO$_2$ as catalyst). This shows that the heterogeneously catalyzed reduction of biomass-derived aqueous GA solutions can be a promising alternative for the renewable production of EG.

Introduction

Glycolic acid (GA) is the smallest α-hydroxy carboxylic acid and best known as a monomer for the production of biodegradable polymers, mainly poly(glycolic acid) and poly(lactic-co-glycolic acid).[1,2] To mitigate the dependence on fossil resources, several biomass-based concepts for a more sustainable production of GA have been reported. In that context, De Clercq et al.[3] as well as Dusselier et al.[4] review processes applying heterogeneous catalysis to obtain GA from biomass. Phosphomolybdic acid catalysts, e.g., can be used to convert biomass into GA with a yield of around 30%.[4] On the other hand, Becker et al.[5] provide an overview of biotechnological approaches for the production of GA, which have reached concentrations up to ca. 5 wt.% (≈ 0.7 mol L$^{-1}$). Moreover, employing a new concept, algae cells have recently been used as photobioreactors that selectively convert CO$_2$ into glycolate and directly excrete it into the surrounding aqueous medium, where it accumulates (so far up to ca. 0.2 wt.%).[6] All biomass-based GA production pathways give access to diluted aqueous solutions of GA with typical concentrations between 0.1 and 5 wt.%. To circumvent water removal and GA purification, which requires intricate and costly procedures typical for biomass-based carboxylic acid production,[7] aqueous GA solutions could be converted directly into other compounds of interest. This was suggested, e.g., by Huo and Shanks[8] as a general strategy.

Based on the availability of diluted GA solutions, the heterogeneously catalyzed hydrogenation of GA over supported metal catalysts was investigated. This reaction was first successfully conducted over Ru-based catalysts by Carnahan et al.[9] several decades ago. The main product was EG, an important bulk chemical for which a sustainable production pathway is highly demanded.[10] More recently, Takeda et al.[11] applied Ru/C (5 wt.% Ru) and modified Ru-MoO$_3$/C catalysts in the aqueous-phase hydrogenation of 5 wt.% (0.7 mol L$^{-1}$) GA solutions. It should be noted that this study was primarily focused on the hydrogenation of lactic acid (LA) into propylene glycol (PG). At 120 °C and 80 bar H$_2$ pressure, 18% GA conversion of 20 g solution over 100 mg Ru/C was obtained after 2 h in combination with 88% selectivity for EG. The Mo-modified catalyst showed increased conversion of 85% and 92% selectivity for EG. Acetic acid (AA) and gaseous compounds were formed as side products, which indicates that AA is accessible by this approach as well, another important chemical compound with several industrial applications. Overall, the amount of data on the catalytic hydrogenation of GA is very limited. In particular, carbon-supported noble metals as well as unsupported RuO$_2$ are the only catalysts investigated so far.

Taking into account available literature on hydrogenation reactions of similar molecules, in particular of LA to PG, there is clear evidence that several monometallic catalysts could be candidates for the aqueous-phase hydrogenation of GA, e.g., Pd[12,13], Pt[14], Ni[15] and Ru[16]. In all comparative studies on LA hydrogenation supported Ru catalysts provided the highest catalytic activity, similar to other examples for this type of hydrogenation reaction.[17,18] In the aqueous-phase hydrogenation of succinic acid Re was also found to be active.[19] One part of this study is therefore an investigation of Ru, Pt, Pd and Re as potentially active metals for the hydrogenation of GA.

Besides the active metal phase, the support material was shown to be a major factor influencing the catalytic behavior in
similar reactions. Considering only Ru-based catalysts for the hydrogenation of LA, several studies dedicated to support effects are available. Studies by Iqbal et al.\textsuperscript{[13]} and Jang et al.\textsuperscript{[14]} on different carbon-supported Ru catalysts show that catalytic activity strongly depends on metal dispersion. In the latter study, a clear correlation was observed between high specific surface area of the support, resulting in high Ru dispersion, and high LA conversion.\textsuperscript{[15]} Furthermore, a morphology of small Ru nanoparticles was found to be preferable to raft-like morphology.\textsuperscript{[16]} In contrast, an earlier study by Zhang et al.\textsuperscript{[17]} indicated that metal dispersion is not a decisive property. Both a commercial and a self-prepared carbon-supported Ru catalyst showed similar activity despite the commercial catalyst having a threefold higher metal dispersion. Moreover, these carbon-based catalysts were 1.5 times as active as Ru/Al\textsubscript{2}O\textsubscript{3}. In this study, Ru/TiO\textsubscript{2} showed hardly any catalytic activity, which is in sharp contrast to other investigations. Primo et al.\textsuperscript{[18]} developed a highly active TiO\textsubscript{2}-supported Ru catalyst with low Ru content (<1 wt.%) that outperformed a commercial Ru/C catalyst (5 wt.% Ru). This was explained by a combination of small Ru particle size of Ru on TiO\textsubscript{2}, which was further proven by a controlled variation of Ru particle size, and a direct role of the support, which is able to adsorb and activate the carboxylic group of LA. Ru/TiO\textsubscript{2} was also among the most active catalyst in a recent study by Liu et al.\textsuperscript{[19]} who investigated Ru on several supports for the aqueous-phase hydrogenation of LA. Based on temperature-programmed reduction (TPR) profiles they suggest that the high activity of Ru/TiO\textsubscript{2} could also be attributed to the high reducibility of Ru on TiO\textsubscript{2}. Moreover, the data in the study of Liu et al.\textsuperscript{[19]} show a strong influence of the support material on the product selectivity of the reaction. In case of Ru/TiO\textsubscript{2}, the crystal phase of the support (anatase/rutile) was also found to have significant influence.\textsuperscript{[20]} Besides the previously discussed catalyst properties, the acidity of the support was found to be an important factor in other aqueous-phase hydrogenation reactions.\textsuperscript{[21]} Overall, it is evident that the choice of support material has significant influence on the catalytic behavior. However, it is often speculative which particular property of a catalyst is responsible.

Therefore, in this study a systematic investigation into the influence of several material properties on the catalytic behavior of supported Ru-based catalysts in the aqueous-phase hydrogenation of GA was conducted. In particular, the role of textural properties, metal dispersion, support acidity and Ru redox behavior were analyzed to contribute to this discussion. Ru on carbon as well as on several oxidic support materials (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2} and zeolite H-Y) was used as catalyst. To the best of our knowledge, this is the first time any support material besides carbon was successfully used for this reaction. Furthermore, a general assessment of the influence of temperature and H\textsubscript{2} pressure is reported.

Results and Discussion

Catalytic activity of different metals supported on activated carbon

Ru, Pt, Pd and Re supported on AC were employed in the hydrogenation of aqueous GA to investigate which metals are suited as catalysts (Figure 1, Table S1). Clearly, the most active metal is Ru showing a metal content-adjusted GA consumption (\(n_{\text{conv},\text{GA}}/n_{\text{metal}}\)) of 22 (corresponding to 21 % GA conversion) after 4 h at 150 °C and 40 bar H\textsubscript{2}. The measure of metal content-adjusted GA consumption was introduced, on the one hand, to take into account differences in the metal loadings of different catalysts and, on the other hand, to adequately compare different metals (see also experimental section). Compared to Ru/AC, metal content-adjusted GA consumption over Re/AC is about 50 % lower and even more than 80 % lower over Pd and Pt. Furthermore, selectivity for EG, which is the main liquid-phase product for all four catalysts, is highest over Ru/AC (73 %) followed by 50 % over Re/AC. Over all catalysts besides Re/AC AA was formed but in low selectivity (<10 %). Besides EG and AA, small amounts of ethanol and methanol (<5 % combined selectivity) could be detected.

It should be noted that with these quantified compounds the liquid-phase components of the reaction mixture the carbon balance could not be closed. Up to 80 % of converted GA could not be identified, which is also the case for the investigation of different support materials below. In that way the results here are comparable to the study of Liu et al.\textsuperscript{[17]} on LA hydrogenation who also could not close the carbon balance at elevated temperatures (>120 °C). Furthermore, Santos et al.\textsuperscript{[22]} recently investigated the hydrogenation of oxalic acid to ethylene glycol over a Ru-based catalyst and found 87 % selectivity for gas-phase compounds at 150 °C. It will be shown below that optimized reaction conditions provide almost closed carbon balances (>95 %). While elemental analysis showed that only up to 3 % of GA was converted into carbon deposits on the catalyst (Table S2), GC of selected gas-phase samples revealed the presence of unquantifiable amounts of methane and ethane, but no presence of CO or CO\textsubscript{2}.

This product distribution is very similar to the findings of Takeda et al.\textsuperscript{[23]} which confirms that EG can be targeted as the main product of GA hydrogenation. It should be noted,
however, that the reaction conditions are not directly comparable. In particular, initial acid concentration is 10 times lower in this study and reaction temperature is 150 °C compared to 120 °C. The finding that Ru is the most efficient metal is also consistent with the study by Carnahan et al.,[19] who obtained 68% EG yield over a Ru-based catalyst at similar reaction temperature (ca. 150 °C) but very high pressure (ca. 680 bar H2). However, they could not identify any EG formed over Pd and Pt, which were found in small yields (< 1%) in this study. In case of the hydrogenation of GA, two studies agree that Ru is the most active metal among supported Ag, Co, Cu, Ni, Pt and Pd.[13,14]

In general, the exceptionally high activity of Ru in aqueous-phase hydrogenation reactions is well documented in literature. Starting from the experimentally confirmed superior activity of Ru in C=O hydrogenation reactions especially in water, Michel and Gallego[18] discuss the role of the aqueous medium. They conclude that H2O itself engages in the hydrogenation mechanism, either through coadsorbed water lowering energy barriers of the hydrogenation reaction or by an increased concentration of adsorbed hydrogen atoms due to H2O dissociation. Either way, the combination of Ru as active hydrogenation metal and water as solvent leads to a facilitated hydrogenation.[19] The results in this study show that the aqueous-phase hydrogenation of GA is yet another example where this is the case.

Based on this finding, Ru was chosen as the active metal for the investigation of support effects.

**Influence of support material on catalytic activity and selectivity**

Ru supported on AC and various oxidic supports (TiO2, ZrO2, SiO2, Al2O3, zeolite H-Y) was investigated regarding the catalytic behavior in the aqueous-phase hydrogenation of GA with H2. In addition to the six catalysts synthesized in this study, a commercial Ru/C catalyst (ABCR, 5 wt.% Ru) was included. Figure 2 shows the metal content-adjusted GA conversion of the catalysts and the corresponding selectivity for EG and AA (data also available in Table S1).

Among the catalysts in Figure 2, both catalytic activity and selectivity differ significantly. Ru content-adjusted GA consumption ranging from ca. 20 (Ru/AC and Ru/H-Y) up to 88 (Ru/ZrO2) and 113 (Ru/TiO2) was obtained. These values correspond to GA conversions of 22% (Ru/AC, Ru/H-Y) up to almost complete conversion of 96% (Ru/TiO2) and 98% (Ru/ZrO2). Previous studies on the analogous aqueous-phase hydrogenation of LA also found Ru/TiO2 to be comparatively active among other supported Ru catalysts,[13,17] however not in every case.[14] Furthermore, comparing the two carbon-based catalysts, it is apparent that the commercial Ru/C catalyst shows threefold higher Ru content-adjusted GA consumption than Ru/AC synthesized in this study.

Comparing the Ru content-adjusted GA consumptions obtained here with the most recent study on GA hydrogenation by Takeda et al.[11] the Ru/TiO2 catalyst reported here, i.e., \( n_{\text{conv. GA}} \left( n_{\text{Ru}} \right)^{-1} = 113 \) after 4 hours, is significantly more active than Takeda’s monometallic Ru/C catalyst (42 after 2 hours). However, the Mo-modified catalyst reported in the same study has even higher catalytic activity (190 after 2 hours).

Another interesting finding is the influence of the support material on the product selectivity. For most catalysts, EG is the main product in the liquid phase with selectivity for EG up to 73% over Ru/AC followed by ca. 40% over Ru/C and Ru/SiO2. On the other hand, Ru/ZrO2 and Ru/Al2O3 clearly show a tendency towards AA formation with AA being the main liquid-phase product at selectivity up to 30%.

Interestingly, selectivity for the main side product AA found in the hydrogenation of GA here is in general much higher than typical values of selectivity for propionic acid in the aqueous-phase LA hydrogenation to PG.[11,14,16–18,21,26,27] Only at significantly higher temperatures (200–350 °C) significant amounts of propionic acid were obtained in vapor-phase processes.[12,28] This indicates that reduction of the α-hydroxyl group may be favored for primary alcohols.

It should be noted that there was no indication for the most commonly observed types of catalyst deactivation, i.e. catalyst degradation and fouling.[29] Elemental (CHN) analysis (Figure 52) showed negligible deposition of carbon-containing deposits on Ru/TiO2 and Ru/Al2O3. Moreover, less than 1 mol-% of Ru was leached from the catalysts during the reaction (Ru/C comm., Ru/TiO2 and Ru/Al2O3 were investigated).

Combining the information on both catalytic activity and selectivity obtained for the series of supported Ru-based catalysts, it can be concluded that the differences in product selectivity do not directly correlate to changes in activity. Furthermore, there is no straightforward correlation between metal content-adjusted GA consumption and selectivity (Figure S1 and Figure S2). Therefore, the support material must play a crucial role in determining the catalytic selectivity.

To understand which properties of the supported Ru catalysts govern their catalytic behavior several key properties will be assessed regarding their respective influence on the catalytic activity and selectivity reported above. An overview of all characterization data is provided in Table 1.

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**Figure 2.** Ru content-adjusted GA consumption \( (n_{\text{conv. GA}}) \left( n_{\text{Ru}} \right)^{-1} \) of Ru on different support materials (left) and the corresponding selectivity for the products EG and AA (right). Reaction conditions: \( m_{\text{cat}} = 150 \text{ mg}, V = 80 \text{ mL}, c_{\text{GA}} = 0.07 \text{ mol L}^{-1}, t = 4 \text{ h}, T = 150 ^\circ \text{C}, p_{\text{H2}} = 40 \text{ bar.} \)
Metal dispersion

Firstly, the role of metal dispersion, which is often considered a highly important parameter, is investigated. In Figure 3 both specific surface area and specific active metal surface area are displayed. No correlation between these two properties for this specific surface area and specific active metal surface area are highly important parameter, is investigated. In Figure 3 both metal dispersions for similar supported Ru catalysts also from other studies as well.

Despite the calculated Ru crystallite sizes being significantly higher (Table 1), XRD patterns reveal no signs of large Ru crystallites > 5 nm or other Ru-containing phases (Figure S4). This discrepancy was resolved by TEM. A representative TEM image of Ru/AC (Figure S5) shows smaller nanoparticles (ca. 4–5 nm) forming larger agglomerates (ca. 30 nm), which are more in the range of the calculated particle size from chemisorption (77 nm). This is a reasonable explanation for the absence of XRD reflexes of Ru-phases despite low metal dispersion. In case of commercial Ru/C, the TEM images confirm the high dispersion of Ru on the support (Figure S6).

Even though it is possible to use the dispersion data to calculate turnover frequencies (TOF) for the Ru-based catalysts (Table S1, Figure S7) it appeared not reliable enough to base the evaluation of catalytic activity on TOF due to the estimated high uncertainty (probably > 20%) of the obtained specific active metal surface areas as a result of the very low absolute values and the extrapolation method that was used to determine them. However, the TOF values obtained were significantly higher (ca. 1000 h⁻¹ for Ru/TiO₂ and Ru/SiO₂; ca. 2000 h⁻¹ for Ru/ZrO₂) than those reported by Takeda et al.[11] (up to 95 h⁻¹), who observed Ru dispersion > 50%. On the other hand, Ru/TiO₂ showed slightly higher activity taking into account only Ru content but not dispersion, as discussed in the previous section.

In Figure 4, the Ru content-adjusted GA consumptions are plotted against the specific active metal surface area. Comparing first only the two carbon-based catalysts, the threefold

### Table 1. Characterization data of Ru supported on different support materials.

| Catalyst | Ru content[a] [wt.%] | Spec. surface area[b] [m² g⁻¹] | Spec. pore volume[c] [cm³ g⁻¹] | Average pore width[d] [nm] | Spec. active metal surface area[e] [m² g⁻¹] | Ru metal dispersion[f] [%] | Ru crystal size[g] [nm] | Main Ru reduction peak[h] [°C] | Acid site density[i] [μmol g⁻¹] |
|----------|----------------------|---------------------------|-------------------------------|-------------------|--------------------------------|-------------------|------------------|---------------------|-----------------------------|
| Ru/AC    | 3.8                  | 563                       | 0.75                          | 5                 | 0.2                           | 1.8               | 77               | 218                 | n.d.[i]                  |
| Ru/C     | 4.6                  | 824                       | 0.74                          | 4                 | 5.3                           | 32                | 4                | 192                 | n.d.[i]                  |
| Ru/TiO₂  | 3.2                  | 49                        | 0.33                          | 27                | 0.4                           | 3.3               | 40               | 150                 | 15                        |
| Ru/ZrO₂  | 4.2                  | 100                       | 0.27                          | 11                | 0.3                           | 1.8               | 73               | 144                 | 80                        |
| Ru/SiO₂  | 4.8                  | 390                       | 0.83                          | 9                 | 0.3                           | 1.5               | 89               | 164                 | 8                          |
| Ru/AC    | 3.8                  | 196                       | 0.54                          | 11                | 0.3                           | 2.5               | 54               | 180                 | 22                        |
| Ru/H-Y   | 3.4                  | 505                       | 0.29                          | 2                 | 0.4                           | 3.2               | 42               | 189                 | 1190                      |

*From [a] ICP-OES elemental analysis, [b] N₂ sorption, [c] H₂ chemisorption, [d] TPR-H₂, [e] TPD-N₂, [f] n.d. – not determined.*
higher activity of commercial Ru/C is probably caused mainly by differences in metal dispersion. This is supported by previous findings for carbon-supported Ru catalysts\cite{14,16} but other factors like Ru particle morphology or differences in the carbon support material may also play a role.

Among the catalysts with comparable Ru dispersion on different supports prepared in this study, Ru/\textit{ZrO}_\textit{2} stands out as the most active catalyst followed by Ru/TiO\textit{2}. The lack of correlation between Ru dispersion and Ru content-adjusted GA consumption for the catalysts prepared in this study (which show a comparable Ru dispersion below 5\%) prove that other catalyst properties also affect the catalytic behavior. While no \textit{ZrO}_\textit{2}-supported Ru catalysts are reported for the analogous aqueous-phase hydrogenation of LA, Ru/TiO\textit{2} is reported to show exceptionally high activity, which was either explained by the redox behavior of the catalyst\cite{15} or by direct interactions of the support material with the adsorbed acid, which might activate the C=O functionality.\cite{17,18}

While the results for the two carbon-supported catalysts indicate that Ru dispersion is an important criterion for high catalytic activity, other catalyst properties must be highly, in some cases even more, influential. In addition to that, there is no indication that the observed differences in product selectivity are governed by Ru dispersion (Figure S8).

### Porosity and textural properties

One of the major differences between the different support materials studied is their textural properties. As already discussed above, supports providing a high specific surface area do not show higher metal dispersion.

There is also no significant correlation between specific surface area and selectivity (Figure S9) or activity (Figure 5, left) for all catalysts. However, when excluding the commercial catalyst due to its high Ru dispersion, GA consumption appears to be inversely dependent on the specific surface area (all relevant correlation parameters of linear fitting listed in Table S4). This finding contradicts an earlier study on LA hydrogenation\cite{20} and there is no obvious underlying scientific explanation for this finding. Thus, it is suggested that this correlation may be coincidental.

In addition, a similar assessment of the effect of average pore width on the catalytic activity was conducted (Figure 5, right), which indicates that GA consumption is inversely correlated to pore width. This could be an indication of internal mass transfer limitations. To investigate this, the influence of catalyst grain size on catalytic activity was studied exemplarily for Ru/SiO\textit{2}. GA conversion was not significantly different for the previously discussed powder catalyst (80\%) and two different larger grain sizes (50–100 \(\mu\)m: 81\%; 200–300 \(\mu\)m: 91\%). Thus, limitations by internal mass transfer were not confirmed. Moreover, no significant correlation between selectivity for EG and average pore width was found (Figure S9).

In addition, no correlation between pore volume and both catalytic activity and selectivity was apparent (Figure S11). Overall, this indicates that the textural properties and the porosity of the support material are only of indirect or subordinate influence. However, this does not serve as proof that mass transfer limitations are completely negligible, especially for microporous materials. However, a thorough investigation of this particular aspect is beyond the scope of this study.

### Acid properties

Among the support materials included in this study, especially the proton-form zeolite is renowned for its pronounced acid properties. TPD-NH\textsubscript{3} confirms that the zeolite H-Y-based catalyst has by far the highest acid site density (ca. 1190 \textit{μmol g}\textsuperscript{-1}) of the catalysts investigated but at the same time shows comparatively low metal content-adjusted GA consumption of 30. The behavior of the catalysts based on oxidic supports does not indicate a correlation between acid site density and neither Ru content-adjusted GA consumption nor selectivity for EG (Figure 6).

For other aqueous-phase hydrogenation reactions, bifunctional catalysts with pronounced acid properties are beneficial,\cite{21,22} however in these cases other acid-catalyzed reaction steps besides metal-catalyzed hydrogenation or hydro- genolysis occur. For the hydrogenation of GA, such undesired acid-catalyzed reaction pathways could result in the formation of esters or ethers from condensation reactions, possibly even oligomer formation, which might also contribute to the gap in

![Figure 5](image5.png) Ru content-adjusted consumption of GA (\(n_{\text{conv, GA}}\) to \(n_{\text{RU}}\))\textsuperscript{-1} during the aqueous-phase hydrogenation of GA plotted against specific surface area (left) and average pore width (right) of the corresponding supported Ru catalysts. Reaction conditions: \(m_{\text{cat}}=150\) mg, \(V=80\) mL, \(c_{\text{GA}}=0.07\) mol L\textsuperscript{-1}, \(t=4\) h, \(T=150^\circ\text{C}, p_{\text{H}}=40\) bar.

![Figure 6](image6.png) Ru content-adjusted GA consumption (\(n_{\text{conv, GA}}\) to \(n_{\text{RU}}\))\textsuperscript{-1} (left) and selectivity for EG (right) plotted against the acid site density of supported Ru catalysts. Reaction conditions: \(m_{\text{cat}}=150\) mg, \(V=80\) mL, \(c_{\text{GA}}=0.07\) mol L\textsuperscript{-1}, \(t=4\) h, \(T=150^\circ\text{C}, p_{\text{H}}=40\) bar.
the carbon balance described above. However, only up to 3% of GA was found to be converted into carbon deposits on the catalyst during the reaction as elemental analysis showed for Ru/TiO$_2$ and Ru/Al$_2$O$_3$ (Table S2). A study by Chen et al.$^{[33]}$ of supported Ru catalysts in the aqueous-phase hydrogenation of propionic acid found that Lewis acidic catalysts favor the C=O hydrogenation compared to decarbonylation of propionic acid. That would in case of the hydrogenation of GA result in C1 products, which were detected only in marginal amounts. While the role of support acidity remains ambiguous and several effects appear plausible, acid site density in general does not appear to influence the catalytic behavior of the aqueous-phase hydrogenation of GA in a significant manner.

Redox behavior

The redox properties of Ru species on several supports was investigated by TPR with H$_2$. The resulting profiles in Figure 7 (left) show that the reduction of the precursor Ru$^{3+}$ to Ru is clearly influenced by the support. On TiO$_2$ and ZrO$_2$ the peaks of maximum H$_2$ consumption correspond to temperatures < 150 °C while the carbon-supported catalysts show the highest main reduction peaks at around 200 °C. The trend among the oxidic materials matches other studies investigating the redox behavior of Ru on different support materials.$^{[17,30]}$ While it is known that dispersion is one factor that can influence the reduction temperature of supported metal catalysts,$^{[30,33]}$ it is apparent that on the other hand the nature of support itself must play a role given the comparable metal dispersion of most catalysts.

Based on that, the Ru content-adjusted GA consumption was plotted against the temperature at which maximum H$_2$ consumption is observed (Figure 7, right). There appears to be an almost linear correlation linking low Ru reduction temperature to catalytic activity (correlation coefficients in Table S4). Therefore, it can be concluded that it is beneficial to use a support that promotes the redox properties of Ru, which is indicated by a lower reduction temperature in TPR. The observed effect on catalytic activity may be caused by a promotion of Ru reduction but it is also possible that the reduced species is stabilized under reaction conditions.

An influence on the catalytic selectivity is not apparent (Figure S12). A correlation between redox properties of supported Ru catalysts and catalytic activity in aqueous-phase hydrogenation reactions was already suspected in previous publications on similar reaction systems,$^{[17,27]}$ however with smaller ranges of support materials. The effect is probably caused by strong metal-support interactions. Another reasonable explanations for the promoting effect on Ru reduction observed on TiO$_2$ and ZrO$_2$ could also be H$_2$ spillover.$^{[30,33]}

The results show that the support material strongly influences activity and selectivity of the heterogeneously catalyzed hydrogenation of GA in aqueous phase. Independent of the support material, it is suggested that high metal dispersion is beneficial for high catalytic activity. Taking into account the nature of the support, Ru/TiO$_2$ and Ru/ZrO$_2$ are highly active. This is mainly due to more facile reduction of Ru on these supports, which is probably caused by strong metal-support interactions. On the other hand, carbon-supported catalysts show higher selectivity for EG compared to Ru/ZrO$_2$ and Ru/Al$_2$O$_3$, which favor the formation of AA.

Influence of reaction conditions on catalytic behavior

Besides taking a close look at support effects, one major goal of this study was to investigate whether hydrogenation of GA to EG is feasible at both high conversion and high product selectivity, i.e. in high yields. Therefore, to study the influence of reaction conditions, i.e., H$_2$ pressure and temperature, two catalysts were used that showed both high activity but different selectivity towards EG (commercial Ru/C) and AA (Ru/ZrO$_2$).

The influence of reaction temperature on the catalytic behavior of commercial Ru/C and Ru/ZrO$_2$ is displayed in Figure 8 (data also in Table S3), two catalysts showing significantly different product selectivity. From here on “conventional” GA conversion will be used to compare catalytic activity since the focus is no longer on the comparison of different materials. As can be expected, regardless of the catalyst, conversion of GA is greatly enhanced at higher temperatures. With increasing temperature from 120 °C to 180 °C, GA conversion is increased by a factor of 16 (Ru/C) and 14 (Ru/ZrO$_2$), respectively. At the
same time, product selectivity is strongly affected. On the one hand, the combined selectivity for the main products in the liquid phase, i.e., EG and AA, is decreasing with increasing temperature from ca. 70% at 120 °C to ca. 20% at 180 °C, similar to observations by Santos et al.[21]

On the other hand, selectivity towards EG compared to AA also decreases with increasing temperature regardless of the catalyst. Over commercial Ru/C, selectivity for EG decreases from 62% at 120 °C to 6% at 180 °C while selectivity for AA increases from 6% to 15%. Results for Ru/ZrO₂, which always favors the formation of AA over EG, show that higher temperatures are also detrimental to AA selectivity. A factor to consider is that while the formation of the diol requires two equivalents of H₂, hydrogenolysis to the corresponding aliphatic carboxylic acid requires only one H₂ equivalent. Therefore, decreased H₂ solubility with increasing temperature may contribute to lower EG selectivity.

In agreement with previous investigations on the aqueous-phase hydrogenation of LA,[14,17,18] there is also a clear trade-off here in terms of reaction temperature between high conversion of GA and high selectivity for EG, which is independent of the catalyst used. On the other hand, the selective production of AA is more challenging since it appears to be limited at low temperatures by high selectivity for EG and at high temperatures by other unwanted side reactions.

Furthermore, the catalytic behavior of Ru/C and Ru/ZrO₂ was investigated at different H₂ pressures from 10 bar to 80 bar (Figure 9, Table S3). Even though there appears to be a slight increase in GA conversion with higher pressure, the differences are within the range of experimental uncertainty. Significant differences, however, can be observed regarding product selectivity. Increasing pressure from 10 bar to 40 bar results in an increase in both combined selectivity for EG and AA (from 28% to 61%) and in particular in selectivity for EG (from 16% to 49%). Further increase in pressure to 80 bar does not have significant influence anymore in case of Ru/C. Looking at Ru/ZrO₂, there is a similar shift in product ratio between EG and AA. While at 80 bar similar amounts of AA and EG are formed, the ratio is 7:1 at 10 bar. These findings support the previously discussed possible influence of H₂ solubility, which may also play a role when changing the reaction temperature.

In general, the trends observed match previous studies on LA hydrogenation.[14,17,18] High H₂ pressure is required to obtain high selectivity for the diol. A beneficial effect of higher pressure also on the conversion, which is not significant here, was reported in one of the earlier studies.[14]

An additional set of experiments was performed to maximize the yield of EG to assess the technical viability of the production of EG from renewable GA. To improve EG yields, two approaches were pursued. First, the catalyst showing the highest selectivity for EG was chosen (Ru/AC) and the reaction time was prolonged (>20 h) to obtain higher GA conversion. Second, more active catalysts that showed lower selectivity for EG but still favor EG over AA formation (commercial Ru/C and Ru/TiO₂) were used at a lower reaction temperature (105 °C). For both approaches H₂ pressure was elevated to 60 bar.

It is apparent from Figure 10 that applying either strategy EG yield is increased to at least 75%, which is considerably higher compared to all results discussed previously. In case of Ru/AC, increasing the reaction time to 24 h at 150 °C expectedly leads to high GA conversion (85%). At the same time, selectivity for EG does not drop but is even higher (89%) compared to the short-term experiment (73% after 4 h at 22% conversion), probably due to the increase in H₂ pressure to 60 bar. This corresponds to an EG yield of 75%.

Conducting the hydrogenation of GA over commercial Ru/C or Ru/TiO₂ at the comparatively mild temperature of 105 °C results in even higher yield. Over both catalysts at optimized reaction conditions, EG yield reaches 90% as a combination of 95% GA conversion and 94% selectivity for EG. This shows that almost quantitative conversion of GA to EG is feasible, however at the cost of long reaction times. In agreement with the results shown above, Ru/TiO₂ is slightly more active than commercial Ru/C since less catalyst was required (150 mg compared to 200 mg) and reaction time was slightly shorter (23 h compared to 25 h).

An additional positive side effect of these results is that the carbon mass balance could almost completely be closed (> 95% for Ru/C and Ru/TiO₂). This is similar to results reported by Liu et al.,[17] who only after adjusting the reaction conditions

**Figure 9.** GA conversion and selectivity for EG and AA over commercial Ru/C (left) and Ru/ZrO₂ (right) at three different values of H₂ pressure. Reaction conditions: mₜₐₐₐ = 150 mg, V = 80 mL, c₀₁₈ = 0.07 mol L⁻¹, t = 1 h, T = 150 °C.

**Figure 10.** GA conversion and selectivity for EG, AA and ethanol over different catalysts at reaction conditions adjusted to each catalyst for obtaining high yields of EG. Reaction conditions: Ru/AC: mₜₐₐₐ = 200 mg, V = 80 mL, c₀₁₈ = 0.07 mol L⁻¹, t = 24 h, T = 150 °C, p₀₉₈ = 60 bar; Ru/C comm.: mₜₐₐₐ = 200 mg, V = 80 mL, c₀₁₈ = 0.07 mol L⁻¹, t = 25 h, T = 105 °C, p₀₉₈ = 60 bar; Ru/TiO₂: mₜₐₐₐ = 150 mg, V = 80 mL, c₀₁₈ = 0.07 mol L⁻¹, t = 23 h, T = 105 °C, p₀₉₈ = 60 bar.
were able to close the gap between conversion and quantified product yields for the analogous hydrogenation of LA. This was in parts due to the formation of volatile side products via hydrogenolysis and further hydrogenation analogous to the results presented here for GA.

**Reaction scheme**

Based on the obtained products and the observed influence of the reaction conditions a reaction scheme is proposed (Scheme 1). Both EG and AA are direct hydrogenation products of GA from competing reductions of either the carboxylic or the hydroxyl group and were previously identified in this reaction.[11] The results above showed that temperature, pressure as well as the properties of the catalyst influence the product ratio of EG and AA.

Ethanol could be formed from either EG or AA by overhydrogenation, which matches the time-resolved conversion and selectivity data, where ethanol was only observed at reaction times $> 2$ h when the selectivities for AA and EG in particular are decreasing (Figures S2 and S3). Even further reduction will eventually lead to light alkanes. Furthermore, it is known, e. g. from the hydrolysis of glycerol, that Ru-based catalysts can catalyze C–C cleavages of polyols under similar reaction conditions.[34] In the case of EG this results in methanol formation, which was observed in small yields ($< 2\%$), e. g. over the highly active commercial catalyst Ru/C.

In terms of gas-phase products, which are increasingly formed with increasing temperature and long reaction times, only methane and ethane could be qualitatively observed. No CO or CO$_2$ formation could be detected; therefore, decarboxylation and decarbonylation were not included in Scheme 1.

**Conclusions**

A variety of supported metal catalysts comprising different metals as well as, for the first time, different support materials was investigated for the aqueous-phase hydrogenation of GA. Ru-based catalysts are at least twice as active in the heterogeneously catalyzed reduction of GA as catalysts containing Re, Pt or Pd as active metal phase, which is a common finding for similar reactions. Furthermore, the catalytic properties of Ru catalysts can be strongly influenced by the choice of support material. Catalytic activity was found to be highest over Ru on TiO$_2$ and ZrO$_2$, which can be explained by altered redox properties as there exists a clear correlation between the low reduction temperature of the Ru species and high catalytic activity. Strong metal-support interactions are suggested to play a role in facilitating Ru reduction and possibly in stabilizing its reduced state. So far, previous studies on similar reactions could not identify the outstanding role redox properties play in governing the hydrogenation activity over supported metal that was shown here. Furthermore, high Ru dispersion is an additional catalyst property that is commonly expected to generally benefit catalyst activity but this effects was only apparent here in case of carbon-supported Ru catalysts. For oxidic catalyst supports, in particular the redox properties of the support outweighed the effect of dispersion. On the other hand, porosity and acid properties of the catalyst appear to be hardly relevant. The catalyst support also influences the selectivity of the reaction. While over Ru/ZrO$_2$ and Ru/Al$_2$O$_3$ AA is formed in larger amounts than EG, most Ru-based catalysts convert GA into EG as the main product in the liquid phase with selectivity up to 70\% at 150\°C.

Selectivity for EG can be improved, regardless of the catalyst, by ensuring high H$_2$ pressure ($> 40$ bar) and by decreasing the reaction temperature ($< 120\degree$C). Under adjusted reaction conditions (105\°C, 60 bar H$_2$ pressure, 23 h, Ru/TiO$_2$ as catalyst) nearly complete conversion (94\%) of GA into EG (selectivity 95\%) can be obtained. This proves that the heterogeneously catalyzed reduction of GA has the potential to selectively provide EG from renewable GA. However, further research into more active catalysts appears to be necessary to improve the efficiency of the process and reduce the long reaction times.

**Experimental Section**

**Catalyst preparation**

The following materials were used as catalyst supports: activated carbon (AC) (Sigma-Aldrich, type Darco, from lignite, granular), SiO$_2$ gel (Sigma-Aldrich, Davisol grade 635, 60–100 mesh, > 99\%), Al$_2$O$_3$ (Alfa Aesar, γ-phase, high surface area, 1/8” pellets), TiO$_2$ (Alrich, P25, nanopowder, 21 nm, > 99.5\%), ZrO$_2$ (Alfa Aesar, monoclinic phase, 1/8” pellets) and zeolite H-Y (CBV-400, Zeolyst Int.). Besides TiO$_2$, which was already available in powder form, all materials were milled and sieved to obtain particles < 100 μm. Incipient wetness impregnation was conducted by dissolving the amount of RuCl$_3$·H$_2$O (ABCR, 99.9\%) corresponding to a Ru content of 5 wt.\% in an appropriate amount of H$_2$O (previously determined by wetting experiments) and adding the solution to the support powder under continuous mixing. As an example, for Ru/AC, 254 mg Ru precursor in 1.2 mL H$_2$O were used. Afterwards, the impregnated materials were dried at 100 \°C for 20 h. In case of TiO$_2$ and ZrO$_2$, the impregnation required two consecutive steps due to the low pore volume of these supports.

A series of ca. 5 wt.\% of each Pt, Pd and Re on AC was prepared by the same incipient wetness impregnation procedure using the following precursors: H$_2$PtCl$_6$·6H$_2$O (Sigma-Aldrich, 37.5 wt.\% Pt), PdCl$_2$ (Alfa Aesar, 99.9\%) and ReCl$_3$ (ABCR, 99.8\%).

Prior to catalytic experiments the Ru-based catalysts and Pd/AC were reduced for 2 h in a tubular furnace at 250\°C in a flow of H$_2$
The catalytic hydrogenation of GA in aqueous phase was conducted in a batch setup using a 250 mL steel autoclave (Berghof BR-200) with a 200 mL Teflon liner. This reactor was equipped with a magnetic stirrer, a heater and a dip tube for liquid-phase sampling and was connected to N2 and H2 gas supply.

All catalytic experiments were conducted as follows: 150 mg of prereduced (see preparation section for conditions) catalyst and 80 mL of 0.07 mol L⁻¹ (0.5 wt.%); aqueous GA solution (solid GA: Alfa Aesar, 98%) were filled into the reactor. The concentration was chosen in the range of biomass-derived GA solutions from emerging technologies rather than from the most advanced approaches (up to 5 wt.%; 0.7 mol L⁻¹). After loading the reactor, it was closed, purged with N2 and heated up to the desired reaction temperature. To start the hydrogenation reaction, H2 pressure was added to the autoclave. Typically, after 4 h the reactor was rapidly cooled down in a water bath and the product mixture was collected and filtered for GC and HPLC analysis. During most experiments, additional liquid-phase samples were taken at regular intervals via the dip tube. After each sampling, H2 was supplied to keep the pressure constant.

GC analysis of liquid samples was conducted using a Shimadzu GC-2010 equipped with a CP-Sil 8 CB column and a flame ionization detector. EG, ethanol and methanol could be detected by GC. HPLC was applied to detect GA and AA using a Shimadzu Prominence HPLC (LC-20A) with a photodiode array detector (SPD-M50 A, wavelength 210 nm) and a Macherey-Nagel Nucleodur PolarTec column. Aqueous H2SO4 (5 mmol L⁻¹) was used as mobile phase. Concentrations of each compound were derived from GC and HPLC based on respective external calibrations.

As a measure of catalytic activity, the metal-adjusted GA consumption was calculated as follows: \( (\text{n}_{\text{GA, conv.}} \div \text{n}_{\text{metal}}) \), i.e., the molar amount of substance of converted GA per molar amount of substance of metal in the catalyst determined by ICP-OES. This way differences in metal loading are normalized, different atomic weights are considered and better comparability to literature values is possible. For example, 96% conversion of GA (80 mL of 0.07 mol L⁻¹ aqueous solution) was obtained after 4 h over 150 mg of Ru/TiO2, which has a Ru content of 3.2 wt.%. Based on that the GA conversion adjusted to metal content was calculated as follows: 
\( (\text{n}_{\text{GA, conv.}} \div \text{n}_{\text{metal}}) = (0.96 \times 5.60 \text{ mmol}) \div (0.0475 \text{ mmol}) = 113 \text{ (mol mol}^{-1}) \).

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Conflict of Interest

The authors declare no conflict of interest.

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