RING-OPENING AND DECARBOXYLATION OF BIOMASS DERIVED LACTONES AND PYRONES

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Abstract

Density Functional Theory (DFT) simulations predicted the formation of an oxocarbenium ions in acid catalyzed ring-opening of saturated lactones such as γ-valerolactone(GVL). The ring-opening proceeds in two steps where oxocarbenium ion ring-opens to form a stable carbenium ion, which on subsequent hydrogen elimination from the neighboring carbon leads to the formation of alkenoic acid. In biomass derived partially saturated 2-pyrones such as 5,6 dihydro-4-hydroxy-6-methylpyran-2-one (5DHHMP) ring-opening and decarboxylation occurs readily via a retro-Dels-Alder (rDA) reaction. The role of solvent and substituents in stabilizing the respective transition states versus the reactant state was studied to develop an understanding on the reactivity of the partially saturated 2-pyrene molecule via rDA reaction. Experimentally, catalytic conversion of a 2-pyrene molecule, that can be derived via direct fermentation of biomass (sugarcane bagasse), was carried out to produce a high value chemical with 93% conversion at 473 K. In order to develop an integrated bio and chemo-catalytic process, the interaction of biogenic impurities such as amino acids and proteins on a heterogeneous catalyst surface was studied by DFT simulations. DFT study shows that methionine a sulfur containing amino acid binds through sulfur on the hydrogenation catalyst surfaces like Ru and Ni and may further decompose to SCH3 and elemental sulfur and hence deactivate the catalyst irreversibly.

Keywords

Biomass, density functional theory, lactone, oxocarbenium ion, biogenic impurities.

Introduction

Strategies for the conversion of biomass solely based upon chemical or biological methods have been studied extensively in the past (Schwartz et al., 2014) with their limits in achieving high conversion to a desired product. Chemically derived platform molecules produced from biomass such as saturated lactones (e.g. GVL) in presence of Brønsted acid catalysts such as SiO2/Al2O3 at 648 K undergo ring-opening and decarboxylation to produce 1-butene (Wang et al., 2013). In contrast, more recently a new strategy has been proposed to integrate fermentation and chemical catalysis to achieve high conversion and product selectivity (Anbarasan et al., 2012). In this regard, researchers at the Center for Biorenewable Chemicals, Ames, USA have suggested 2-pyrones as platform molecules derived from biomass fermentation with high yield and can be used for selective conversion to high value chemicals. Dumesic and co-workers have shown that TAL can undergo ring-opening and decarboxylation to 2,4-pentanedione at relatively mild conditions (T<100°C), even without requirement of an acid catalyst (Chia et al., 2013). It was proposed that key structural features of the 2-pyrene such as the position of the double bond and the substituents at C3 and C5 in the ring can significantly effect the reactivity of the 2-pyrene molecules. However, the impurities present in the biomass derived platform molecules feedstock pose a challenge to the catalytic conversion process (Zhang, Jackson, & Miller, 2008). The impurities originate from the fermentation or reaction media and have a substantial effect on the catalyst activity.

In one of the study loss of activity for Ru-catalyzed hydrogenation of lactic acid was seen when fermentation derived lactic acid was used as feedstock.

Motivated from aforesaid studies, we have undertaken a detailed density functional theory (DFT) based mechanistic study to unravel the mechanism of the ring-opening of saturated lactones and 2-pyrones and to study the mechanism by which biogenic impurities interfere with the catalyst surface. In order to experimentally demonstrate the integration of fermentation and catalytic processing a fermentation derived 2-pyrene molecule was subjected to catalytic processing via ring-opening, decarboxylation to produce a high value chemical.

Results and discussion

DFT calculations predicted that the ring-opening reaction in saturated lactones such as GVL proceeds via formation of stable oxocarbenium ion intermediate. The apparent activation barrier for the two step ring-opening reaction for GVL was calculated to be 81 kJ/mol which compares well with the experimental measured value of 85 kJ/mol (Bond et al., 2011) (Figure 1a). Further investigation by ab-initio molecular dynamics simulations in explicit aqueous environment showed stable oxocarbenium ion formation, which were observed to remain intact for 5 ps of simulation time, Figure 1b. On the contrary 2-pyrones showed a relatively high barrier (>200 kJ/mol) for ring-opening via the formation of an
oxocarbenium ion. TAL on partial hydrogenation forms 5,6 dihydro-4-hydroxy-6-methylpyran-2-one (5DHHMP) which contains a double bond at C=C position, which readily decarboxylates via rDA at 343 K. In order to study the effect of substituents at C3 and C5 three different 2-pyrones were selected. The 2-pyrones molecules, can be derived from polyketide biosynthetic routes via direct fermentation of biomass or the fermentation of biomass derived aqueous sugars by an appropriate microorganism. These molecules differs in terms of the substituent at C3 and C5 and are listed as: Methyl triacetic lactone (MTAL), tetra-acetic acid lactone (TAAL) and 3,6-dihydro-4,6,6-trimethyl-2H-pyran-2-one (DTMP). On ring-opening and decarboxylation these molecules form hexa-2,4-dien-3-ol, heptanes-2,4,6-trione and 1,3-pentadiene. Interestingly the HUMO-LUMO gap between the diene and dienophile which in turn depends on the type of substituent present on the ring serves as a good descriptor for their activity in vapor phase. DFT calculations showed that TAL forms a stable zwitterions in water and ring−opens with an activation barrier of 61 kJ/mol. On the other hand in n-hexane it follows a concerted route with an activation barrier of 86 kJ/mol (Figure 2a). The ring-opening activation barrier was found to decrease with increasing dielectric constant, which clearly highlights the solvent effect (Figure 2b).

Figure 1. a) DFT calculated barriers for the ring-opening of GVL in water for 5ps b) ab initio MD simulation of oxocarbenium ion of GVL in water for 5ps

DFT study showed that amino acids containing sulfur such as methionine, cysteine present in the fermentation media binds to the catalyst surface and deactivates it irreversibly. The binding energy through sulfur for methionine and cysteine on Ru (0001) surface was calculated to be -134 kJ/mol and 89 kJ/mol. Furthermore, it could be envisaged that methionine may decompose to SCH3 with an activation barrier of 85 kJ/mol on Ni (111) surface (Figure 2c). In the presence of an acid catalyst, the 2-pyrene was converted into long chain hydrocarbon fuels by ring-opening and decarboxylation with a 93% conversion and 30% selectivity at 473 K in a batch reactor, Table 1.

Table 1. Reactivity of 2-pyrene to produce fuel.

<table>
<thead>
<tr>
<th>Reaction (hr)</th>
<th>Temperature (K)</th>
<th>Conversion</th>
<th>% Selectivity</th>
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<tr>
<td>12</td>
<td>473</td>
<td>93</td>
<td>30</td>
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Batch reactions, 2wt % catalyst and 1.5wt% reactant

Conclusion

DFT study suggest routes for possible ring-opening and decarboxylation of saturated lactones and 2-pyrene. The product molecules can be used as precursors, fuel additives and, flavoring agent.

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References


