Reaction Pathways for the Deoxygenation of Biomass-Pyrolysis-Derived Bio-oil on Ru: A DFT Study using Furfural as a Model Compound

Banerjee, Arghya; Mushrif, Samir Hemant

2017

Banerjee, A., & Mushrif, S. H. (2017). Reaction Pathways for the Deoxygenation of Biomass-Pyrolysis-Derived Bio-oil on Ru: A DFT Study using Furfural as a Model Compound. ChemCatChem, 9(14), 2828-2838.

<https://hdl.handle.net/10356/83376>

<https://doi.org/10.1002/cctc.201700036>

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. This is the author created version of a work that has been peer reviewed and accepted for publication by ChemCatChem, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1002/cctc.201700036>].

Downloaded on 26 Apr 2023 21:57:40 SGT

Reaction pathways for the deoxygenation of biomass pyrolysis derived bio-oil on Ru: A DFT study using furfural as a model compound

Arghya Banerjee and Samir H. Mushrif *

Abstract: Fast pyrolysis is emerging as a promising route for the production of liquid fuels from biomass. However, pyrolysis derived bio-oil needs to be upgraded prior to its utilization as a fuel and hydrodeoxygenation (HDO) is an important catalytic step in it. Design of suitable catalysts with high activity and selectivity for the HDO process would require detailed understanding of the underlying catalytic reaction mechanism. Since Ruthenium (Ru) based catalysts have been proposed to be the most effective HDO catalysts, the complete reaction network for HDO of furfural, a representative of furanic compounds present in bio-oil, is elucidated in this study on Ru(001) surface, using first principles Density Functional Theory calculations. Reaction pathways for the formation of Furfuryl alcohol (FA), Tetrahydrofurfuryl alcohol (THFA), Methyltetrahydrofuran (MTHF), Methylfuran (MF), Cyclopentanol, 1,2 and 1,5 pentane diols, Furan and Pentanes are established. Furan ring opening is facile on Ru surfaces and our calculations predict pentane formation to be thermodynamically and kinetically favoured in the vapour phase hydrodeoxygenation of furfural on Ru surfaces.

1. Introduction

1.1 Biomass pyrolysis and bio-oil

The rapid depletion of fossil fuel resources globally, coupled with growing energy demands, has led to the search for alternate sustainable fuel sources. Biomass is emerging as a potential feedstock for the production of chemicals and liquid fuels. Thermochemical methods, particularly the fast pyrolysis of biomass is a promising, low cost route for the processing of biomass^[1-3]. It also has an added advantage of being able to be deployed in a decentralized manner, since transportation of biomass may not be economically feasible. Along with char and non-condensable gases, *bio-oil* is the dominant product (~70% yield) of fast pyrolysis and contains variety of oxygenated compounds like aldehydes, ketones, acids, leuoglucosan, along with furanic (e.g. furfural, HMF) and phenolic derivatives (e.g. guaiacol, phenol).^[4-6] However, the high viscosity and corrosiveness of bio-oil renders it unstable, making its transportation and storage difficult. Besides, the high oxygen content (~45%) of bio-oil results in a poor heating value (20 MJ/kg

relative to 47 MJ/kg for gasoline), thus limiting its direct usability as a fuel^[7].

1.2 Catalytic Upgrading of Bio-oil

Aforementioned drawbacks associated with the direct usability, storage and transportation of pyrolysis based bio-oil can be overcome by upgrading it via catalytic cracking (using zeolite as a catalyst)^[8-10] or hydrodeoxygenation (HDO)^[11]. Catalytic cracking of bio-oil, using zeolites, results in a significant loss of carbon due to coke formation and thus, gives a low bio-oil yield^[11-12]. HDO, on the other hand, can result in excellent oil yields with high H/C ratios, but requires high hydrogen pressures. Hydrodeoxygenation has an additional advantage of being similar to hydrotreating and can be easily implemented into the existing refinery infrastructure.

Transition metal catalysts like Cu, Co, Ni, Pt, Pd, and Ru^[1, 13-30] have been explored for the hydrodeoxygenation of biomass derived compounds; but most of those studies were conducted in a condensed^[1, 19-24] or aqueous phase^[13-16, 18, 29] environment. However, catalytic upgrading of bio-oil is expected to be a gas phase reaction since bio-oil exiting from the pyrolysis reactor is in vapor phase and it is economically preferable to upgrade it catalytically in the presence of hydrogen before its condensation. Majority of aqueous or condensed phase bio-oil upgrading studies have focused on Ru, Pt and Pd catalysts primarily due to their excellent hydrogenation and deoxygenation capabilities,^[1, 18-20, 22-24, 31] along with high oil yields. Carbon supported Ruthenium catalysts were reported to have the highest oxygen removal ability from bio-oil, along with a moderately high bio-oil yield at reaction temperature of 350 °C and 200 bar H₂ pressure^[23]. The upgraded bio-oil contained long chain aliphatic compounds and a reduced O content of upto 6 wt%^[19, 22-24]. Relative to Ru, on Pd catalysts, higher CO₂ yields and greater aliphatic character were reported^[23]. The former is suggestive of the strong decarbonylation characteristic of Pd catalysts. To further minimize the gas and coke yield from bio-oil HDO, Sanna et al.^[20] proposed a condensed phase two-step hydrogenation process over Ru/C and Pt/C catalysts. In the first step, bio-oil is hydrogenated over Ru at low temperatures of ~ 125 °C to convert the aldehydes and ketones to corresponding alcohols. The second hydrogenation step over Pt at higher temperatures of ~250 °C yield alkanes (gasoline cut) and C2 to C6 diols.

One of the major challenges in bio-oil upgrading is to develop catalysts which can achieve the dual objective of reducing the oxygen content and also to selectively produce feedstocks which can either be directly used as transportation fuels or blended into conventional fuels like gasoline. Some of the desired target

Dr. Arghya Banerjee and Prof. Samir H. Mushrif*
School of Chemical and Biomedical Engineering
Nanyang Technological University
62 Nanyang Drive, Singapore 637459
E-mail: shmushrif@ntu.edu.sg

Supporting information for this article is given via a link at the end of the document.

Figure 1. Furfural adsorption configurations (top and side views) on Ru(001) surfaces and the corresponding Gibbs free energy of adsorption (kJ/mol) at 500 K and 1 bar. (a) flat, fcc hollow site; (b) flat, hcp hollow site; (c) vertical, parallel to surface; (d) vertical, perpendicular to surface. (a) and (b) are the $\eta^2(\text{C-O})$ and (c) and (d) are the $\eta^1(\text{-O})$ adsorption modes. Ru atoms are represented as green balls, C in grey, O in red and H in white.

products for blending into straight run gasoline obtained from refinery complexes include $\text{C}_5 - \text{C}_{12}$ hydrocarbons comprising of alkanes and olefins. In order to achieve this objective, an in depth understanding of the underlying reaction chemistry occurring on the catalyst surface is required^[21, 32-33]. Multiple theoretical investigations to elucidate the reaction mechanism of HDO on Cu, Ni and Pd surfaces have been reported. For example, activities of Cu, Ni and Pd catalysts for the vapor phase HDO of bio-oil have been investigated for model compounds like furfural^[25-28]. Furfural (*cf.* Figure 1) is one of the major components present in bio-oil^[34-36] and is a precursor to the formation of methylfuran (MF), which is an excellent gasoline additive. Cu catalysts predominantly formed furfuryl alcohol (FA) with small amounts of MF, while aliphatic alcohols and furans were the main products on Ni and Pd catalysts, respectively. The difference in the selectivity was attributed to different adsorption configurations of furfural on Ni, Pd and Cu^[27]. DFT studies on Cu^[28, 37], Ni^[25] and Pd^[17, 26] surfaces reveal that furfural adsorbs in a $\eta^1(\text{-O})$ orientation through the formyl O on the Cu(111) surface, while on Ni(111) and Pd (111) surface the $\eta^2(\text{C-O})$ configuration is preferred in which both, the formyl group and the ring interact with the metal (*cf.* Figure 1). The weak adsorption of the furan ring on Cu(111) surface prevents ring activation while low hydrogenation barriers of 52 and 106 kJ/mol were reported for the two step hydrogenation of furfural to furfuryl alcohol^[37]. In contrast, the strong ring-metal interaction on Ni weakens the C – O bond and results in ring opening to form aliphatic alcohols. On Pd(111) surfaces, the formation of furfuryl alcohol and furan is competitive with highest computed barriers of 77 and 92 kJ/mol^[17]. However, the formation of furan is thermodynamically favored on Pd surfaces, in agreement with experimental observations^[26-27]. Computational studies detailing the mechanism of furfural hydrodeoxygenation to furfuryl alcohol, furan and MF have also been reported on Pt^[38] and Ru^[13-14] surfaces. Cai et al.^[38] calculated activation barriers for furfural

hydrogenation on flat Pt(111), stepped Pt(211) and Pt₅₅ clusters and concluded the hydrogenation to furfuryl alcohol to be kinetically favored at terrace and step sites while furan formation is favorable at corner sites. Recently, Mironenko et al.^[14] reported C – O scission and hydrogenation barriers for the formyl group of furfural on Ru(001) surfaces. C – O scission of the ring-CH₂O species was found to be facile with barriers of 65 kJ/mol, relative to the ring-CH₂O hydrogenation to furfuryl alcohol, on Ru surfaces. It has to be noted that all the aforementioned computational studies have been largely limited to the formation of FA, MF and/or furan compounds and did not evaluate the formation of alternate products like Tetrahydrofurfuryl alcohol (THFA), Methyltetrahydrofuran (MTHF), 1,2 and 1,5 pentane diols, cyclopentanol, pentanol and pentane in their calculations.^[39] To the best of our knowledge, a systematic kinetic and thermodynamic evaluation of multiple competitive pathways leading to the formation of aforementioned products is rarely done.

1.3 Scope of this study

Ruthenium based catalysts have been proposed as potential candidates for the condensed phase HDO of bio-oil^[22-23]. The desired products from HDO would include compounds which can be either directly used as transportation fuels or blended as fuel additives (in gasoline). However, the vapor phase upgrading of bio-oil occurs at temperatures between 200 – 400 °C in the presence of hydrogen, and simultaneous competitive reactions would lead to the formation of multiple products. The product distribution/selectivity would be governed by both, kinetics and thermodynamics, which in turn are governed by activation barriers and reactions energies, in terms of Gibbs free energy. Hence, in this work, we develop a comprehensive reaction map and compute energetics of individual reaction steps for the catalytic conversion of furfural - a model aromatic oxygenate derived from bio-oil, using Density Functional Theory (DFT). Free energy

Figure 2. Schematic illustrating possible reaction pathways for the first activation of furfural (within the dotted line) and listing potential final products to be obtained. The 6 possible pathways by which furfural can activate are shown here: C^1-O hydrogenation, C_{ring} hydrogenation, C^1-O scission, $C_{ring}-O$ scission, C^1-C^2 dissociation and C^1-H scission. The nomenclature for the carbon atoms is shown in the central furfural molecule. FA: Furfuryl alcohol; THFA: Tetrahydrofurfuryl alcohol; THF: Tetrahydrofuran; THFu: Tetrahydrofurfural; MF: Methylfuran; MTHF: Methyltetrahydrofuran.

barriers and reaction free energies for the transformation of furfural to FA, THFA, MF, MTHF, 1,2 and 1,5 pentane diol, cyclopentanol, pentanol, pentane and furans are reported. The reaction mechanisms/pathways and energetics computed in this paper will guide experimentalists to understand the activity of Ru quantitatively and its selectivity qualitatively. Additionally, our calculations suggest that the formation of pentanes is kinetically and thermodynamically favored during the vapor phase hydrodeoxygenation of furfural on Ru surfaces.

2. Results and Discussion

Furfural ($(C_4H_3O)-CHO$) can adsorb on the Ru(001) surface in two possible configurations: i) a flat parallel configuration in which both, the ring and the $C=O$ group interact with the metal surface - $\eta^2(C-O)$, and ii) a vertical configuration in which the furan ring does not interact with the surface, $-\eta^1(-O)$. Figure 1 shows these adsorption configurations and corresponding adsorption free energies. $\eta^2(C-O)$ is the most stable configuration (Figure 1a). The furan ring preferably adsorbs over the hollow fcc site. Note that in this configuration, the ring hydrogens and oxygen buckle out of the plane. The formyl group is bound in a $\eta^2(C-O)$ mode which is typical of group VIII metals^[17, 26,40].

Furfural activation can take place via 6 possible pathways, namely (i) C^1-O and (ii) C_{ring} hydrogenation, (iii) C^1-O and (iv) $C_{ring}-O$ scission, (v) C^1-C^2 dissociation and (vi) C^1-H scission (see Figure 2 for the nomenclature of carbon atoms). Each of these pathways can further lead to the formation of a number of platform chemicals, as depicted in Figure 2. Table 1 reports the activation and reaction free energies for these 6 pathways. Hydrogenating

the C^1HO to C^1H_2O and opening of the furan ring via a $C_{ring}-O$ scission are the most facile furfural activation pathways, with barriers of 81 and 64 kJ/mol, respectively. They can lead to the formation of FA, THFA, MF, MTHF or cyclopentanols, diols, pentanols and pentanes. However, note that the first activation step may not be the rate determining step and hence the selectivity of Ru towards either of these products would require the analysis of the energetics of the complete reaction network for all the possible products. In this study, we investigate multiple pathways for the HDO of furfural, resulting in the formation of FA, THFA, MF, MTHF, 1,2 and 1,5 pentane diol, cyclopentanol, pentanol, pentane and furans, as illustrated in Figure 2.

2.1 FA and THFA formation (C^1-O and C_{ring} hydrogenation)

Furfural hydrogenation to THFA can proceed via two pathways (i) Hydrogenation of the ring, followed by C^1-O hydrogenation, or (ii) C^1-O hydrogenation followed by ring hydrogenation, as shown in Figure 3. Hydrogenation of the C^1-O group occurs either at the C or at the O centre to form $(C_4H_3O)-CH_2O$ or $(C_4H_3O)-CHOH$ intermediates, respectively. Hydrogenating the carbon has a free energy barrier of 81 kJ/mol while O hydrogenation has a barrier of 115 kJ/mol (Figure 3). Recent studies by Mironenko et al. on Ru(001) surfaces report electronic energy barriers of 75 and 123 kJ/mol for the former and latter pathways.^[14] Also, $(C_4H_3O)-CHOH$ is 38 kJ/mol less stable than $(C_4H_3O)-CH_2O$, making $(C_4H_3O)-CHOH$ formation both thermodynamically and kinetically less favorable than $(C_4H_3O)-CH_2O$. $(C_4H_3O)-CH_2O$ hydrogenates further to form FA ($(C_4H_3O)-CH_2OH$) with a barrier of 126 kJ/mol. FA formation is 60 kJ/mol endergonic relative to furfural. Further hydrogenating the ring of FA leads to the formation of THFA with hydrogenation barriers of

Table 1. DFT calculated activation barriers and reaction free energies for the first step of (C₄H₃O)-CHO and (C₄H₃O)-CH₂O activation.

	(C ₄ H ₃ O)-CHO		(C ₄ H ₃ O)-CH ₂ O	
	ΔG_a	ΔG_{rxn}	ΔG_a	ΔG_{rxn}
	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)
C¹ – O hydrogenation	81 ^a	40	126	20
C¹ – O scission	169	-13	80	-84
C^{ring} hydrogenation (at C³)	113	41	85	19
C^{ring} – O scission (C⁵ – O/C² – O)	64/116	-9/-43	51/63	-28/-72
C¹ – H cleavage	103	77	41	-40
C¹ – C² cleavage	121	12	91	40

[a] Hydrogenation at the carbon end

103, 67, 67 and 64 kJ/mol for the addition of the 1st, 2nd, 3rd and 4th hydrogen, respectively. THFA is 110 kJ/mol endergonic relative to furfural. Alternatively, furfural can undergo ring hydrogenation prior to the formyl group hydrogenation, to form THFA. Furfural ring hydrogenation proceeds with barriers of 113, 95, 104 and 92 kJ/mol to form Tetrahydrofurfural (THFu). Note that the sequence in which the ring carbon atoms are hydrogenated does not affect the overall kinetics and thermodynamics significantly (refer to Table S7 in the supporting information). THFu sequentially hydrogenates at the carbon (THFu-CH₂O) and oxygen centres of the C¹HO group with barriers of 80 and 116 kJ/mol, respectively, to form THFA. The formation of a THFu-CHOH species is 30 kJ/mol less stable than THFu-CH₂O. The effect of a partial (One Hydrogen added at a C³ position) or fully hydrogenated ring on the C¹ – O hydrogenation barriers, and a hydrogenated C¹ – O moiety (-C¹H₂OH) on the ring hydrogenation barriers was also calculated. Hydrogenation of the ring does not affect the C¹ – O hydrogenation barriers significantly. The hydrogenation of the CHO group to -CH₂O proceeds with barriers of 81, 90 and 80 kJ/mol for an unsaturated ring (furfural moiety), partially hydrogenated ring (1H added at a C³ position) and fully saturated ring (THFu moiety), respectively. Conversely, hydrogenating the C¹ – O moiety first to -C¹H₂OH lowers the ring hydrogenation barriers by around 10 – 37 kJ/mol. The order of hydrogenation however, does not affect the overall kinetics of THFA formation significantly.

Liquid ^[41,43-45] and gas phase^[42] furfural hydrogenation studies suggest THFA formation to proceed via furfuryl alcohol intermediate on Ru^[41,45] and on other transition metal systems ^[42-44]. Since, the rate determining steps for THFA formation, via FA and THFu pathways, have competitive barriers of 126 kJ/mol and 116 kJ/mol, respectively (*cf.* Figure 3), THFA formation can proceed by either pathway.

2.2 Methyl Furan (MF) and Methyl Tetrahydrofuran (MTHF) formation (C¹ – O scission)

MF can form either by direct C¹–O cleavage or via hydrogenation of the C¹–O group, followed by C¹–O scission. The direct cleavage of the C¹–O bond of furfural ((C₄H₃O)-CHO → (C₄H₃O)-CH + O) has a significantly high barrier of 169 kJ/mol. (C₄H₃O)-

Figure 3. Gibbs free energy profile for the formation of THFA from furfural via the THFu and FA pathways. The THFu (bold line) and FA (dotted line) routes are kinetically competitive with the highest barriers of 116 and 126 kJ/mol, respectively. The free energy barriers for each step are also indicated. H atoms are omitted for clarity purpose. FA: Furfuryl alcohol; THFu: Tetrahydrofurfural; THFA: Tetrahydrofurfuryl alcohol.

CH hydrogenates to MF ($(\text{C}_4\text{H}_3\text{O})\text{-CH}_3$) with barriers of 105 and 72 kJ/mol. The high C – O scission barrier makes this pathway kinetically unfavorable for MF formation. Hydrogenating the CO group prior to $\text{C}^1\text{ – O}$ scission have shown to reduce C – O scission barriers significantly^[46–47]. Our calculations also show that the scission barriers indeed decrease to 100 and 80 kJ/mol for the $(\text{C}_4\text{H}_3\text{O})\text{-CHOH}$ and $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2\text{O}$ species (Figure 4). Furfuryl alcohol can also dehydroxylate to $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2$ with a barrier of 91 kJ/mol. Besides the direct dehydroxylation pathways to remove the OH group, an H assisted pathway leading to elimination of a water molecule can also be envisaged (hydrogenolysis). However, hydrogenolysis barrier of 161 kJ/mol was considerably higher than the direct dehydroxylation pathway. The $(\text{C}_4\text{H}_3\text{O})\text{-CHOH}$ or $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2\text{O}$ species can either hydrogenate to furfuryl alcohol ($(\text{C}_4\text{H}_3\text{O})\text{-CH}_2\text{OH}$) or cleave the C – O bond to form $(\text{C}_4\text{H}_3\text{O})\text{-CH}$ and $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2$, respectively. $(\text{C}_4\text{H}_3\text{O})\text{-CHOH}$ hydrogenation to furfuryl alcohol is kinetically (92 vs 100 kJ/mol) more favorable but thermodynamically less favorable (-18 vs -100 kJ/mol) over $\text{C}^1\text{ – OH}$ scission. Unlike $(\text{C}_4\text{H}_3\text{O})\text{-CHOH}$, $\text{C}^1\text{ – O}$ scission to $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2$ is kinetically (80 vs 126 kJ/mol) and thermodynamically more favorable (-84 vs 20 kJ/mol). The kinetic and thermodynamic favorability of $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2\text{O}$ formation over $(\text{C}_4\text{H}_3\text{O})\text{-CHOH}$ (as described in the previous section) suggests furfural would preferably hydrogenate to $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2\text{O}$ and immediately undergo C – O cleavage to form a $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2$ intermediate rather than forming furfuryl alcohol (*cf.* Figure 4). The subsequent hydrogenation of $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2$ to MF ($(\text{C}_4\text{H}_3\text{O})\text{-CH}_3$) is 13 kJ/mol exergonic with a free energy barrier of 72 kJ/mol. Hence, our calculations indicate that the preferred pathway for MF formation from furfural proceeds via hydrogenation to the $(\text{C}_4\text{H}_3\text{O})\text{-CH}_2\text{O}$ intermediate, followed by $\text{C}^1\text{ – O}$ scission. Furfuryl alcohol is thus unlikely to form as an intermediate in the pathway for MF formation.

MTHF can form by two pathways: a) via a MF intermediate where C¹ – O scission precedes ring hydrogenation (bold lines in Figure 5) or b) via a THFu intermediate in which C¹ – O scission follows the ring hydrogenation (dotted lines in Figure 5). The former pathway is kinetically favored with the highest calculated barrier of 110 kJ/mol for the ring hydrogenation of MF. In the latter

Figure 4. Gibbs free energy profile indicating the competitive pathways of C¹ – O scission and C¹ – O hydrogenation in the transformation of furfural to furfuryl alcohol. The scission pathway is indicated by dashed lines. Free energy barriers for each step are shown. H atoms are omitted for clarity purpose.

pathway, the highest barrier of 156 kJ/mol corresponds to C¹ – O scission, thereby suggesting that ring hydrogenation increases the scission barrier significantly. For e.g., ring hydrogenation leads to THFu which further hydrogenates to THFu-CH₂O before undergoing the C¹ – O scission to form a saturated ring-CH₂ intermediate. Subsequent hydrogenation to MTHF proceeds with a barrier of 33 kJ/mol. Alternatively, THFu-CH₂O can hydrogenate to THFA with a barrier of 116 kJ/mol. The lower hydrogenation barriers indicates that THFu-CH₂O, if formed, would preferentially hydrogenate at the oxygen end to THFA than undergoing the C¹ – O scission (116 vs 156 kJ/mol). MTHF formation is energetically downhill relative to furfural by 13 kJ/mol. Higher C – O scission barriers of the saturated ring molecule than that of the unsaturated ring is not surprising and is attributed to the loss of aromaticity of the furan ring (π electrons)^[14]. For the unsaturated ring, the furfuryl radical formed at the transition state is stabilized by the favorable overlap of the π orbitals of formyl carbon and the furanic ring leading to a conjugated system. This delocalizes the unpaired electron and stabilizes the transition state, thereby lowering C – O cleavage barriers. Ring saturation destroys the conjugation and hence increases the C – O cleavage barrier. Both MTHF and THFA readily desorb from the surface with a calculated Gibbs free energy of -38 and -42 kJ/mol for desorption, at 500 K and 1 bar.

In summary, C¹ – O scission proceeds after hydrogenation at the carbon end. The reasonably low scission barriers ~80 kJ/mol provide evidence of the excellent deoxygenation capability of the Ruthenium catalyst, in agreement with experimental studies^[23]. The lower scission barriers also suggest furfuryl alcohol formation to be kinetically less favorable as a product. Hydrogenating the furan ring prior to the scission increases this barrier significantly. Ring hydrogenation succeeds C¹ – O scission in the dominant pathway for MTHF formation.

2.3 Ring opening reactions (C_{ring} – O scission)

2.3.1 Diol formation

Linear and branched chain alcohols and ketones have also been reported as products during the aqueous phase hydrogenation of

Figure 5. Gibbs free energy profile for the formation of MTHF from furfural via two pathways. The MF route (bold line) is the preferred pathway where ring hydrogenation proceeds after C¹ – O scission. Free energy barriers for each step are shown. The red lines indicate the C¹ – O scission steps. H atoms are omitted for clarity purpose. THFu: Tetrahydrofurfural; MTHF: Tetrahydrofuran; MF: Methylfuran.

furfural on Ruthenium surfaces^[48-49]. The formation of alcohol derivatives is initiated by a C_{ring} – O cleavage, followed by the hydrogenation of the open chain product to form linear (C² – O cleavage) or branched chain (C⁵ – O cleavage) alcohols. The C⁵ – O cleavage has a significantly low barrier of 64 kJ/mol, while C² – O cleavage proceeds with a barrier of 116 kJ/mol, in reasonable agreement with recent studies on Ru^[13]. Besides the direct cleavage of the C_{ring} – O bond, a hydrogen assisted ring opening pathway has also been proposed for the ring opening in glucose, in which a surface hydrogen attacks the ring oxygen and cleaves the C – O bond^[50-52]. However, unlike glucose, our calculations show that the C_{ring} – O barrier rises to 126 kJ/mol for the C² – O and C⁵ – O scission in the surface hydrogen attack pathway for furfural. The much lower C_{ring} – O cleavage barriers in the furan ring relative to the attached formyl group can be explained by the strong interaction of the ring π electrons with the metal d orbitals, which weakens the C_{ring} – O bond^[53]. The resulting open chain product hydrogenates at the oxygen ends of the two carbonyls with barriers of 95/132 kJ/mol (at C²/C¹) and 101/80 (at C⁵/C¹) to form 1,2 (C⁵ – O scission) and 1,5 (C² – O scission) alkene diols. Subsequent sequential hydrogenation of the unsaturated carbon atoms leads to 1,2 and 1,5 pentane diols (in Figure 6, pathway for 1,2 diol is only shown). An alternate pathway for the formation of diols is via ring opening of monohydrogenated furfural (C₄H₃O-CH₂O), followed by sequential hydrogenation of the oxygen and carbon atoms (*cf.* Figure 9). Furfuryl alcohol (C₄H₃O-CH₂OH) was also proposed to be an intermediate for the formation of 1,2 and 1,5 pentane diol over supported Pt catalysts.^[54-55] (C₄H₃O)-CH₂O undergoes C² – O and C⁵ – O cleavages with barriers of 63 and 51 kJ/mol, respectively. The significantly lower barrier for C² – O scission for the monohydrogenated furfural intermediate (63 kJ/mol vs 116 kJ/mol for furfural) makes it the kinetically favored pathway for the formation of 1,5 pentane diols (Figure S1). The formation of 1,2 pentane diol has similar barriers via both the pathways. The highest barrier in the 1,5 pentane diol pathway is considerably lower than that of 1,2 pentane diol pathway and involves the hydrogenation of the terminal C⁵ carbon (102 kJ/mol vs 137 kJ/mol). However, the first activation barrier in the 1,2 pentane diol formation pathway (64 kJ/mol) is slightly lower than that in 1,5 pentane diol formation (81 kJ/mol). Hence we believe

Figure 6. Gibbs free energy profile for the formation of pentane (bold lines) and 1,2 pentane diol (long dashed line) from furfural. Ring opening of furfural is the first activation step where C^5-O scission is kinetically favorable over the C^2-O scission. The C^2-O scission pathway and H atoms are omitted for clarity purpose. The open chain product either hydrogenates to the 1,2 pentane diol or deoxygenates to pentene which further hydrogenates to pentane. The dotted green box indicates the competitive barrier between the diol and pentane formation. The formation of pentane is thermodynamically and kinetically favored over 1,2 pentane diol. Free energy barriers for each step are shown.

that the formation of both the diols would be kinetically competitive under reaction conditions. The formation of diols is endergonic with a reaction free energy of 79 and 74 kJ/mol for 1,2 and 1,5 diol, respectively, relative to furfural.

2.3.2 Pentane formation

Instead of hydrogenation to produce diols, open chain products from the ring opening of furfural can undergo two deoxygenation steps to remove the ring and C^1 oxygen, leading to the formation of linear pentenes. After a C^5-O scission of furfural, deoxygenation proceeds via the hydrogenation of two carbonyl groups to C^2OH and C^1H_2O , followed by C^2-OH and H_2C^1-O cleavage (cf. Figure 6). An alternate pathway involves hydrogenation at the carbon atom to form HC^2O and C^1HOH species. However, HC^2O and C^1HOH are calculated to be 80 and 46 kJ/mol less stable than C^2OH and C^1H_2O and hence are not considered in our analysis. The direct C^1-O or C^2-O scission of the ring opened product is kinetically difficult, as discussed in Section 2.2 and hence is not considered either. C^2-OH and H_2C^1-O scission have barriers of 70 and 35 kJ/mol respectively. The formed pentenes further hydrogenate to form pentane with barriers between 40 – 106 kJ/mol (not shown in Figure 6 for clarity). Pentane formation is also thermodynamically highly favorable, with a reaction free energy (relative to furfural) of -67 kJ/mol.

2.3.3 Cyclopentanol and Pentanol formation

Ring opening also opens up the route for the formation of cyclopentanone derivatives. Hronec et al.^[56] obtained high yields of cyclopentanone in aqueous phase catalytic hydrogenation of furfural over supported Ru and Pt catalysts. Cyclopentanone yield decreased on changing the solvent from water to other polar solvents, thus suggesting a strong role of water in the reaction mechanism. The authors proposed cyclopentanone formation to proceed via the formation of a 3-hydroxy-4-cyclopentenone intermediate^[57]. However, the vapor phase furfural hydrogenation

Figure 7. Gibbs free energy profile for the formation of a pentene (long dashed line) and cyclopentanol (bold line) from furfural. Ring opening of furfural is the first activation step where C^5-O scission is kinetically favorable over C^2-O scission. The open chain product undergoes a single deoxygenation step followed by ring closure via a C^1-C^5 coupling to form a cyclopentenone derivative. The red lines indicate the C^1-O scission steps. The formation of 2-cyclopentenone is thermodynamically more favorable than pentenes but is kinetically limited with a highest barrier of 135 kJ/mol. Ring hydrogenation of 2-cyclopentenone to cyclopentanol is thermodynamically uphill. Free energy barriers for each step are indicated. The H atoms are omitted for clarity purpose.

would be in the absence of water (and not in a condensed phase environment) and hence an alternative mechanism is likely to exist for cyclopentanone formation. In our proposed pathway, ring opening (C^5-O scission) is followed by the C^2-OH scission to remove one of the oxygen groups (cf. Figure 7). Subsequent dehydrogenation from C^1 , followed by ring closure via C^1-C^5 coupling and the final C^2 hydrogenation proceeds with barriers of 98, 88 and 135 kJ/mol respectively. Further hydrogenation of the furanic ring leads to 2-cyclopentenone which is 100 kJ/mol exergonic relative to furfural. Alkene formation is still kinetically more favorable (cf. Figure 7) than the formation of 2-cyclopentenone. Hydrogenation of the unsaturated ring and the ketonic oxygen to form cyclopentanol proceeds with ring hydrogenation barriers between 70 – 147 kJ/mol and the O hydrogenation barrier of 130 kJ/mol. Starting from furfural, the formation of cyclopentanol is 62 kJ/mol endergonic with the highest barrier of 147 kJ/mol. Instead of a C^1-C^5 coupling, ring closure via a C^1-O coupling leads to a 6 membered cyclic ring which is 82 kJ/mol less stable than the cyclopentenone intermediate and, hence, is not considered in this analysis.

Pentanol can also be produced after a single deoxygenation step of the open chain product, followed by the hydrogenation of unsaturated carbon atoms. 1-pentanol can be formed via both a C^2-O or a C^5-O cleavage while 2-pentanol can be produced via a C^5-O cleavage. 1-pentanol and 2-pentanol are 120 and 112 kJ/mol endergonic relative to furfural. Hydrogenation of unsaturated carbon atoms have not been computed separately and are expected to have similar barriers as those of the diols. For brevity, the complete energetics of 1-pentanol formation is not shown in Figure 7.

In summary, ring opening of furfural opens up pathways for the formation of linear and branched pentane diols, pentanols, pentanes and cyclic alcohols. The selectivity towards pentane vs a pentane diol or cyclopentanol/pentanol formation is determined

Figure 8. Gibbs free energy profile for the formation of furan from furfural. The preferred pathway involves a C¹ – H cleavage followed by C¹ – C² cleavage (bold line). Free energy barriers for each step are shown and hydrogens are omitted for clarity purpose.

by comparing the O hydrogenation (for diols) and C – C coupling barriers (for cyclopentanol) vs C – O scission barriers, after the furfural ring opening. The former has higher barriers (O hydrogenation for 1,2 diol: 132 kJ/mol and C – C coupling: 88 kJ/mol) then the latter (70 and 35 kJ/mol), making pentane formation kinetically favorable over diols/alcohols (cf. Figure 6 and 7). In addition, pentane formation is also thermodynamically more favorable than both diols and cyclopentanols (Pentane: -67 kJ/mol; 1,2 diol: 79 kJ/mol; Cyclopentanol: 62 kJ/mol). Thus, pentane formation is both kinetically and thermodynamically favorable on Ruthenium surfaces, in agreement with the condensed phase bio-oil HDO studies which have also observed their formation^[23]. The authors observed a high concentration of aliphatic hydrocarbons and limited alcohol yields in the hydrodeoxygenated oil, thus validating our predictions.

2.4 Furan formation (C¹ – C² and C¹ – H scission)

Furan formation can proceed via 2 main pathways - a) C¹ – C² bond cleavage followed by hydrogen addition to the C² or b) dehydrogenation of the C¹HO group followed by C¹ – C² cleavage and C² hydrogenation. C¹ – C² cleavage of furfural has a free energy barrier of 121 kJ/mol (cf. Figure 8). Dehydrogenating the CHO group prior to C¹ – C² cleavage, leads to the formation of an acyl species in which the carbonyl group attaches to the metal surface only via carbon (cf. Figure 8). Such an acyl species have been proposed to be the precursor for the decarbonylation reaction to form furans on Pd surfaces^[58-59]. The formation of the acyl species drastically lowers the C¹ – C² cleavage barrier to 40 kJ/mol. However, the first dehydrogenation step is significantly endothermic at 77 kJ/mol, with a barrier of 103 kJ/mol. The final hydrogenation at the C² position to produce furan has a very high barrier of 164 kJ/mol and is the rate limiting step for furan formation via both pathways. The formation of furan, though thermodynamically favorable, is thus limited by the high free energy barriers and is hence not kinetically competitive with the formation of any of the products discussed above. Besides furfural, the direct C¹ – C² scission of (C₄H₃O)-CH₂O, (C₄H₃O)-CH₂OH, (C₄H₃O)-CH₂ and (C₄H₃O)-CH₃ were also computed with the lowest reported barrier of 91 kJ/mol for (C₄H₃O)-CH₂O (Table S4,

Table 2. DFT calculated activation barriers and reaction free energies for all products analyzed. G_{ini-barrier} is the free energy barrier of activation for the first step and G_{highest barrier} is the highest barrier of activation in the reaction network of the respective products.

Product	G _{ini-barrier} (kJ/mol)	G _{highest barrier} (kJ/mol)	ΔG _{rxn} (kJ/mol)
FA	81	126	60
THFA	81	126	110
MF	81	81	-21 ^a
MTHF	81	110	19 ^a
1,2 Pentane Diol	64	137	79
1,5 Pentane Diol	81	102	74
2- Cyclopentenone	64	135	-100 ^a
Pentane	64	106	-67 ^a
Furan	103	164	-71

[a] reported with O removed as H₂O (g)

Reaction 49). Similar barriers have been reported by Vlachos et al. on Pd surfaces^[17].

2.5 Proposed Reaction Pathways

We now present the complete free energy landscape for different furfural conversion pathways on Ruthenium (001) surface, as shown in Figure 9. Table 2 summarizes the reaction free energies (ΔG_{rxn}), free energy barriers for the first activation step (G_{ini-barrier}) and the rate determining step free energy barrier (G_{highest barrier}) for all the products analyzed in this study. MF (via C¹ – O scission), 2-cyclopentenone and pentane (via C⁵ – O scission) are thermodynamically favored over Ru surfaces. In addition, the above three products also have the lowest first activation barriers (G_{ini-barrier}). The product selectivity on Ru surfaces would be determined by comparing the highest barriers (G_{highest barrier}) for each of these products in their respective pathways. Among all the products studied, MF and pentane have the lowest G_{highest barrier} of only 81 and 106 kJ/mol and are also thermodynamically favored, thus, suggesting them to be the favored products of furfural HDO on Ru. The selectivity of pentane and MF on Ru can be further determined by revisiting their reaction pathways starting from furfural. The low C⁵ – O scission and C¹ – O hydrogenation barriers of 64 and 81 kJ/mol for furfural suggest that both the pathways are kinetically competitive. Next, we focus on the potential reaction pathways originating from a C⁵ – O scission and C¹ – O hydrogenation. The open chain product after the C⁵ – O scission can either hydrodeoxygenate to pentanes or hydrogenate to form diols. As discussed in earlier sections, the former is both, thermodynamically and kinetically favored. On the other hand, the (C₄H₃O)-CH₂O species formed after C¹ – O hydrogenation can activate by the 6 pathways similar to that of furfural (cf. Table 1). Ring opening (C⁵ – O or C² – O scission) would lead to pentane formation, whereas C¹ – O scission would form MF. The former has a barrier of 51 and 63 kJ/mol, while the latter proceeds with a barrier of 80 kJ/mol. The lower ring opening barriers results in a ring opened aliphatic chain which deoxygenates to form pentane as the thermodynamically and kinetically favored product (bold lines in Figure 9). Thus, pentane is suggested to be the dominant product via both kinetically

Figure 9. Proposed reaction pathway for furfural activation on Ru(001) surfaces. Kinetically favored pathways for the formation of FA, THFA, MF, MTHF, 1,2 and 1,5 pentane diols, 2-cyclopentenone, furan and pentane are shown here. Free energy barriers and reaction free energies (in parenthesis) in kJ/mol are indicated above the arrow lines. Our calculations suggest that pentanes are kinetically and thermodynamically favored (indicated by bold arrows) on Ru surfaces. All the studied pathways and the corresponding activation free energies are tabulated in Table S4 in the supporting information.

favorable pathways from furfural.

In summary, ring opening of furfural is the preferred route for furfural activation on Ru(001) surfaces (Figure 9). Removal of oxygen groups of furfural occurs *after* the ring opening. Although hydrogenation of the aliphatic chain produced after the ring opening leads to the formation of pentane diols, deoxygenation of the aliphatic chain to form alkenes and further hydrogenation to alkanes remains the preferred pathway. The above results also explain the significant increase in the intensities of the aliphatic –CH₂ and –CH₃ groups in the hydrotreated oil in the condensed phase experimental studies of HDO of pyrolysis oils over Ru/C catalysts^[23]. The good oxygen removal capability of Ru catalyst thus makes it an excellent choice for bio-oil upgrading. We thus

propose the formation of alkanes to be the dominant product in the gas phase hydrogenation of furfural on Ruthenium surfaces. One of the possible routes of the utilization of the formed alkanes is the direct blending into straight run gasoline in existing petroleum complexes.

3. Conclusions

In this study, a detailed reaction network, involving multiple possible pathways for furfural hydrodeoxygenation on Ru(001) surface is developed using first principles DFT calculations. Reaction free energies and free energy barriers for the catalytic

conversion of furfural to FA, THFA, MF, MTHF, 1,2 and 1,5 pentane diols, cyclopentanol, pentanol, pentanes and furan were computed. The first activation of furfural can take place via 6 possible reaction pathways, namely C¹ – O or C_{ring} hydrogenation, C¹ – O or C_{ring} – O scission, C¹ – C² dissociation and C¹ – H scission. Hydrogenation of the formyl group followed by ring hydrogenation leads to THFA formation, with the highest barrier of 126 kJ/mol. The preferred pathway for furan formation proceeds via a C¹ – H cleavage followed by a C¹ – C² cleavage. Furan formation, though thermodynamically favored, is kinetically limited by the high ring carbon hydrogenation barrier of 164 kJ/mol. C⁵ – O scission (Ring opening of furfural) and C¹ – O hydrogenation are facile and kinetically competitive with barriers of 64 and 81 kJ/mol. Ring opening before or after C¹ – O hydrogenation, opens up the pathway for the formation of pentane diols, cyclopentanol and pentanes. Pentane formation proceeds after ring opening by removal of the oxygen via deoxygenation to form pentenes, which hydrogenate to form pentanes. The deoxygenation of furfural molecule proceeds *after* ring opening and provides evidence of the excellent oxygen removal ability of Ruthenium. Our calculations indicate that pentane formation is both thermodynamically and kinetically favored over diols and is likely to be the dominant product in the vapor phase hydrogenation of furfural over Ru catalysts. The results are in agreement with experimental studies of bio-oil upgrading on Ru/C catalysts where long chain aliphatic compounds have been identified in the upgraded bio-oil. Our present model assumes a low H coverage on the surface and hence can be assumed to be an acceptable model at low H₂ pressures, typical of vapor phase HDO studies. The present study provides mechanistic understanding into the overall free energy landscape for HDO of furfural on Ruthenium surfaces for the *first* time and will stimulate further experimental studies for the vapor phase upgrading of bio-oil.

Computational Methods

Spin restricted Density Functional Theory calculations were performed using plane wave energy cut off of 450 eV and a projector-augmented wave method, as implemented in the Vienna Ab-initio Simulation Package (VASP)^[60-61] developed at the Fakultät für Physik of Universität Wien. In order to account for the significant non-local interactions present in model systems like furfural, the vdW-DF functional^[62-63] was employed in our calculations. Conventional functionals like PBE may not capture dispersion interactions associated with adsorption of aromatic compounds on transition metal surfaces. Liu et al. have shown the PBE functional to underestimate furfural adsorption energies significantly on Pd(111), Pt(111) and Cu(111) surfaces^[64]. The vdW-DF functional has been shown to work well for describing CO adsorption on Co(0001)^[65-66] and Pt(111)^[67] surfaces and also for thiophene adsorption on Cu(110)^[68]. To the best of our knowledge, no experimental data for the adsorption of furanics on Ru surfaces exist. However, on the Pd(111) surfaces, the computed adsorption energy of furan (-93 kJ/mol) using the vdW-DF functional is in excellent agreement with the experimental values of -91 and -99 kJ/mol^[62, 69]. Furfural adsorbs in the η² (C-O) configuration on both Ru and Pd surfaces and hence we believe the vdW-DF functional would be a good descriptor for furfural adsorption on Ru surfaces too. A (3x3x1) Monkhorst pack grid with a smearing width of 0.2 eV was found to be sufficient for sampling the Brillouin zone. Geometry optimization was carried out using

the conjugate gradient algorithm, with a force convergence criteria of 0.15 eV/Å. A stricter force convergence criteria of 0.03 eV/Å changed the energy of selected intermediates by less than 2 kJ/mol. Vibrational frequencies of all the reactants and products were also carefully analyzed and no imaginary frequencies were observed (refer to Table S6 in the supporting information).

Ruthenium was modelled as a 3 layer, p(4x4) unit cell by considering its most stable facet, the Ru (001) surface. A 10 Å vacuum was maintained between repeated slabs. The bottom layer was kept fixed and the top two layers were relaxed in all our calculations. The optimized lattice constant for Ru was computed to be 2.744 Å with a c/a ratio of 1.58. Energy convergence calculations with thicker slabs and larger unit cells led to no significant change in the total energies (*cf.* Table S2 and Table S3 in the supporting information). Transition state structures were estimated using the climbing image Nudged Elastic Band (NEB) method^[70]. 6-8 transition state structures were used in the NEB and the forces were minimized to 0.1 eV/Å. The NEB image closest to the transition state was further optimized using the quasi Newton algorithm and vibrational frequency analysis was done to confirm the transition state (Table S5). All reaction energies and activation barriers are reported as the Gibbs free energy change between the transition state/products and the reactants in separate unit cells at reaction conditions of 500 K and 1 bar pressure (Equation 1). The zero point energy, entropy and enthalpy correction for different adsorbed configurations are calculated from statistical thermodynamics.^[71] Harmonic vibrational frequencies were calculated by considering the adsorbed species as a harmonic oscillator and replacing the translational or rotational modes of the molecule with the vibrational modes corresponding to frustrated translation and rotation on the surface.^[72-73] This assumption is valid for strongly bound adsorbate species for which the diffusion barriers over the surface are large relative to the thermal energy of the adsorbate (k_BT), as proposed by Blaylock et al.^[72] Furfural adsorbs strongly on the Ru(001) surface (binding energies of -130 kJ/mol) which corroborates the use of the standard harmonic oscillator partition function for calculating entropies of the adsorbed species. The procedure for the calculation of the adsorption free energies and Gibbs free energies is presented in detail in the supporting information (SI.1).

Acknowledgements

This research is supported by the Ministry of Education, Singapore, under the Academic Research Fund (AcRF) Tier-2 grant (Grant No. T2-1-082).

Keywords: Biomass, DFT, Hydrodeoxygenation, Ruthenium, Mechanism

- [1] T. P. Vispute, H. Y. Zhang, A. Sanna, R. Xiao, G. W. Huber, *Science* **2010**, 330, 1222-1227.
- [2] G. W. Huber, S. Iborra, A. Corma, *Chemical Reviews* **2006**, 106, 4044-4098.
- [3] A. V. Bridgwater, *Chemical Engineering Journal* **2003**, 91, 87-102.
- [4] Y. S. Choi, P. A. Johnston, R. C. Brown, B. H. Shanks, K. H. Lee, *Journal of Analytical and Applied Pyrolysis* **2014**, 110, 147-154.
- [5] D. Mohan, C. U. Pittman, P. H. Steele, *Energy Fuels* **2006**, 20, 848-889.

- [6] S. Czernik, A. V. Bridgwater, *Energy Fuels* **2004**, *18*, 590-598.
- [7] P. M. Mortensen, J. D. Grunwaldt, P. A. Jensen, K. G. Knudsen, A. D. Jensen, *Applied Catalysis a-General* **2011**, *407*, 1-19.
- [8] Y. T. Cheng, G. W. Huber, *ACS Catalysis* **2011**, *1*, 611-628.
- [9] J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo, G. W. Huber, *Journal of Catalysis* **2011**, *279*, 257-268.
- [10] C. Mukarakate, M. J. Watson, J. ten Dam, X. Baucherel, S. Budhi, M. M. Yung, H. X. Ben, K. Lisa, R. M. Baldwin, M. R. Nimlos, *Green Chemistry* **2014**, *16*, 4891-4905.
- [11] M. W. Nolte, B. H. Shanks, *Energy Technology* **2016**.
- [12] A. V. Bridgwater, *Biomass & Bioenergy* **2012**, *38*, 68-94.
- [13] A. V. Mironenko, M. J. Gilkey, P. Panagiotopoulou, G. Facas, D. G. Vlachos, B. J. Xu, *Journal of Physical Chemistry C* **2015**, *119*, 6075-6085.
- [14] A. V. Mironenko, D. G. Vlachos, *Journal of the American Chemical Society* **2016**, *138*, 8104-8113.
- [15] P. Panagiotopoulou, N. Martin, D. G. Vlachos, *Chemsuschem* **2015**, *8*, 2046-2054.
- [16] P. Panagiotopoulou, D. G. Vlachos, *Applied Catalysis A-General* **2014**, *480*, 17-24.
- [17] V. Vorotnikov, G. Mpourmpakis, D. G. Vlachos, *ACS Catalysis* **2012**, *2*, 2496-2504.
- [18] S. Oh, H. Hwang, H. S. Choi, J. W. Choi, *Fuel* **2015**, *153*, 535-543.
- [19] C. A. Mullen, A. A. Boateng, S. E. Reichenbach, *Fuel* **2013**, *111*, 797-804.
- [20] A. Sanna, T. P. Vispute, G. W. Huber, *Applied Catalysis B-Environmental* **2015**, *165*, 446-456.
- [21] T. P. Vispute, G. W. Huber, *Green Chemistry* **2009**, *11*, 1433-1445.
- [22] J. Wildschut, M. Iqbal, F. H. Mahfud, I. Melian-Cabrera, R. H. Venderbosch, H. J. Heeres, *Energy Environ. Sci.* **2010**, *3*, 962-970.
- [23] J. Wildschut, F. H. Mahfud, R. H. Venderbosch, H. J. Heeres, *Industrial & Engineering Chemistry Research* **2009**, *48*, 10324-10334.
- [24] J. Wildschut, I. Melian-Cabrera, H. J. Heeres, *Applied Catalysis B-Environmental* **2010**, *99*, 298-306.
- [25] S. Sitthisa, W. An, D. E. Resasco, *Journal of Catalysis* **2011**, *284*, 90-101.
- [26] S. Sitthisa, T. Pham, T. Prasomsri, T. Sooknoi, R. G. Mallinson, D. E. Resasco, *Journal of Catalysis* **2011**, *280*, 17-27.
- [27] S. Sitthisa, D. E. Resasco, *Catalysis Letters* **2011**, *141*, 784-791.
- [28] S. Sitthisa, T. Sooknoi, Y. G. Ma, P. B. Balbuena, D. E. Resasco, *Journal of Catalysis* **2011**, *277*, 1-13.
- [29] D. C. Elliott, T. R. Hart, *Energy Fuels* **2009**, *23*, 631-637.
- [30] R. C. Runnebaum, T. Nimmanwudipong, D. E. Block, B. C. Gates, *Catalysis Science & Technology* **2012**, *2*, 113-118.
- [31] D. C. Elliott, T. R. Hart, G. G. Neuenschwander, L. J. Rotness, A. H. Zacher, *Environmental Progress and Sustainable Energy* **2009**, *28*, 441-449.
- [32] N. Li, G. A. Tompsett, G. W. Huber, *Chemsuschem* **2010**, *3*, 1154-1157.
- [33] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446-1450.
- [34] R. H. He, P. Ye, B. C. English, J. A. Satrio, *Bioresource Technology* **2009**, *100*, 5305-5311.
- [35] N. Lohitharn, B. H. Shanks, *Catalysis Communications* **2009**, *11*, 96-99.
- [36] J. Adam, M. Blazso, E. Meszaros, M. Stocker, M. H. Nilsen, A. Bouzga, J. E. Hustad, M. Gronli, G. Oye, *Fuel* **2005**, *84*, 1494-1502.
- [37] Y. Shi, Y. L. Zhu, Y. Yang, Y. W. Li, H. J. Jiao, *ACS Catalysis* **2015**, *5*, 4020-4032.
- [38] Q. X. Cai, J. G. Wang, Y. G. Wang, D. H. Mei, *AIChE Journal* **2015**, *61*, 3812-3824.
- [39] Y. Nakagawa, M. Tamura, K. Tomishige, *ACS Catalysis* **2013**, *3*, 2655-2668.
- [40] J. W. Medlin, *ACS Catalysis* **2011**, *1*, 1284-1297.
- [41] V. V. Ordonsky, J. C. Schouten, J. van der Schaaf, T. A. Nijhuis, *Applied Catalysis a-General* **2013**, *451*, 6-13.
- [42] Y. Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, *ChemCatChem* **2012**, *4*, 1791-1797.
- [43] Y. Nakagawa, K. Takada, M. Tamura, K. Tomishige, *ACS Catalysis* **2014**, *4*, 2718-2726.
- [44] N. S. Biradar, A. M. Hengne, S. N. Birajdar, P. S. Niphadkar, P. N. Joshi, C. V. Rode, *ACS Sustain. Chem. Eng.* **2014**, *2*, 272-281.
- [45] R. Alamillo, M. Tucker, M. Chia, Y. Pagan-Torres, J. Dumesic, *Green Chemistry* **2012**, *14*, 1413-1419.
- [46] O. R. Inderwildi, S. J. Jenkins, D. A. King, *Journal of Physical Chemistry C* **2008**, *112*, 1305-1307.
- [47] P. Van Helden, J. A. Van Den Berg, I. M. Ciobăcă, *Catalysis Science and Technology* **2012**, *2*, 491-494.
- [48] R. Q. Fang, H. L. Liu, R. Luque, Y. W. Li, *Green Chemistry* **2015**, *17*, 4183-4188.
- [49] Y. Nakagawa, K. Tomishige, *Catalysis Today* **2012**, *195*, 136-143.
- [50] X. H. Qian, *Journal of Physical Chemistry B* **2013**, *117*, 11460-11465.
- [51] S. H. Mushrif, J. J. Varghese, D. G. Vlachos, *Physical Chemistry Chemical Physics* **2014**, *16*, 19564-19572.
- [52] Q. T. Trinh, B. K. Chethana, S. H. Mushrif, *Journal of Physical Chemistry C* **2015**, *119*, 17137-17145.
- [53] M. K. Bradley, J. Robinson, D. P. Woodruff, *Surface Science* **2010**, *604*, 920-925.
- [54] T. Mizugaki, T. Yamakawa, Y. Nagatsu, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *ACS Sustain. Chem. Eng.* **2014**, *2*, 2243-2247.
- [55] W. J. Xu, H. F. Wang, X. H. Liu, J. W. Ren, Y. Q. Wang, G. Z. Lu, *Chemical Communications* **2011**, *47*, 3924-3926.
- [56] M. Hronec, K. Fulajtarova, *Catalysis Communications* **2012**, *24*, 100-104.
- [57] M. Hronec, K. Fulajtarova, T. Liptaj, *Applied Catalysis A-General* **2012**, *437*, 104-111.
- [58] J. L. Davis, M. A. Barteau, *Journal of the American Chemical Society* **1989**, *111*, 1782-1792.
- [59] R. Shekhar, M. A. Barteau, R. V. Plank, J. M. Vohs, *Journal of Physical Chemistry B* **1997**, *101*, 7939-7951.
- [60] G. Kresse, J. Furthmüller, *Physical Review B: Condensed Matter* **1996**, *54*, 11169-11186.
- [61] G. Kresse, J. Furthmüller, *Computational Material Science* **1996**, *6*, 15-50.
- [62] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, *Physical Review Letters* **2004**, *92*, 246401.
- [63] J. Klimeš, D. R. Bowler, A. Michaelides, *Physical Review B* **2011**, *83*, 195131.
- [64] B. Liu, L. Cheng, L. Curtiss, J. Greeley, *Surface Science* **2014**, *622*, 51-59.
- [65] G. T. K. K. Gunasooriya, A. P. van Bavel, H. P. C. E. Kuipers, M. Saeys, *Surface Science* **2015**, *642*, L6-L10.
- [66] A. Banerjee, A. P. van Bavel, H. P. C. E. Kuipers, M. Saeys, *ACS Catalysis* **2015**, *5*, 4756-4760.
- [67] P. Lazic, M. Alaei, N. Atodiresei, V. Caciuc, R. Brako, S. Blugel, *Physical Review B* **2010**, *81*.
- [68] P. Sony, P. Puschnig, D. Nabok, C. Ambrosch-Draxl, *Physical Review Letters* **2007**, *99*.
- [69] R. M. Ormerod, C. J. Baddeley, C. Hardacre, R. M. Lambert, *Surface Science* **1996**, *360*, 1-9.
- [70] G. Mills, H. Jónsson, *Physical Review Letters* **1994**, *72*, 1124-1127.
- [71] K. I. Karl, *Appendix B. In Computational Thermochemistry ACS Symposium Series 677 Washington DC, 1998*.
- [72] D. W. Blaylock, T. Ogura, W. H. Green, G. J. O. Beran, *Journal of Physical Chemistry C* **2009**, *113*, 4898-4908.
- [73] C. R. Chang, Z. J. Zhao, K. Kohler, A. Genest, J. Li, N. Rosch, *Catalysis Science & Technology* **2012**, *2*, 2238-2248.

FULL PAPER

Entry for the Table of Contents

FULL PAPER

Complete reaction network of the catalytic hydrodeoxygenation of biomass pyrolysis derived bio-oil on Ruthenium catalyst is elucidated using Density Functional Theory calculations. Reaction pathways for the formation of Furfuryl alcohol, Tetrahydrofurfuryl alcohol, Methylfuran, Methyltetrahydrofuran, Cyclopentanol, 1,2 and 1,5 pentane diols, Furan and Pentanes are established.

Arghya Banerjee, Samir H. Mushrif*

Page No. – Page No.

Title: Reaction Pathways for the Deoxygenation of Biomass Pyrolysis Derived Bio-Oil on Ru: A DFT study using furfural as a model compound