Mechanism of glycerol dehydration and dehydrogenation: an experimental and computational correlation

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Abstract
Experimental formation of hydroxyacetone (HA) from glycerol over La2CuO4 catalyst under mild experimental conditions (533 K, N2 atmosphere) was correlated with molecular modeling results with the aim to propose reaction pathways. Based on these results, a novel mechanism in terms of elementary reactions is proposed for gaseous phase process. The results suggest that there are two main routes that contribute to HA formation. The main and more feasible reaction pathway corresponds to the direct 1,2-dehydration of glycerol. The second pathway involves the dehydrogenation of glycerol to produce glyceraldehyde, which is then dehydrated toward HA through the formation of a six-membered cyclic transition state during the hydrogenation step. Finally, the pyruvaldehyde formation pathway was found to be a parallel reaction to the HA formation which could be displaced by tuning the reaction conditions. HA formation as a result of pyruvaldehyde hydrogenation was also proposed, but it was found to be a less important route.

Keywords: hydroxyacetone formation mechanism; glycerol dehydration; glycerol dehydrogenation; glycerol conversion; biomass valorization.

1. Introduction

The catalytic or bio-catalytic transformation of biomass, mainly composed of polyhydroxylated molecules such as carbohydrates, represents one of the most important processes to produce chemicals and biofuels. Particularly, glycerol, considered to be the smallest polyhydroxylated compound and the main by-product in biodiesel synthesis, has been used as a model compound in experimental and theoretical studies for a deeper understanding of the chemistry of carbohydrates and glycerol itself under different reaction conditions [1–6].

Currently, the catalytic conversion of glycerol in gas phase is carried out under mild reaction conditions (around 550 K and atmospheric pressure) to produce some value-added liquid...
Hydroxyacetone (HA), as primary products [4,16,17], of glycerol leads to the formation of acrolein and two water molecules [16,17,20,21]. Nimlos et al. [4], supported the importance of Brønsted acid sites on the catalyst surface for the selective production of acrolein under mild reaction conditions using quantum chemistry calculations at the B3LYP/6-311G-(d,p) level of theory. They proposed a dehydration reaction mechanism for neutral and protonated glycerol based on the results of energy calculations. It has been shown that the catalytic dehydration reaction of glycerol leads to the formation of acrolein and hydroxyacetone (HA), as primary products [4,16,17]. However, the selectivity towards these products depends mainly on the acid-base properties of the catalyst [10,18,19]. For instance, it was proposed that the formation of acrolein from glycerol consists of a double dehydration reaction catalysed by Brønsted acid sites (proton donors) where the mechanism proceeds through the protonation of the secondary hydroxyl group to form the 3-hydroxypropanal, which is an unstable intermediate compound. Once formed, a second dehydration reaction could give rise to formation of acrolein and two water molecules [16,17,20,21].

The results of that study showed a complete glycerol conversion, where the number of formed species was reduced and only HA, glyceraldehyde, and pyruvaldehyde were obtained with a carbon balance higher than 95 %. The selectivity toward HA (76 %) was the highest among these three products.

According to the above-mentioned observations, the authors suggested that over a heterogeneous basic catalyst, the reaction may proceed directly through a dehydration step on Lewis acid-base sites or by dehydrogenation step on Brønsted basic sites leading to the formation of HA and glyceraldehyde, respectively. But, the additional increase in HA selectivity observed in their experiments suggests that this may be caused by a subsequent dehydration with further hydrogenation steps involving glyceraldehyde and pyruvaldehyde as intermediate species according to the reaction scheme described in Fig. 1.

However, the mechanism of reaction for HA formation on basic catalysts is still in discussion and some of the proposed reaction pathways have been based only on experimental results and few on computational chemistry studies [16,17,23,24]. Therefore, the aim of this paper is to get some insights about the HA formation mechanisms involving not only the direct dehydration of glycerol, but also the subsequent dehydrogenation/dehydration and rehydrogenation pathways from glyceraldehyde and pyruvaldehyde, as starting molecules.

2. Methodology

This study is based on the correlation of some experimental results with thermodynamic and kinetic data obtained by quantum chemistry calculations. Although all calculations correspond to the gas phase, taking as starting point the gas species obtained by catalytic tests, the thermodynamics of the process do not change by the presence of a catalyst, indicating validity of the inferential analysis performed here. As perspective for future work, there are still some questions that need to be addressed related to the effect of catalyst on activation energies provided by the surface-interaction pathways between the catalyst and the glycerol molecule besides the type of surface complexes and resulting transition states. It is important to highlight that to the knowledge of the authors, this is the first time that experimental results on dehydrogenation of glycerol using a basic catalyst are correlated to computational calculations.
2.1. Experimental

In a previous experimental work [22] three major products (HA, pyruvaldehyde, and glyceraldehyde) coming from glycerol conversion in gas phase using La$_2$CuO$_4$ as catalyst at 533 K were identified and quantified. However, to confirm that the trend observed for glycerol conversion and that HA selectivity can also be promoted by subsequent reaction pathways involving glyceraldehyde and pyruvaldehyde, some complementary reactions were proposed to: 1) evaluate the behavior of selectivity for the three species involved in the reaction mechanism as a function of residence time varying the catalyst mass. 2) Evaluate the change of reaction atmosphere (from N$_2$ to H$_2$) to verify the possible hydrogenation pathways leading to the HA formation as proposed in Fig.1. 3) Evaluate subsequent dehydration/dehydrogenation reactions using pure HA and, in a different experiment employing 10 % (w/w) glyceraldehyde-glycerol solution as starting substrates. Standard compounds of glycerol, HA, and glyceraldehyde to perform the experiments were obtained from Sigma-Aldrich.

All reactions were carried out during 2.5 hours at atmospheric pressure using 20 % v/v of substrate (glycerol, HA, or glyceraldehyde-glycerol solution) in the carrier gas (N$_2$ or H$_2$) over a catalyst bed located inside of a quartz reactor. This reactor was placed into an oven with two heating zones. In the first zone, each substrate was previously vaporized without decomposing before arriving to the reaction zone. The temperature of the first zone was adjusted depending on the substrate. 573 K for glycerol and glyceraldehyde-glycerol solution and 419 K for HA. Once the substrate was vaporized, the vapours enter the second heating zone where the catalytic reaction takes place at 533 K.

Liquid phase products were recovered by condensation in two cold traps located at the reactor outlet for further analysis. Separation and quantification of main organic compounds in liquid phase were performed using a gas chromatograph (Varian 430GC) equipped with a CPWAX58CB capillary column (50 m × 0.25 mm × 0.2 µm) and a FID detector. Pyruvaldehyde and glyceraldehyde also present in liquid phase were analysed using a gas chromatograph (Varian 356-LC) equipped with refractive index and UV detectors.

2.2. Computational

A molecular modelling study of the reactions that could explain the formation of detected products from glycerol transformation was carried out. All calculations (energies, optimizations, and frequencies) were performed at B3LYP density functional theory level (DFT), using the 6-311++G(d,p) basis set implemented in Gaussian 09 software [25]. This basis set was selected based on a previous work published by Chelli et al. [3] who calculated the structural and vibrational properties of glycerol with high level of accuracy and computational efficiency using a similar basis set. Calculations of transition states for each elementary reaction were done to obtain thermodynamic and kinetic information (using the transition state theory) that fits the experimental results. All structures were optimized in their electronic ground state, which correspond to the multiplicity with the lowest energy. From the frequency calculations it was verified that stable structures have no imaginary frequencies and that transition states have only one imaginary frequency that corresponds to the transformation from reactants to products, verified by intrinsic reaction coordinate (IRC) calculations allowing with certainty that the transition states correspond to the studied reactions.

3. Results

3.1. Experimental results

3.1.1. Effect of residence time on selectivity

To evaluate the effect of residence time on products selectivity, some reaction tests at 533 K using different amounts of La$_2$CuO$_4$ as catalyst were carried out. The selectivity toward HA, pyruvaldehyde, and glyceraldehyde as a function of glycerol conversion is described in Fig. 2.

In general, it is possible to observe that the selectivity toward HA increases until reaching a maximum value around 76 % at complete glycerol conversion (1000 mg of catalyst). This trend indicates that reaction pathways leading to HA formation from glycerol are thermodynamically favourable, even though the global kinetic reaction is rather slow, since a long contact time is required to obtain high yields. On the other hand, the selectivity toward glyceraldehyde and pyruvaldehyde was relatively low and constant with the glycerol conversion, indicating that although these compounds are coming from reactions that are thermodynamically unfavourable, once they reach their maximum yield, they can participate as intermediate species on consecutive reactions leading to HA formation under catalytic conditions.

Alhanash et al. [26] and Kinage et al. [11] proposed, on the basis of their observations, that the formation of HA from glycerol can be catalysed not only by acid sites, but also over basic sites. However, an optimum number of acidic and basic sites on catalyst surface must be taken into account to obtain high selectivity toward HA formation. Given this result, it is reasonable to think that on the La$_2$CuO$_4$ catalyst the reaction takes place at 533 K.

![Figure 2. Selectivity of products vs glycerol conversion over La2CuO4 catalyst at 533 K, atmospheric pressure, 2.5 h of reaction and catalyst mass (in mg): (a) 80, (b) 100, (c) 200, (d) 400, (e) 600, and (f) 1000. Source: Own source](image-url)
used in this study, a balance between both Lewis acid-base sites and Brønsted basic sites should exist.

It has also been reported that the main reaction pathway that contributes to the selective HA formation from glycerol occurs through a direct dehydration over Lewis acid sites [17,21]. However, other reaction pathways involving sequential dehydrogenation/dehydration steps on Brønsted basic sites can also contribute to the increase in HA selectivity as reported in Fig. 2. For instance, the glycerol dehydrogenation over Brønsted basic sites leads to the formation of glyceraldehyde which is then dehydrated to form an enol intermediate that is reorganized to give pyruvaldehyde.

Finally, the pyruvaldehyde is hydrogenated to HA or 1,2-propanediol depending on H2 content as it was proposed by Auneau et al. [27] and Kinage et al. [11]. But, according to Albuquerque et al. [28], the reaction from HA to pyruvaldehyde can also be possible under alkaline conditions in liquid phase, which leads us to believe that this reaction step can be reversible.

However, none of these authors detected the formation of glyceraldehyde or pyruvaldehyde in their studies, probably due to the oxidant reaction conditions used. The experimental results obtained from the evaluation of some reaction pathways discussed above will be presented in the next section to verify their validity.

3.1.2 Complementary reactions toward HA formation

With the aim to understand possible reaction pathways from glycerol to HA, a series of complementary reactions were carried out using glyceraldehyde and HA as reactants. The reactivity of glycerol under hydrogen and nitrogen as carrier gases was also evaluated. The results of conversion, selectivity, and carbon balance are gathered in Table 1.

All experiments were carried out using 1000 mg of La2CuO4 catalyst corresponding to the best result reported in Fig. 2. Entry 1 shows the reference values corresponding to the reaction performed under N2 atmosphere, condition at which the complete glycerol conversion and higher selectivity towards HA were obtained.

Entry 2 shows how the change of carrier gas from N2 to H2 increases the selectivity toward HA followed by a decrease in glyceraldehyde and pyruvaldehyde formation. This result agrees with the mechanism of Auneau et al. [29] and others [6,11,17] implying that the hydrogenation of these two species toward HA can proceed as proposed in Fig. 1. However, due to the hydrogen-rich environment used in Entry 2, the extension of hydrogenation reaction can promote the formation of 1,2-propanediol from HA. It is important to highlight that the detection of 1,2-propanediol was carried out by GC and its quantification is within the 18% of other products. Something similar is expected to occur under N2 atmosphere, since the H2 coming from initial dehydrogenation step from glycerol will promote the subsequent hydrogenation reactions, but the extension of the reaction will be limited only toward HA formation since the H2 content is lower than the one used in Entry 2.

Similarly, the formation of pyruvaldehyde was also experimentally investigated using HA and 10% glyceraldehyde-glycerol solution as reactants. Entry 3 shows that HA is a very stable compound since only 10% was transformed mostly to pyruvaldehyde, indicating that the dehydrogenation of HA to pyruvaldehyde is highly selective but kinetically unfavorable under our reaction conditions. In fact, Auneau et al. [27] proposed that equilibrium must exist between pyruvaldehyde and HA that in the presence of hydrogen could shift the equilibrium in favor of HA formation. On the other hand, the addition of glyceraldehyde to glycerol as reactant does not significantly modify the selectivity of pyruvaldehyde but increases the selectivity to HA, when compared to the reference values reported in Entry 1. This suggests that the reaction leading to HA from glyceraldehyde can be much more favorable than the one leading to pyruvaldehyde under our reaction conditions.

With the aim to having more detailed information of reaction pathways described above leading to HA formation from glycerol, we performed a computational analysis involving different routes of glycerol transformation at gas phase looking for the same products. Therefore, in terms of elementary reactions, intermediate species, transition states, reaction coordinates, and thermodynamics of the process, we performed a computational analysis that will be described in the next section.

Table 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Carbon balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HA</td>
<td>Pyr</td>
</tr>
<tr>
<td>1</td>
<td>Pure glycerol</td>
<td>99.8</td>
<td>76.5</td>
<td>14.0</td>
</tr>
<tr>
<td>2</td>
<td>Pure glycerol</td>
<td>98.9</td>
<td>79.9</td>
<td>0.98</td>
</tr>
<tr>
<td>3</td>
<td>Pure HA</td>
<td>10.1</td>
<td>------</td>
<td>93.3</td>
</tr>
<tr>
<td>4</td>
<td>10% glyceraldehyde-glycerol Solution</td>
<td>96.3</td>
<td>79.5</td>
<td>13.7</td>
</tr>
</tbody>
</table>

HA= hydroxyacetone, Pyr= pyruvaldehyde, Gly= glyceraldehyde, Others = 1,2-propanediol, ethylene glycol, methanol, and glycidol, a = N2 atmosphere, b = H2 atmosphere.

Source: the authors
3.2. Computational results

This section starts with a description of the results concerning the initial stages of reaction involving the dehydration and dehydrogenation of glycerol. Thereafter, the subsequent dehydration/dehydrogenation and re-hydrogenation reactions of the species coming from the initial steps leading to HA formation are described.

According to the work of Callam et al. [30] there are 126 glycerol conformers which have been characterized by computational analysis using different theory levels. They found that a cyclic structure forming three internal hydrogen bonds is the conformer structure with the lowest energy. Therefore, in this work we used this glycerol structure as starting point. From this reference molecule, the dehydration and dehydrogenation reactions of glycerol in gas phase were studied at a reaction temperature of 533 K taking into account the products identified in experimental results.

3.2.1 Glycerol dehydration

According to the experimental results, HA was the main product under our reaction conditions. Therefore, the formation of HA could occur through a 1,2-dehydration mechanism, where only the terminal hydroxyl group is lost as it was proposed in [4,16,17]. Eq. (1) shows that the first step of glycerol dehydration (structure 1) to form an enol intermediate (2,3-hydroxypropene, int1) proceeds through a four-membered cyclic transition state (TS1). This transition state structure is in agreement to that proposed at 0 K by Nimlos et al. [4]. At 533 K the Gibbs free energy barrier of the transition state is $\Delta G_{533,TS1} = 273.2$ kJ mol$^{-1}$, which means that this reaction (at gas phase) is expected to be rather slow. We also found that $\Delta H_{533,\text{reaction}} = 21.3$ kJ mol$^{-1}$, indicating the endothermicity of this elementary reaction. Therefore, due to this and the activation energy obtained for TS1, it is possible to suggest that this reaction would be favored at high temperatures. This result agrees with the findings of Nimlos et al. [4] who suggested that this reaction is favored at temperatures near to those used for pyrolysis (around 873 K).

However, our experimental results showed a high selectivity to HA even at low temperatures (533 K). This could be attributed to two factors. The first one is related to the thermodynamics of the elementary reaction which shows a $\Delta G_{533,\text{reaction}} = -67.8$ kJ mol$^{-1}$, indicating that the reaction is exergonic and therefore spontaneous. The second factor is related to the inherent catalytic effect of the La$_2$CuO$_4$ type-perovskite to decrease the energy barrier perhaps due to the presence of Lewis acid-base pair on the catalyst surface, from which glycerol has a single dehydration reaction to form the enol intermediate (2,3-hydroxypropene, int1) as reported by Katryniok et al. [21].

On the other hand, the eq. (2) corresponds to the second reaction step. It involves a keto-enol tautomerism of int1 through TS2 to form HA as the most stable product. For this elementary reaction, the energy barrier is lower than the one obtained for eq. (1) ($\Delta G_{533,TS2} = -219.7$ kJ mol$^{-1}$) and associating this result to the fact that this reaction is also exergonic ($\Delta G_{533,\text{reaction}} = -60.7$ kJ mol$^{-1}$) it is possible to suggest that once 2,3-hydroxypropene is formed, it is easily transformed to HA at 533 K.

3.2.2. Glycerol dehydrogenation

The dehydrogenation reaction of glycerol (structure 1 in eq. (3)) leads to the formation of glyceraldehyde (structure 2). This reaction has been reported as the key step for the production of other products such as lactic acid and therefore is favored under strong alkali conditions [31]. However, under our reaction
conditions it could be possible that the formation of glyceraldehyde takes place over the Brønsted basic sites on the La$_2$CuO$_4$ surface. Eq. (3) shows that the dehydrogenation of glycerol also takes place through a four-membered cyclic transition state TS$_3$, where the hydrogen atom of terminal hydroxyl group and the hydrogen atom of carbon adjacent to this hydroxyl group are lost to produce H$_2$.

For this reaction step, the activation Gibbs free energy is $\Delta G_{TS3} = 354.4$ kJ mol$^{-1}$, which is even higher than the one obtained for the first step in the dehydration reaction. Additionally, the reaction is slightly endergonic ($\Delta G_{\text{reaction}} = 1.7$ kJ mol$^{-1}$), indicating that under our reaction conditions the dehydration reaction is more viable in comparison with dehydrogenation reaction of glycerol.

3.2.3. Subsequent reaction pathways for HA formation

a. Glyceraldehyde dehydration

Although in a previous work [22] it was proposed that HA is formed directly from glyceraldehyde, computational results suggest that after the dehydration reaction of glyceraldehyde (structure 2) an intermediate (int$_2$) is formed, which is shown in eq. (4). From int$_2$, the results show two competitive reactions (eq. (5),(6)), which correspond to a tautomerism step that leads to the formation of pyruvaldehyde (structure 3) and a hydrogenation step that leads to the formation of int$_3$. The transition state (TS$_4$), which leads to int$_2$, is similar to that for the dehydration of glycerol, i.e. a four-membered cyclic transition structure with an activation energy of $\Delta G_{TS4} = 239.3$ kJ mol$^{-1}$. This result implies that if the dehydration of glycerol is possible to form int$_1$ at 533 K in eq. (1), then it is expected that the dehydration reaction of glyceraldehyde to form int$_2$ is also favorable, since the energy barrier is lower.

Additionally, due to the same transition state structure it is possible that the energy barrier for this dehydration reaction could also be affected by the presence of Lewis acid-base pair on the catalyst surface.

Eq. (5) involves a breaking of an H-H bond in a hydrogen molecule that requires a large amount of energy ($\Delta G = 406.7$ kJ mol$^{-1}$) to proceed. However, if there is a hydrogen molecule near to two electronegative atoms, it is expected that the electron interaction would decrease the dissociation energy compared to that required for the isolated hydrogen molecule. In the same context, it is also possible to suggest that the metal sites on the catalyst surface contribute to the dissociation of the hydrogen molecule. Therefore, this hydrogenation step would be favored through a catalytic effect. In this reaction, a six-membered cyclic transition state (TS$_5$) structure was obtained, with an energy
barrier of ΔG₅₃₃,TS₅ = 236.4 kJ mol⁻¹, which is lower than that for four-membered cyclic transition states. This result is expected since six-membered cyclic structures have less geometric stress.

On the other hand, the energy barrier for the tautomerism step (eq. (6)) is ΔG₅₃₃,TS₆ = 241.0 kJ mol⁻¹, which is very similar to the hydrogenation step in eq. (5). This suggests that both pathways are thermodynamically feasible.

However, it was observed in the experimental results (Table 1) that when hydrogen was used as carrier gas, the selectivity to pyruvaldehyde decreases to nearly zero followed by an increase in the HA selectivity. This result implies that it is possible to avoid the pyruvaldehyde formation when hydrogen content in the reaction medium is high. Another aspect that can suggest the pathway of these two reactions is associated to the exothermicity. For eq. (5) ΔH₅₃₃ = -64.0 kJ mol⁻¹ while for eq. (6), ΔH₅₃₃ = -18.4 kJ mol⁻¹. These results suggest that the hydrogenation reaction that leads to int₃ can be slightly favored under low temperatures and a hydrogen atmosphere.

Finally, HA is formed from int₃ as the most stable product through a tautomerism reaction as it is shown in eq. (7). This reaction has a relatively low energy barrier (ΔG₅₃₃,TS₇ = 154.4 kJ mol⁻¹) suggesting that once the int₃ is formed, the conversion to HA at 533 K should be rather easy.

Fig. 3 corresponds to a Gibbs free energy plot where all the previous reaction pathways are included. From computational results, it is possible to conclude that the dehydration reaction (grey line) is the most probable pathway to obtain HA as the most favorable product of glycerol transformation. However, it was found that it is possible to obtain HA through a second pathway that involves the formation of glyceraldehyde after dehydrogenation of glycerol (continuous black line), which corresponds to the most difficult step due to its high energy barrier. Nevertheless, once glyceraldehyde is formed it may undergo a dehydration reaction that conducts to an intermediate (int₄) from which there are two competitive reactions that lead to pyruvaldehyde (dotted line) formation or to another intermediate (int₃) which finally may tautomerize to form HA.

b. Hydrogenation of pyruvaldehyde

We studied the possibility of producing HA from the hydrogenation of pyruvaldehyde as it is proposed in the literature [28]. It was found that this hydrogenation step is thermodynamically favorable but kinetically controlled due to the high energy barrier (ΔG₅₃₃,TS₈ = 356.8 kJ mol⁻¹) that has to be overcome. This result is in agreement with the experimental result reported in Entry 1 and Entry 2 (Table 1), implying that even in the presence of catalyst, the hydrogenation reaction of pyruvaldehyde toward HA depends on the H₂ partial pressure (Entry 2).

In this way, it is concluded that under our reaction conditions, the hydrogenation of pyruvaldehyde toward HA is unfavorable since the H₂ content was low. A similar analysis for the reverse reaction, from HA to pyruvaldehyde, can be performed. In this case, the dehydrogenation step is much less favorable than the hydrogenation step described above since the energy barrier is higher (ΔG₅₃₃,TS₈,r = 387.0 kJ mol⁻¹). This agrees with the experimental result obtained in Entry 3 (see Table 1) indicating that although the selectivity toward pyruvaldehyde was high, the HA conversion was relatively low (10 %).
Figure 3. Gibbs free energy plot for the reactions of dehydration (grey line) and dehydrogenation (continuous black and dotted lines) of glycerol. All energies are relative to glycerol.

Source: Own source
The hydrogenation step that leads to the formation of 1,2-propanediol from HA was also studied. It was found that this reaction also has a high energy barrier \((\Delta G^\ddagger = 390.8 \text{ kJ mol}^{-1})\) and agrees with the low selectivity obtained for this product in the experimental results. Particularly, for these two hydrogenation reactions similar transition structures were found as can be observed in eq. (8), (9), i.e. four-membered transition states (TS8 and TS9). These results compared to those obtained for six-membered cyclic transition state would suggest that the energy barrier of the hydrogenation steps depends strongly on the transition state geometry.

4. Conclusions

In this work, strong correlations were obtained between experimental results of HA formation from glycerol using a heterogeneous catalyst at mild reaction conditions (533 K and atmospheric pressure) and computational results of HA formation from glycerol in gas phase, which contribute to understanding or establishing possible reaction pathways.

The main and more feasible reaction pathway corresponds to direct 1,2-dehydration of glycerol, probably over Lewis acid-base pair on the catalyst surface. The second pathway involves the dehydrogenation of glycerol that may take place over strong Brønsted basic sites to produce glyceraldehyde which is subsequent dehydrated toward HA through the formation of a six-membered cyclic transition state during the hydrogenation step. The pathway of pyruvaldehyde formation was found to be a parallel reaction to the HA formation pathway which could be oriented by tuning the reaction conditions.

HA formation from pyruvaldehyde hydrogenation was possible as a third pathway but under our reaction conditions was found to be less important. It is worth mentioning that, although computational calculations do not include the catalyst effect, thermodynamic comparison is still valid. Kinetic observations should be analyzed in more detail.

5. Acknowledgements

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