On the effect of Alkaline Earth Metal Cations in the Hydrogenolysis of Glycerol over Pt/C – an Experimental and Theoretical Study

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Glycerol can be converted to propylene glycol via metal and base catalyzed hydrogenolysis. The nature of the base has a profound influence on the outcome of the reaction. We have tested a range of alkaline (LiOH, NaOH and CsOH) and alkaline earth (Mg(OH)2, Ca(OH)2, Sr(OH)2 and Ba(OH)2) metal hydroxides in combination with Pt/C. The data reveal that alkaline earth metal hydroxides exhibit a much higher activity and improved selectivity. DFT calculations confirm that the coordination of reactive intermediates to divalent cations is responsible for the observed behavior. In the study, the effect of the cation on hydrogenolysis was elucidated for the first time.

Introduction

Glycerol (GLY), a bio-based polyol and the major side product of biodiesel production, can be converted to several value added chemicals such as propylene glycol (PG),[2–7] 1,3-propanediol,[8–10] n-propanol[11] and propyl acetate.[12] In particular, PG finds wide application in cosmetics, as monomer, anti-freeze and food additive. Apart from a few exceptions, mainly heterogeneous catalysts are used for the hydrogenolysis of GLY to PG.[10–13] The employed catalysts are typically based on the noble metals Ru/Re,[14] Pd[15–16] and Pt[17–18] or the non-noble metals Ni[19–20] and Cu.[21] Next to the metal catalyst, a basic or acidic co-catalyst is added to enable the reaction. Additionally, efforts were made to produce bifunctional catalysts combining both metal and acid or base functionality, for example hydro-talcite precursor supported Pt catalyst have been developed.[22] Depending on the nature of the used co-catalyst, two distinct reaction mechanisms have been postulated. Under acidic conditions, the reaction is considered to proceed via a dehydration-hydrogenation mechanism, with acetal as the main intermediate.[23–26] Under basic conditions, a dehydrogenation-dehydrogenation-hydrogenation mechanism is proposed. The mechanism is based on studies carried out by Montassier et al. in the early 1990s using Ru catalysts.[25–26] The group suggested that GLY is dehydrogenated to glyceraldehyde (GLA), dehydrated and isomerized to form propylene glycol (PA). From here on, two reaction pathways are possible: either a benzilic acid rearrangement (i.e. a hydride shift) to the by-product lactate (LA)− or a metal-catalyzed hydrogenation to PG (Scheme 1). Additionally, side-products can be formed via the base-catalyzed retro-aldol reaction. Products are ethylene glycol (EG) and formaldehyde, which in water reacts to methane diol and can be dehydrogenated to CO2 and H2 over Ru, Pt or Au catalysts under mild conditions.[27–29] The influence of base has been studied extensively. Sautet et al. showed in a combined experimental and theoretical study that, under basic conditions, dehydrogenation is preferred over dehydration on a Rh surface.[30] Maris et al. found that the addition of base enhances the rate of the reaction when a Pt/C catalyst is applied.[31] For high amounts of base, an increased selectivity to LA was found. A study by Ukitu and Miyadera on the dehydrogenation of 2-propanol over noble metal catalysts showed that bases also assist the dehydrogenation reaction.[32] The groups of Feng and Marinoiu additionally observed varying reaction rates for differ-

Scheme 1. Hydrogenolysis of GLY to PG and LA− catalyzed by metal catalyst and base.
ent bases (LiOH, NaOH, KOH and CaO). They suggested that the base speeds up the dehydrogenation of GLY so that more GLA is formed. Additionally, they suspected that the activity differences can be associated with the size of the used metal cations. In a subsequent study, Feng et al. investigated the hydrogenolysis of GLY over Pt/C in combination with alkaline metal bases. They found the best selectivity and activity for LiOH. To explain this observation, they developed the chelation-hydrogenolysis-mechanism (based on the dehydrogenation-dehydration-hydrogenation mechanism). Here the cation is involved in the dehydrogenation of GLY by stabilizing the formed alkoxide. Also in our previous study on the hydrogenation of LA to PG over Cu/SiO₂, a facilitating effect of the Mg²⁺ cation could be shown. Although many studies address the influence of base in hydrogenolysis reactions, the molecular mechanism and role of chelation to the cation is still not fully understood. So far only a small selection of bases was tested and a comprehensive study is missing. Also, most of the proposed mechanisms are primarily based on experimental data, so that a kinetic and theoretical study is of high interest. Here, we present an experimental study with kinetic investigations that is complemented by DFT calculations which focuses largely on the base-catalyzed reaction occurring in the liquid phase.

**Results and Discussion**

**Catalyst characterization and base screening**

A series of alkaline (LiOH, NaOH, CsOH) and alkaline earth (Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂) metal hydroxides was tested in the aqueous hydrogenolysis of GLY using a commercial 5 wt% Pt/C catalyst. Pt was chosen as it typically exhibits good stability and is the most selective among noble metals. The catalyst was fully characterized using N₂-physisorption, ICP-OES, XPS, H₂-chemisorption, XRD, TEM and EDX. The obtained results are shown in the ESI (Figures S1–S5 and Table S1).

H₂-chemisorption, XRD and TEM confirm a narrow particle size distribution with an average size of the Pt-particles between 2.6 and 3.2 nm. N₂-physisorption confirms a high specific surface area of the catalyst of 1485 m²/g. Reactions were carried out at 170 °C and 80 bar H₂, the amount of OH⁻ was kept constant for all reactions. The results of the base screening are shown in Table 1, selectivity is calculated carbon-based (see eq. S2–S4 in the ESI). A high pH value of ≥13 was found for all bases except for the poorly soluble Mg(OH)₂. PG and LA are the main products and EG was obtained as minor side product with a maximum selectivity of 9%. Glycolic acid was observed only in traces and the analysis of the gas phase revealed no gaseous products such as CO, CO₂ or CH₄ (exemplarily a GC diagram of the gas phase after 4 h of reaction with Sr(OH)₂ is shown in Figure S6 in the ESI). Via acidification of the reaction solution, any formed carbones were decomposed to gaseous CO₂ and quantified by the evolved gas volume (see Eq. S5 and S6 in the ESI). Due to the combination of different analytical methods, the carbon balance may not be closed or may even exceed 100%. All alkaline metal bases show a comparable hydrogenolysis activity. With decreasing pKₐ the selectivity to PG increases at the expense of LA to a value of 51% for CsOH.

| Base         | pKₐ  | t [h] | X [%] | S [%] | PG | LA | EG | CO₂ |
|--------------|------|------|------|------|----|----|----|-----|
| LiOH         | 0.18 | 3    | 47   | 38   | 61 | 2  | 1  |     |
| NaOH         | −0.56| 4    | 39   | 47   | 51 | 2  | 7  |     |
| CsOH         | −1.76| 4    | 53   | 51   | 45 | 3  | 3  |     |
| Mg(OH)₂      | 1.80 | 16.75| 4   | 39   | 0  | 0  | n.d. |     |
| Ca(OH)₂      | 1.37 | 3    | 51   | 53   | 36 | 12 |     |     |
| Sr(OH)₂      | 0.30 | 0.5  | 65   | 63   | 24 | 4  | 7  |     |
| Ba(OH)₂      | 0.15 | 1    | 54   | 71   | 20 | 4  | 4² |     |

[a] after 4 h, [b] after 1 h.

For alkaline earth metal bases the pKₐ values are in general higher than for alkaline metal bases, but also here the selectivity to PG improves significantly with decreasing pKₐ to 71% for Ba(OH)₂. For all bases CO₂ is formed as side-product with low to moderate selectivity of up to 12%. Additionally, a significant increase in activity is observed that might additionally result from an increasing solubility. To highlight the striking difference in activity and selectivity between alkaline and alkaline earth metal hydroxides the course of the reaction for CsOH and Ba(OH)₂ is shown in Figure 1. While with CsOH a conversion of 55% is obtained after 4 h, Ba(OH)₂ converts 69% GLY within 1 h. At comparable conversion CsOH reaches a selectivity to PG and LA of 51% and 45%, respectively, while for Ba(OH)₂ an increased selectivity to PG of 65% is obtained at the expense of LA (S = 22%). A comparison of the activity of all screened bases over a reaction time of 4 h is shown in Figure S7 in the ESI. It is also important to note that when Ba²⁺ in the form of Ba(OAc)₂, which by itself is not active (see Figure S8a in the ESI), is added to a reaction with CsOH, conversion and PG selectivity increase drastically (Figure S8b in the ESI). This confirms the important role of alkaline earth metal cations in the catalysis.

![Figure 1. Reaction course of the hydrogenolysis of GLY using Pt/C and CsOH (a) or Ba(OH)₂ (b). Conditions: 170 °C, 80 bar H₂, 2.2 mmol GLY, 0.2 g Pt/C, 8 mmol OH⁻, 20 mL H₂O.](image-url)
To verify whether Ba\(^{2+}\) and OH\(^{-}\) act as catalysts, an additional reaction was carried out using a lower amount of Ba(OH)\(_2\) of 0.25 mmol (Figure S9 in the ESI). Within the first 24 hours the reaction proceeds rapidly, a conversion of 17% is achieved. Thereafter, the reaction is slowed down (within 8 days, 29% conversion of GLY is achieved), yet the reaction does not stop. In total, 2.6 mol GLY per mol Ba\(^{2+}\) were converted (1.3 mol GLY per mol OH\(^{-}\)), which indicates a slow but catalytic conversion. In addition, it has to be noted that both Ba\(^{2+}\) and OH\(^{-}\) are consumed to a certain extent by the formation of the by-products CO\(_2\) and LA\(^{-}\), which causes an inhibition of the reaction. This becomes apparent from the pH value of the reaction solution, which decreases from 12 to 6 over the course of the reaction. To identify possible reversible reactions, stability tests were performed on LA\(^{-}\) and PG. In the presence of CsOH, both products are stable for at least 3 h under hydrolysis conditions (Figure S10a and b in the ESI). When Ba(OH)\(_2\) is used, LA\(^{-}\) remains stable for over 1 h, whereas PG is converted (14%) with full selectivity to LA\(^{-}\) (Figure S10c and d in the ESI). This should lower the selectivity to PG during the reaction. Hence, the enhanced selectivity to PG over Ba(OH)\(_2\) cannot be explained via reversibility.

**Variation of Pt/C and base amount**

Since the overall hydrogenolysis mechanism consists of metal- and base-catalyzed steps, we varied the amounts of both catalysts to gain insight into their roles. Variation of the amount of base (Figure 2a and b) reveals that CsOH and Ba(OH)\(_2\) affect the reaction to a different extent. In both cases conversion increases with increasing base amount, confirming the dependence on base concentration. For CsOH the selectivity to PG is lowered drastically from 74% (1 mmol OH\(^{-}\)) to 50% (6 mmol OH\(^{-}\)), after which it remains constant. In contrast, for Ba(OH)\(_2\) selectivity to PG only decreases slightly from 73% (2 mmol OH\(^{-}\)) to 67% (12 mmol OH\(^{-}\)). These results confirm that the cation has not only a strong influence on activity but also on the formation of PG and LA\(^{-}\). An experiment without the Pt/C catalyst revealed that the hydrogenation catalyst is needed to enable the reaction as no conversion could be observed in alkaline media (Figure S11 in the ESI). The variation of the amount of Pt/C between 0.1 and 0.6 g (in the presence of CsOH) yielded a roughly linearly increasing conversion with increasing catalyst amount (Figure 2c). This indicates that mass transfer limitations can be excluded. Also, the PG selectivity increases to 62% for 0.4 g of catalyst, after which it remains constant. Thus, the hydrogenation catalyst enables the reaction and improves selectivity.

**DFT calculations**

To gain insight into the reaction mechanism and the effect of the cation on the rate and selectivity of the reaction, the formation of PG and LA\(^{-}\) was studied using DFT (Figure 3, see Chapter 6 in the ESI for calculation results and geometries). For this system it is assumed that Pt/C only catalyzes (de)hydrogenation reactions (which are not included) and that hydrogenation only occurs for neutral molecules. For the liquid phase reactions, first an anionic mechanism without a cation is proposed (OH\(^{-}\) route). This represents the extreme case where cation and anion are always fully dissociated, which should be valid for CsOH given its very low pK\(_a\). In brief, GLY is dehydrogenated to glyceraldehyde (GLA) over Pt/C and deprotonated at the second carbon atom by OH\(^{-}\) (TS0\(^{\dagger}\), +67.7 kJ/mol) to yield the corresponding enolate (IM1\(^{-}\)). Via a reverse conjugate addition (TS1\(^{\dagger}\), +54.1 kJ/mol), IM1\(^{-}\) splits into the enol form of PA and OH\(^{-}\) (IM2\(^{-}\)). In turn, the enol is deprotonated in a barrierless process to yield the much more stable enolate and water (IM3\(^{-}\)). The enolate, in turn is protonated at the carbon atom by water, (TS2\(^{\dagger}\), +65.2 kJ/mol) to yield PA and OH\(^{-}\). Given the fact that hydrogenation of aldehydes and ketones over Pt/C occurs readily at mild conditions (i.e. an enthalpy of activation of 28 kJ/mol was found for the hydrogenation of furfural), it is likely that PA is easily converted to PG. Nevertheless, an OH\(^{-}\) can add to PA, with a very low barrier (TS3\(^{\dagger}\), +5.7 kJ/mol), to yield a significantly more stable acetate (IM4\(^{-}\)). IM4\(^{-}\) is the precursor for lactate (LA\(^{-}\)) which forms via hydride-shift (TS4\(^{\dagger}\), +83.6 kJ/mol). When IM4\(^{-}\) is additionally deprotonated (IM4\(^{\dagger}\)), the barrier for H-shift is lowered considerably (TS5\(^{\dagger}\), +43 kJ/mol). The results also indicate that LA\(^{2-}\) is protonated back to LA\(^{-}\) thereby regenerating one equivalent of base. These results are in line with the observation that the selectivity for LA\(^{-}\) formation increases with

![Figure 2. Variation of the amount of CsOH (a), Ba(OH)\(_2\) (b) and Pt/C (c), in the hydrogenolysis of GLY. Conditions: 170 °C, 80 bar H\(_2\), 2.2 mmol GLY, a, b) 0.2 g Pt/C, c) 8 mmol CsOH, 20 mL H\(_2\)O, selectivity is compared for comparable conversion, conversion is depicted after a reaction time of a) 4 h (CsOH), b) 0.25 h (Ba(OH)\(_2\)), and c) 1 h (Pt/C).](image-url)
base concentration (Figure 2a). In addition, the reverse reaction of IM4 to PA has a barrier of 48.5 kJ/mol, which is quite close to that of TS4. This is reflected in the approximately 1 : 1 ratio between PG and LA observed in Figure 2a. Thus, although the base catalyzed reaction is completed with the formation of PA, it is in fact IM4 that determines the selectivity of the overall reaction.

The same mechanism was also modeled with the [Ba(OH)(H2O)4]+ species as basic catalyst. This cationic tetra-aquo complex was identified as the most stable species by variation of the number of water and hydroxide ligands. It is noteworthy that the water ligands are only weakly bound and positioned around Ba2+ and the geometry of the complexes is mostly distorted between a trigonal bipyramidal and a tetragonal pyramidal geometry. The reaction mechanism is essentially identical to that without a cation, with the exception that the reacting species/groups are held together by the Ba-cation. This route represents the opposite extreme, where the reacting intermediates are always associated with the cation and the overall charge is either cationic or neutral. A noteworthy difference is that the balance between PA formation from IM4 (TS4, + 42.8 kJ/mol) is clearly shifted in favor of PA formation, which is in line with the higher PG selectivity observed for Ba(OH)2 (Figure 2b). Finally the energetic span ES of the base-catalyzed cycle is defined by TS0 (RDTS) and IM4 (RDI) and amounts to 111 kJ/mol for the OH route and 87 kJ/mol for the Ba(OH)+ route (ES = RDTS – RDI + ΔGrcn, whereby the ΔGrcn is that of GLA to PA). This is in line with the enhanced rate observed for the reaction of Ba(OH)2 and the rate enhancement when Ba(OAc)2 is added to the reaction of CsOH.

Kinetic analysis

The experimental Gibbs energy of the overall reaction was determined by measuring the rate of glycerol conversion in a temperature range of 150°C to 200°C using 1 and 8 mmol CsOH or 2 mmol Ba(OH)2. In all cases, ln(c(GLY)) gave a linear trend versus reaction time indicating a pseudo-homogeneous 1st order kinetics (Figure S12 in the ESI).

The results of the regression using the Eyring-equation are shown in Figure 4 (also see eq. S7 - S10 in the ESI). The rates were normalized using the cation concentrations whereas the Pt amount was considered as a constant. For both concentrations of CsOH a comparable Gibbs energy results, indicating that at both high and low base concentrations the reaction proceeds via the same mechanism and that RDTS and RDI do not change. For the Ba-catalyzed reaction, the Gibbs Energy of the reaction is about 15 kJ/mol lower than for the Cs-catalyzed
In summary, the role of alkaline and alkaline earth metal cations in the base- and metal-catalyzed hydrogenolysis reaction is investigated. Variation of the catalyst revealed that the selectivity and rate of the reaction are strongly dependent on valence and pKₐ. Two mechanistic models, which represent the extreme cases (i.e. fully dissociated/anionic and associated/cationic) were proposed and studied using density functional theory. The enhanced selectivity to propylene glycol for divalent cations compared to experiment, which indicates that also the metal-catalyzed steps contribute to the overall mechanism. The experimental and theoretical results confirm that for divalent cations coordination to the metal ion is an important factor, which controls the outcome of the overall catalytic reaction.

Conclusion
In summary, the role of alkaline and alkaline earth metal cations in the base- and metal-catalyzed hydrogenolysis of glycerol was investigated. Variation of the catalyst revealed that the selectivity and rate of the reaction are strongly dependent on valence and pKₐ. Two mechanistic models, which represent the extreme cases (i.e. fully dissociated/anionic and associated/cationic) were proposed and studied using density functional theory. The enhanced selectivity to propylene glycol for divalent cations can be explained by the decreased activation barrier from IM4 to pyruvaldehyde. The energetic span for the calculated base-catalyzed reaction steps is underestimated by 19 to 28 kJ/mol compared to experiment, which indicates that also the metal-catalyzed steps contribute to the overall mechanism. The experimental and theoretical results confirm that for divalent cations coordination to the metal ion is an important factor, which controls the outcome of the overall catalytic reaction.

**Experimental Section**

**Materials and reagents**
5 wt% Pt/C was obtained from Sigma-Aldrich and used as delivered. Chemicals were purchased from Abscr (Ba(OAc)₂, Mg(OH)₂), Acros Organics (GLY, Alfa Aesar (LiOH (trace-metal basis), NaOH,H₂O (trace-metal basis)), AppliChem (HCl), Chemsolutes (H₂SO₄), Fluka (LA), KMF Laborchemiehandel GmbH (Ba(OH)₂, 18H₂O), Sigma-Aldrich (Ca(OH)₂, trace-metal basis), 50 wt% CsOH solution in H₂O (trace-metal basis), Sr(OH)₂·8H₂O (trace-metal basis)), Wacker (Pt) and Westfalen (H₂).

**Characterization**
For N₂-physisorption (Quadrasorb SI by Quantachrome Instruments), materials were degassed in a FloVac Degasser by Quantachrome Instruments in vacuum at 120 °C for at least 4 h. H₂ Chemisorption was measured on a 3flex by Micromeritics (prior to measurement the catalysts were reduced under H₂ at 350 °C for 16 h). XPS was performed by using a Thermo Scientific K Alpha spectrometer equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel delay line detector. Spectra were obtained using an aluminum anode (AlKα = 1486.6 eV) operated at 72 W and a spot size of 400 μm. Survey scans were measured at constant pass energy of 200 eV, and high-resolution scans of the separate regions were measured at 50 eV. The background pressure of the ultra-high vacuum (UHV) chamber was 2·10⁻⁶ mbar. No special precautions were taken to keep the sample under an inert atmosphere during catalyst transfer and handling. Sample charging was compensated for by the use of an electron flood gun, and binding energy calibration was done by setting the peak of graphitic sp² carbon to BE = 284.5 eV. Data treatment and fitting was performed using the software CasaXPS (version 2.3.19). Metal surface, dispersion and crystal size were calculated using the Freundlich and Langmuir models. TEM was measured on a Tecnai G2 F20 S TWIN device. EDX was measured using an Octane T Ultra device. The particle size distribution was determined using the software ImageJ. ICP-OES analysis of the digested Pt/C catalyst was performed using a Spectro ICP Spectroflame D device. XRD was performed using a Siemens D5000 diffractometer with Cu Kα radiation (λ = 0.15409 nm, 40 kV, 40 mA) and a scan width of 0.02° 20. Spectra were recorded in the range from 3 to 90° and each point was measured for 10 s. The average crystallite size of Pt can be calculated from the peak broadening of the Pt(111) reflex using the Scherrer equation (eq. 51 in the ESI).

**Hydrogenolysis procedure**
Hydrogenolysis reactions were carried out in a 50 mL stainless steel autoclave equipped with a Teflon insert and a sampling tube. Typically, reactions were performed at 170 °C while stirring with a magnetic stirrer at 750 rpm. In a typical experiment, the autoclave was charged with GLY (0.20 g, 2.2 mmol), Pt/C catalyst (0.20 g), base (8.0 mmol OH⁻) and water (deionized, 20 mL). The autoclave was flushed 3 times using H₂ and pressurized with 80 bar H₂. Samples were taken periodically and filtered over a syringe filter (Chromafil® PA 45/25).

**Quantification**
HPLC analysis of the reaction solution was performed on a Shimadzu system (Rezex ROA-Organic Acid H⁻ (8 %) with a column by Phenomenex, (eluent: 0.05 M H₂SO₄)). Conversion, carbon-based
yield and selectivity was calculated corresponding to equations S2 to S4 in the ESI. GC analysis of the gas phase was performed on an Agilent HP6890 system with a 2 m Shin carbon ST 100/120 mesh micro packed column using a TCD detector. Helium was used as transport gas with a constant flow rate of 24.6 mL/min. The gas phase of selected reactions was taken with a gas bag and analyzed by GC. pH values of the liquid phase of the reaction were measured using pH rods purchased from Macherey-Nagel. If soluble and insoluble carbonates were analyzed, the reaction solution (liquid and solid phase) was acidified using hydrochloric acid (0.6 M, 6 mL). The gas volume was measured via replaced water volume which was weighed. The reaction apparatus is depicted in Figure S13 and the calculations explained in Eq. S5 and S6 in the ESI.

DFT calculation
All calculations were performed with the NWChem software package based on the DFT method. The geometries of all transition states, reactants and intermediates involved in the reaction were fully optimized with the continuum solvation model of SMD at the B3LYP/(H, C, and O: 6–311 + + G**, Ba: TZVPD_ecp) level of theory with dispersion correction vdW 3. Harmonic frequency calculations were performed at the equilibrium geometries to confirm first-order saddle points and local minima on the potential energy surfaces, by GC. pH values of the liquid phase of the reaction were measured using pH rods purchased from Macherey-Nagel. If soluble and insoluble carbonates were analyzed, the reaction solution (liquid and solid phase) was acidified using hydrochloric acid (0.6 M, 6 mL). The gas volume was measured via replaced water volume which was weighed. The reaction apparatus is depicted in Figure S13 and the calculations explained in Eq. S5 and S6 in the ESI.

Acknowledgements
The authors thank Kalle Vaeßen, Noah Avraham, Simon Petring and Elke Biener for analytical measurements, Markus Hölscher for fruitful scientific discussions and Maximilian Conradt for experimental support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: barium · cations · glycerol · hydrolysis · Pt/C

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Version of record online: March 1, 2022

Manuscript received: February 23, 2021
Revised manuscript received: January 24, 2022
Accepted manuscript online: February 1, 2022