Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Catalytic conversion of biomass into hydrocarbon fuel precursors

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Abstract

We report of a new pyrolytic pathway for biomass conversion to hydrocarbon fuel precursors. The process entails the conversion of multifunctional oxygenates generated from biomass pyrolysis over a metal oxide catalyst into ketonic-rich monofunctional molecules suitable for making hydrocarbon fuel components for gasoline, diesel, and jet fuel. A number of catalysts were explored including anatase TiO_2 nanorods, CeO_x-TiO_2 mixed oxides, pure CeO_2, ZrO_2, and MgO. Under pyrolysis conditions, the ceria-based catalysts were effective in the conversion of hydroxy-carbonyls, anhydrosugars, and carboxylic acids into acetone, 2-butanone, pentanones, C6/C7 ketones, cyclopentanone, and 2-cyclopentenones. The highest carbon yield (23.5%) of ketonoic precursors was achieved on the pure CeO_2.

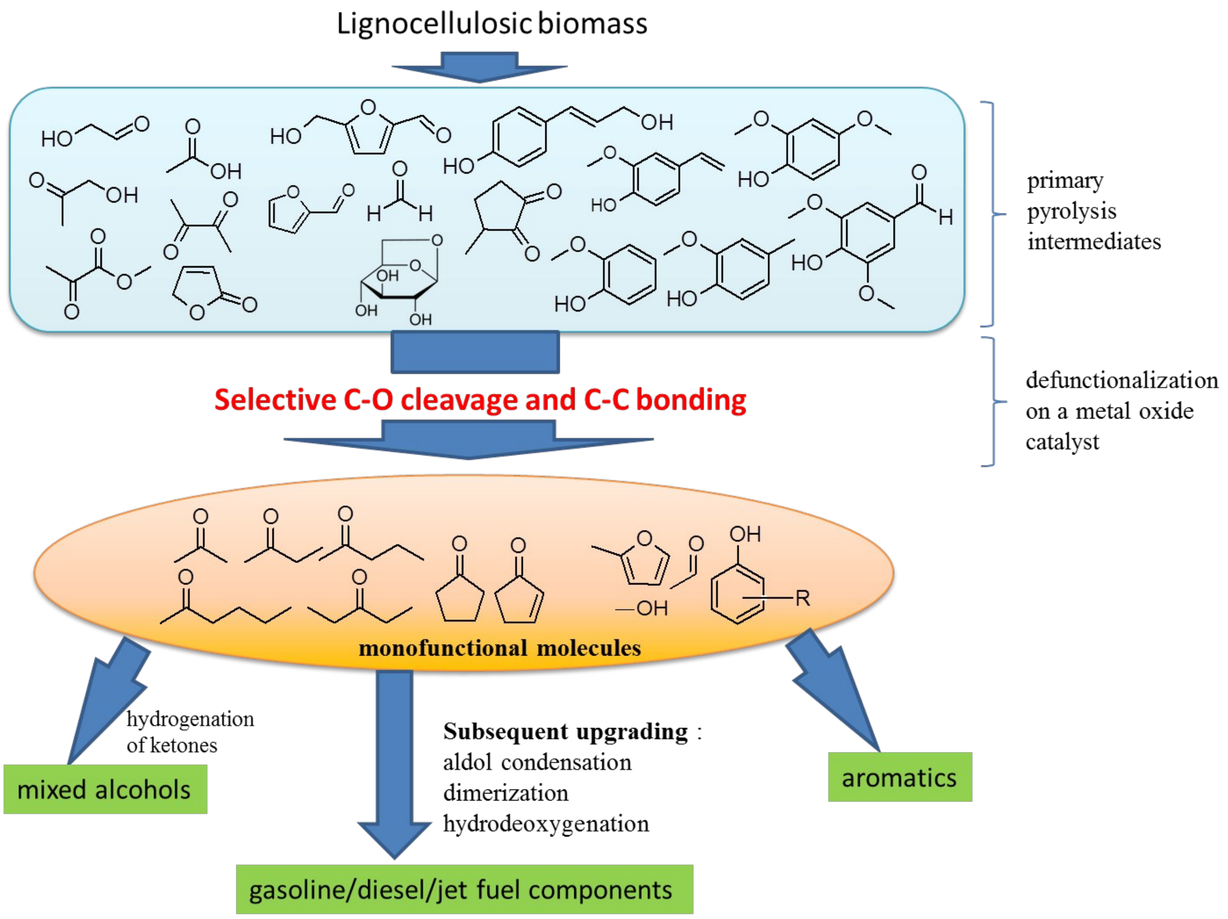
Keywords: Biomass: catalytic pyrolysis; monofunctional molecules;metal oxide catalysts; pyrolysis vapors upgradinig

Direct catalytic upgrading of biomass pyrolysis vapors (*in-situ* or *ex-situ*) is a promising thermochemical pathway for the production of liquid hydrocarbons that could potentially be used as substitutes for gasoline, diesel, and jet fuels. However, current efforts show that the production of fungible liquid hydrocarbons from lignocellulosic biomass via pyrolysis platform continues to be a technological challenge due to the complexity and functionalities of the primary oxygenates[1-7]. In recent years, the conversion of biomass into platform molecules or monofunctional intermediates has become one of the rapidly evolving strategic approaches to producing hydrocarbon biofuels [8, 9]. This attractive strategy has been demonstrated extensively in aqueous phase reforming (APR) of carbohydrate feeds, where a Pt-Re/C catalyst is used at elevated pressures (20-30 bar) and low temperature (210-250 ^oC) to promote C-O cleavage leading to the formation of ketones and alcohols as monofunctional intermediates [9, 10]. These intermediates can then be converted into diesel fuel components using a dual catalytic bed system of $Ce_1Zr_1O_x$ and Pd/ZrO_2 where ketonization, aldol condensation, and dehydration/hydrogenation reactions are promoted. Alternatively, the monofunctional species can be converted to gasoline fuel component by first hydrogenating them to alcohols and then transforming them with ZSM-5 into aromatics/olefins[8]. Conceptually, this strategy which offers increased flexibility in producing hydrocarbons could be adopted to biomass pyrolysis; but it would require the promotion of controlled defunctionalization and deoxygenation of the primary pyrolysis intermediates.

Herein, we propose that ketonic and other useful mono-oxygenated functional molecules could be produced from lignocellulosic biomass as hydrocarbon building blocks in a one-step pyrolytic process at atmospheric pressure without the use of external hydrogen as illustrated in Scheme 1. In this process, the mixture of hydroxy-carbonyls, acids, sugars, and multifunctional phenols formed from the initial pyrolytic breakdown of the biomass are subjected to selective C-O cleavage and C-C bond formation over a suitable metal oxide catalyst. As a result, useful intermediates which could undergo further C-C coupling reactions for subsequent upgrading into hydrocarbons are produced. Ketones are examples of such desirable building blocks that have sufficient functional moieties to undergo C-C bond forming reactions. The advantage of such a strategy is that, different types of fuels/chemicals can then be produced.

In our investigation, we focused on promoting partial deoxygenation reactions such as ketonic decarboxylation and aldol condensation. These well-known reactions which occur over a number of metal oxides are attractive because they promote C-C coupling reactions, with the simultaneous removal of oxygen. Typically, metal oxides such as TiO_2, ZrO_2, CeO_2, MnO_2, Al_2O_3, and Fe_2O_3 are used [9, 11, 12]. It is worth noting that ketonization in particular has received considerable attention for bio-oil upgrading in recent times; but it has been explored mostly for the conversion of carboxylic acids to ketones in an effort to reduce the acidity of bio-oil [9, 13, 14]. On the other hand, the conversion of other pyrolysis oxygenates to ketones have received far less attention from many research groups. For the catalytic strategy proposed herein, the novelty is in the formation of ketonic compounds from other families of oxygenates (hydroxy-carbonyls and sugars) as well; and not just the acid-rich fraction. In fact, the total yield of carboxylic acids produced in biomass pyrolysis are about 3-6 wt % of the biomass [15]; hence it is important that other oxygenates are transformed as well if the goal is to produce ketonic molecules as the primary product. Model studies show that it is possible for aldehydes, alcohols, and esters to be converted to ketones via dimerization [11, 16, 17]. Nevertheless, in a study by Hakim et. al [18] using a CeZrOx mixed oxide catalyst, they observed that common pyrolysis compounds such as furfural have significant inhibition on ketonization while levoglucosan and cresol exhibit negligible conversion over the mixed oxide catalyst.

This finding suggests that ketonization of the entire pyrolysis compounds could be challenging. Nevertheless, a recent study by Wan et. al [19] showed that Ru/TiO_2 has a promising ketonization activity for actual pyrolysis oxygenates in the vapor phase. In their studies, the yields of levoglucosan, acetol, and acetic acid decreased whilst ketones such as acetone (1.62 wt%), butanone (0.8 wt%), and 2-cyclopenten-1-one (1.51 wt%) were increased.



Scheme 1. A pyrolytic strategy for producing monofunctional precursors that is useful in producing gasoline, diesel, and jet fuel hydrocarbon components.

Based on the results from the study by Wan and co-workers, we focused our initial research on anatase titania nanorods to test our hypothesis. A series of synthesized titania rods were screened: TiO_2 nanorods, 1% and 5% Ni/TiO_2 nanorods, and 1% and 5% Pt/TiO_2 nanorods. From these tests, we found that the synthesized nanorods as shown in Table S2 had low catalytic activity for ketonization of the multifunctional oxygenated species. Thus, in the next step, we tested a commercial form of the anatase TiO_2 including its impregnated forms with 5wt% each of Ni and Pt metals. Furthermore, in search for a much better performing catalyst, we conducted an additional investigation with synthesized ceria-titania mixed metal oxides (CeO_x-TiO_2) and pure CeO_2. The results showed that ceria increased the formation of ketonic species. We then compared the performance of ceria catalysts with other commercial forms of oxide catalysts including ZrO_2, MgO, CaO/CeO_2, and rutile 1%Mn/TiO_2. The outcome of these experiments indicated clearly that under pyrolysis conditions, CeO_2 possess higher ketonization activity compared to all the catalysts that were investigated. Also, the effect of pyrolysis temperature on the formation of ketones was studied with cellulose using the CeO_2 metal oxide. Finally, to gain insight into the conversion of non-acidic oxygenates into ketones, hydroxyacetaldehyde was reacted over CeO_2. The vapor phase reaction of the pyrolysis oxygenates from sugar maple over each catalyst studied was conducted using a CDS Analytical Pyroprobe 5200 (CDS Analytical, PA) interfaced with Agilent 7890A Gas Chromatograph and 5975C Mass Spectrometer detector. The physicochemical properties of the sugar maple feedstock used are shown in Table S1. All the reactions over the metal oxide catalysts were performed at 550 ^{o}C and a catalysts-to-feed ratio of 8:1was used.

Table S2 shows the carbon yields of the monofunctional molecules that were quantified by GC/MS analysis in the first experiment. The main linear ketones identified were acetone, 2-butanone, 2-pentanone, 3-pentanone, 3-penten-2-one, and C_6-C_7 ketones. The cyclic ketones include 2-cyclopenten-1-one(s) and cyclopentanone. Other useful monofunctional species such as methanol, acetaldehyde, furan(s), and simple phenols were also detected. From the data in Table S2, it can be seen that the catalytic activities of the TiO_2 nanorods and the impregnated forms with Ni and Pt were low. Nonetheless, the yields of the ketones obtained by the rods were higher than those reported by Wan et. al [19] with the use of Ru/TiO_2. The overall carbon yield of the targeted monofunctional molecules produced by the nanorods were 10.78%, 5.43%, 7.29%, 9.02%, and 12.93% for TiO_2, 1%Ni/TiO_2, 5%NiTiO_2, 1% Pt/TiO_2, and 5%Pt/TiO_2 respectively. The impregnation of the rods with nickel was found to decrease the ketonization activity. Instead, the supported Pt on the rods resulted in a slight increase in the performance of the TiO_2 rods. As mentioned, it was important in this study that other oxygenated species besides the acids undergo ketonic condensation so as to increase the yield of the ketonic products. The conversion analysis of a selected number of the primary pyrolysis oxygenates after the reaction over the rods in Figure S2 generally show that hydroxycarbonyls (particularly, hydroxyacetaldehyde (HAA) and 5-hyroxymethyl furfural (5HMF)), levoglucosan (LG), furanone(FU), and methyl pyruvate (MP) were reactive over the titania rods and underwent significant conversion. For instance, the carbon yield of HAA in the blank run was 9.6%, but in most of the catalytic runs with TiO_2 rods, the yield was less than 1.5% which corresponds to over 85% conversion. In contrast, furfural (FF), acetic acid (HAc), and hydroxyacetone (HA) were less reactive over the TiO_2 rods. In fact, FF was the most unreactive over TiO_2rods. In some cases, the yields of FF increased by 50% after the catalytic reaction.

In comparison with the TiO_2 nanorods, the commercial anatase nanopowder exhibited a promising ketonic decarboxylation activity. In Table 1, it can be seen that a relatively higher carbon yield of ketones was obtained for the TiO_2 nanopowder: acetone (4.5%), 2-butanone (1.86%), C_6-C_7 ketones (0.95%), 2-cyclopentenone (1.45%), and cyclopentanone (0.75%). This suggests that the ketonization reaction under pyrolysis condition may be sensitive to the surface morphology and structure of TiO_2. One thing to note is that, the carbon yield for the cyclic ketones for the nanorods was higher than the commercial nanopowder. It suggests that cyclization is promoted more on the rods. In addition, the combined carbon yields for methanol, acetaldehyde, methylfurans and simple phenols were higher for the rods.

Table 1. Summary of the carbon yields of the primary monofunctional species obtained after reacting biomass pyrolysis vapors over commercial anatase TiO_2 nanopowders:(Reaction conditions: 550 ^oC and catalyst-to-feed ratio of 8:1.

Catalysts	*Blank*	*Anatase TiO_2*	*5 wt% Ni/TiO_2*	*5 wt% Pt/TiO_2*
Monofunctional molecules, Yield (%C)				
Linear ketones				
Acetone	BDL	4.47 ± 0.47	3.40 ± 0.19	1.34 ± 0.28
2-Butanone	BDL	1.86 ± 0.04	1.76 ± 0.25	1.74 ± 0.19
2-Pentanone	BDL	0.18 ± 0.01	0.14 ± 0.01	0.04 ± <0.01
3-Pentanone	BDL	0.22 ± 0.06	0.09 ± 0.01	0.03 ± <0.01
3-Penten-2-one	BDL	0.49 ± 0.04	0.37 ± 0.02	0.40 ± <0.01
C6/C7 ketones	BDL	0.06 ± <0.01	0.12 ± 0.01	BDL
2-Cyclopenten-1-one(s)	BDL	1.45±0.15	2.83 ± 0.35	1.32 ± 0.03
Cyclopentanone	BDL	0.75±0.09	0.58 ± 0.03	0.73 ± 0.01
Other useful monofunctional species				
Methanol		0.68 ± 0.13	0.67 ± 0.01	BDL
Acetaldehyde		0.78 ± 0.10	0.91 ± 0.06	0.11 ± <0.01
Furan(s)		1.57 ± 0.04	1.97 ± 0.13	1.11 ± 0.05
Simple phenols	BDL	0.84 ± 0.12	0.88 ± 0.10	0.56 ± 0.01
Effect on selected primary pyrolysis oxygenates				
Hydroxyacetaldehyde	9.61 ± 1.05	0.03 ± <0.01	0.07 ± <0.01	0.03 ± <0.01
Acetic acid	4.16 ± 0.48	1.57 ± 0.8	1.48 ± 0.81	1.34 ± 0.5
Levoglucosan	4.04 ± 0.39	0.07 ± <0.01	0.20 ± 0.06	BDL
Hydroxyacetone	1.22 ± 0.1	BDL	BDL	0.05 ± <0.01
Methyl pyruvate	0.70 ± 0.06	0.10 ± <0.01	0.01 ± <0.01	0.01 ± <0.01
Furfural	0.55 ± 0.03	0.21 ± <0.01	0.19 ± 0.2	0.09 ± 0.01
5-hydroxymethyl furfural	0.42 ± 0.05	0.02 ± <0.01	BDL	BDL
2(5H)-Furanone	0.36 ± 0.01	0.02 ± <0.01	0.02 ± <0.01	0.02 ± <0.01

BDL=below detection limit

The conversions of the pyrolysis oxygenates over TiO_2 nanopowder were relatively higher than on the TiO_2 nanorods (Figure S3). With the nanopowders, the yields of most of the multi-functional oxygenates decreased significantly, but HAc remained unchanged. This means, the ketonization of the carboxylic acids did not occur readily over both TiO_2 catalysts under the pyrolytic conditions used in the present study. For instance, the conversion of HAc over the nanopowders was about 60%, whilst on the nanorods, the yield of HAc increased up to 50%. One of the reasons for the high yields of HAc after the catalytic reaction may be because it also formed as a product from the ketonization of other oxygenates. In fact, this was observed in the ketonization of hydroxyacetone [18].

The results in Table 1 also show that the impregnation of the nanopowders with Ni and Pt metals at 5wt% level did not enhance the catalytic conversion of the pyrolysis oxygenates into ketones. Rather, the use of Ni/TiO_2 altered the selectivity of the produced ketones; the yield of 2-Cyclopentenones doubled and yields of linear ketones decreased by 20%. The yield of furans and simple phenols also increased slightly. On the other hand, the use of Pt/TiO_2 decreased the overall yield of the ketones and other useful mono-oxygenated species. Besides, other highly oxygenated species such as diketones (2,3-butanedione and 1,2-cyclopentadione), methyl acetates, and multifunctional phenolics including benzenediols were difficult to convert over Pt/TiO_2 at the catalyst-to-feed (C/F) ratio of 8:1 (See Figure S4). The apparent effect of the Pt-promoted TiO_2 was in the formation of aromatic hydrocarbons. This is because the Pt metals increased dehydration/hydrogenation reactions. Hence, at a higher C/F ratio (15:1), we observed that the pyrolysis oxygenates were converted solely to aromatic hydrocarbons without any formation of ketones (not shown). These results indicate that a complex interplay occurs upon metal-oxide (Pt, Ni ←→TiO_2) interaction, which could be used to steer reaction selectivity. Nonetheless, it should be pointed out that the production of aromatics and olefins was not of interest in the present study so it was not pursued further.

In search for a better preforming catalyst that can promote ketonic condensation of the actual biomass oxygenates in the vapor phase under pyrolysis conditions, we then explored CeO_2-TiO_2 ceria based metal oxides even though it was found that certain oxygenates (e.g., furfural and levoglucosan) were unreactive over $CeZrO_x$ and also reduced the ketonization activity[18]. Nevertheless, CeO_2-based catalysts in general have been shown to possess higher ketonization activity [11, 12, 16]. Figure 1 below shows the results from the reaction of the pyrolysis oxygenates over ceria-titania mixed metal oxides ($CeTiO_2$) and pure CeO_2. The incorporation of low loadings of nanostructured ceria into titania seems to improve the conversion into mono-functional compounds. In comparison to anatase TiO_2, the reactions over 15$CeTiO_2$ catalyst specifically produced more 2-butanone and 2-cyclopentenones as well as higher yields of acetaldehyde and simple phenols. However, the highest formation of ketones was observed with pure CeO_2: acetone (5.84%), 2-butanone (4.87%), pentanone (2.37%), C5-C7 ketones (1.01%), 2-cyclopenten-1-one (2.86%), and cyclopentanone (4.31%). Overall, the mono-oxygenated functional intermediates produced with CeO_2 amounted to 23% of the biomass carbon. The ketonic fraction constituted over 90% of the total monofunctional compounds produced as shown in Figure 2. We found that complete conversion of acetic acid, furfural, hydroxycarbonyls, and sugars were achievable over pure CeO_2 under the pyrolysis conditions. This clearly shows that CeO_2 has a higher catalytic activity for the conversion of the multifunctional pyrolysis oxygenated species into ketones relative to the titania-based catalysts used in the study.

The high catalytic activity of CeO_2 in the formation of ketones is typically attributed to its very high oxygen exchange and storage capacity, redox properties (interchangeable Ce^{4+}- Ce^{3+}), and strong Lewis basicity [16, 20, 21]. Ceria also has good chemical stability, refractory properties, resistance to coking, and high propensity towards catalyzing products at very high temperatures[22]. In the conversion of acids over metal oxide catalysts to ketones, it is believed that the reaction either proceeds through the formation of a bulk metal carboxylate or a surface-catalyzed reaction depending on the metal-oxygen bond strength or lattice energy[23]. Nonetheless, it has been recently hypothesized that the production of ketones from acids over CeO_2 is necessitated by the formation of a metal carboxylate intermediate regardless of the pathways (either through the bulk or the surface-catalyzed pathway) [24]. Thus, under the high pyrolytic temperature conditions as used for this work, it is most likely that the hydroxycarbonyls, furfural, sugars, and the acids were transformed to carboxylate type species and hydroxyl groups on the surface of ceria which then underwent adsorbate-adsorbate interactions to form ketonic products and other monofunctional species. Furthermore, considering the different types of oxygen functionalities that reacted and the resultant ketonic product distribution, it suggests that several types of reactions besides the classical ketonization reaction were promoted over CeO_2.

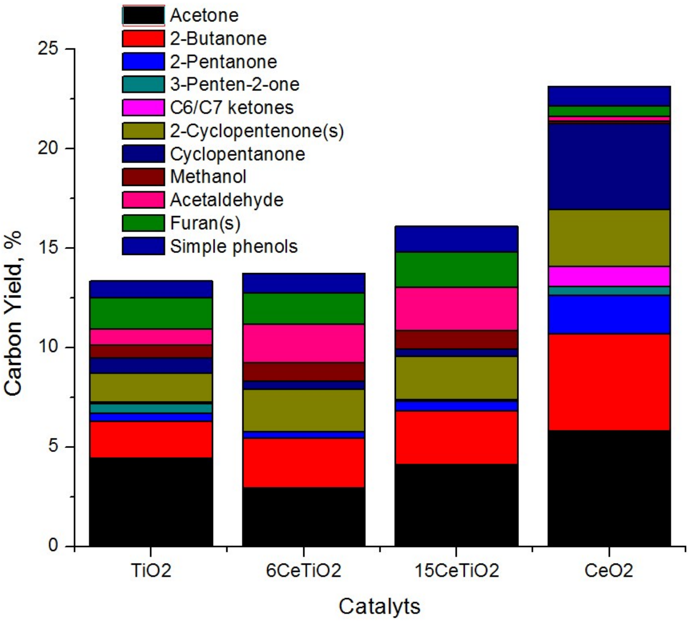


Figure 1. Comparison of the carbon yields of the monofunctional compounds produced from the use of anatase TiO_2 nanopowder, 6%Ce/TiO_2, 15%Ce/TiO_2, and pure CeO_2.

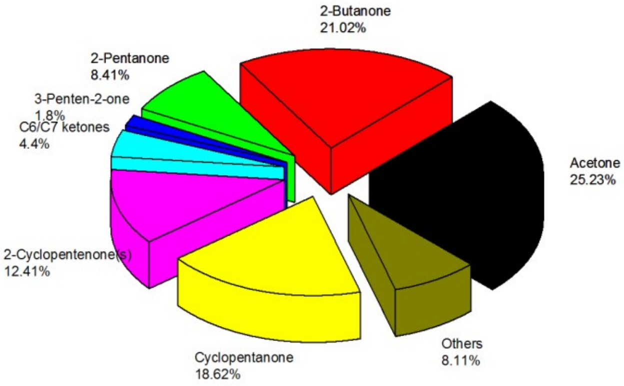


Figure 2. A pie chart of the selectivity of the monofunctional compounds produced from the reaction of the pyrolysis oxygenates over pure CeO_2.

To gain a better understanding of the catalytic transformation of the non-acidic oxygenates over CeO_2 into ketones as demonstrated in this work, we performed under similar reactions an experiment with pure hydroxyacetaldehyde (the highest single chemical compound produced in biomass pyrolysis). The primary reaction products besides CO, CO_2, and H_2O were acetone, hydroxyacetone, 2-butanone, 2-hydroxy-γ-buyrolactone, 2,3-butanedione, acetol acetate, and 2-methylcyclopentenone (Figure 3). At a lower catalysts-to-feed ratio 4:1, it was found that the products were mainly hydroxyacetone, 2-hydroxy-γ-buyrolactone, acetic acid, 2,3-butanedione, and acetates (hydroxy-2-butanone and acetol); which suggests that these species were key intermediates that underwent further conversion to form the ketonic compounds. Based on the product distribution from the reaction of HAA over CeO_2, it can be said that several reactions including dehydrogenation, dehydration, ketonization, aldol condensation, cyclisation, and hydrogenation were promoted on CeO_2. Most of these reactions would have to be necessitated by a transfer hydrogenation reaction as pointed out in a study on the reaction mechanism of acetol over a ceria-based catalysts [18].

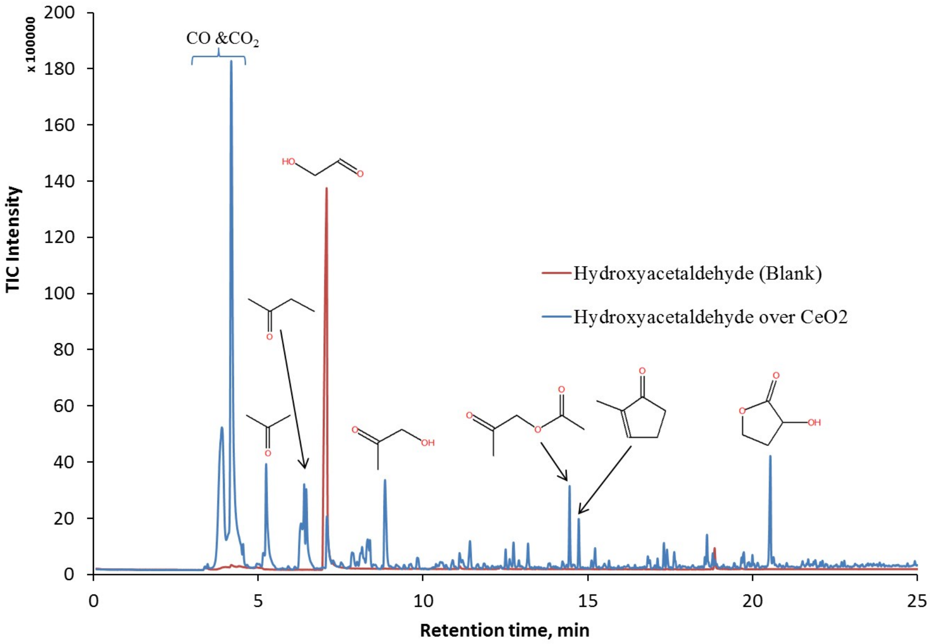


Figure 3. GC/MS chromatogram showing the conversion of hydroxyacetaldehyde over CeO_2 at 550 °C into ketonic products (acetone,2-butanone, and cyclopentenone) and intermediate species (hydroxyacetone, acetol acetate, and 2-hydroxy-γ-buyrolactone)

The reaction temperature was found to influence the conversion of the pyrolysis oxygenates over CeO_2 into ketonic products. In this investigation, pyrolysis oxygenates from cellulose which constituted mainly of LG, HAA, 5-HMF, and FF were reacted over CeO_2 at 450 °C, 550 °C, 600 °C, 650 °C, and 700 °C. Figure 4 shows that the formation of acetone and pentanones increased with increase in temperature. Butanone increased up to 550 °C and a further increase in temperature appeared not to have any influence. On the other hand, the formation of cyclic ketones and higher linear ketones (C_6 and C_7) increased through a maximum between 550 and 600 °C; a further increase in temperature decreased their yields. Overall, the highest amount of ketones was formed at 600 °C. These results suggest that the catalytic activity of CeO_2 increased at higher temperatures possibly due to enhanced reduction of CeO_2 at those reaction conditions, where the catalyst is likely to have a rich concentration of Ce^{3+}.

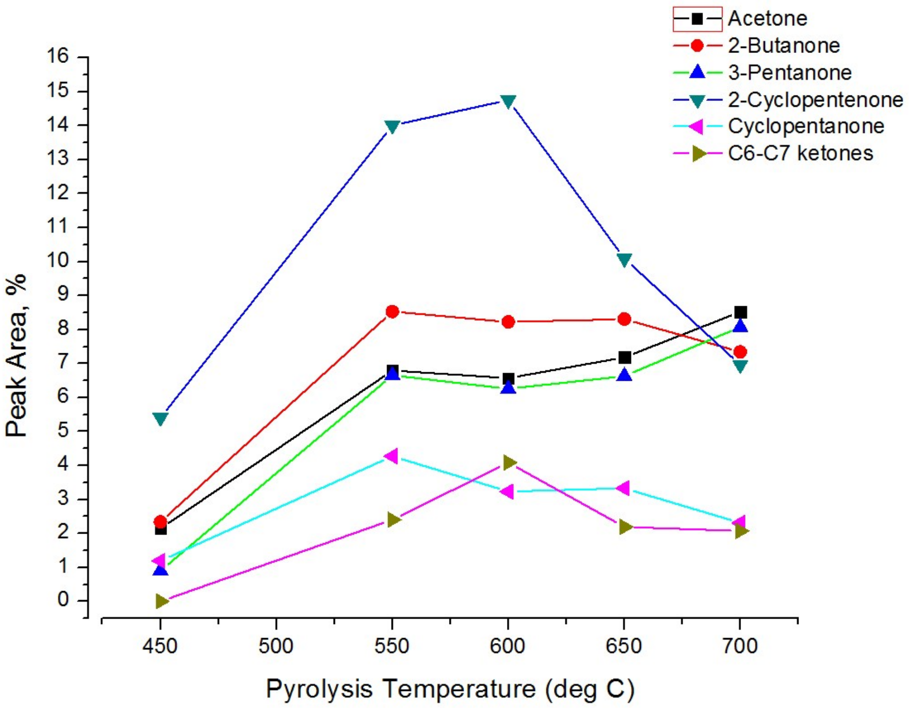


Figure 4. Effect of reaction temperature on the formation of ketones from reactions of cellulose primary pyrolysis oxygenates over pure CeO_2.

Lastly, we compared the performance of pure CeO_2 with several other oxides including ZrO_2, MgO, 1%Mn/TiO_2, and mixed CaO/CeO_2. The results from this test as shown in Table S3 indicated that these set of catalysts were unable to transform the pyrolysis oxygenates into comparable yields of ketonic monofunctional compounds as observed with the pure CeO_2. It was found that the primary pyrolysis oxygenates were less reactive over ZrO_2, MgO and rutile TiO_2. For instance, the highest conversion of acetic acid achieved among these three catalysts was 29%. Consequently, their total carbon yields representing all the monofunctional intermediates produced were very low (less than 8%). In the case of ZrO_2 and MgO, the very poor catalytic performance observed was unexpected because it has been reported that ZrO_2 and MgO are among the most active metal oxides that catalyze the vapor phase ketonization of carboxylic acids [9]. By contrast, the performance of CaO/CeO_2 was much better although the carbon yield (19.59%) of the monofunctional compounds were lower than the pure CeO_2. Specifically, the addition of 25 wt% CaO to CeO_2 decreased the ketonic product yield; acetone, 2-butanone, and cyclopentanone. However, the yields of pentanones, C6/C7ketones, and 2-cyclopentenone increased when CaO was added. The increase in the formation of pentanones and C6/C7 ketones could be an indication that aldol condensation reactions increased which may be attributed to the stronger basic sites on CaO. One of the plausible explanations for the poor catalytic performance of ZrO2, MgO and rutile TiO_2 as observed in this study could be attributed to suppression of the catalytic activity under the upgrading conditions of the pyrolysis vapors. In fact, the high concentration of other oxygenated functionalities, CO_2, and steam under the pyrolysis condition could inhibit their catalytic activity for ketonization and condensation reactions Co-feeding of CO_2, H_2O(g), and other pyrolysis oxygenates in model studies have been shown to inhibit the promotion of ketonization and aldol condensation reactions on a number of metal oxides [18, 25-27]. For instance, in a model study by Liu et al.[25] using acetic acid, it was found that the zirconia based catalyst had a strong CO_2 adsorption strength which resulted in lower activity in the presence of CO_2. It is believed that the formation of carbonates from CO_2 adsorption block the active sites on the surface of the metal oxide. In the same study, it was reported that adsorption of water on the surface of the catalysts also has inhibiting effect on the catalytic activity. Therefore, based on the findings from this work, it can be concluded that the catalytic activity of CeO_2 is less inhibited by pyrolysis conditions and is capable of promoting useful reactions for the conversion of the multifunctional molecules into monofunctional species suitable for upgrading into hydrocarbon fuels.

In summary, this investigation has demonstrated that it is possible to reform the complex mixture of multifunctional oxygenates generated during biomass pyrolysis over a suitable metal oxide into monofunctional precursors that can undergo further downstream processing such as aldol condensation and hydrogenation for conversion into a wide range of hydrocarbon liquid fuels. The ketonic products are desirable because they have sufficient functional moties to undergo C-C coupling with each other or other pyrolysis oxygenates into longer chain aliphatic hydrocarbons. Additionally, the simple phenols and the furans are useful intermediates for forming aromatic hydrocarbons. This demonstrated pyrolytic approach provides a greater degree of flexibility in producing gasoline, diesel, and jet fuels components. The significant finding of the present work is that a variety of pyrolysis oxygenated families (hydroxy-carbonyls and sugars) besides carboxylic acids can be activated to form useful ketonic compounds. Our current results show that not all the known active ketonization catalysts reported in literature are capable of facilitating the formation of ketones even from carboxylic acids under pyrolysis conditions. Among the catalysts tested, we found that ceria-based catalysts are most suitable for the pyrolytic strategy pursued in this work. This suggests that the reducibility of the metal oxide plays an important role in effective conversion of the pyrolysis oxygenates into useful monofunctional precursors. This work opens a new pyrolysis path to renewable fuels or chemicals from biomass.

Experimental Section

A CDS analytical pyroprobe 5200 (CDS Analytical, PA) equipped with a micro reactor was used for the pyrolysis and the reactions over a bed of catalyst. The quantification of products of interest was done with the interfaced Agilent 7890A gas chromatograph and 5975C mass spectrometer detector. The powdered sample of sugar maple (0.2-0.8 mg) was loaded into a quartz tube of 25 mm in length and 1.9 mm in diameter. In the catalytic experiments, the primary vapors from sugar maple pyrolysis were swept through the micro reactor packed with the catalyst under investigation. The loaded sample in the pyroprobe quartz tube and catalyst in the stainless steel tube reactor were held in place at the center with small plugs of quartz wool. The quartz tubes were weighed before and after pyrolysis using a Mettler Toledo MS105 semi-micro balance with sensitivity of 0.01 mg (Mettler Toledo, Greifensee, Switzerland). The Pyroprobe control software was programmed to rapidly heat the sample to the specified temperature and hold for 20 s. The pyrolysis interface zone, valve oven, tenax trap and the transfer line to the GC/MS were all set at 300 ^{o}C.

After the reactions, the vapors and gases were swept by ultra-high purity helium carrier gas into the GC/MS for separation and detection. The products were separated with a 60 m x 0.25 mm DB-1701 capillary column of 0.25 µm film thickness. The GC inlet was set at 275 °C and a split ratio of 75:1 was used. The column followed a temperature program of 40 °C for 1 min, 6 °C/min to 130 °C, 10 °C/min to

275 °C held for 20 min. Column flow was controlled to maintain a constant linear velocity of 1 mL/min. The ion source and the interface of the mass spectrometer detector were held at 230 °C and 250 °C respectively. Electron ionization of the compounds was performed at 69.9 eV and the ions were separated by their mass-to-charge (m/z) ratios in the range of 28 to 350. Each experiment was conducted at least five times to calculate average yields. .The GC column was calibrated with pure forms of selected compounds to allow for quantification and confirmation of peaks present in pyrolysis products from biomass and the catalytic reactions over the catalysts tested. The National Institute of Standards and Technology (NIST) mass spectral library and a library created for the mass spectra of the known compounds were both used in the identification of compounds. Analytical standards for the calibration of the GC/MS system were prepared in accordance to ASTM method D4307. All the yields are reported in terms carbon yield, where it is defined as the percentage of the carbon in the product with respect to carbon in the biomass or feed on mass basis.

The sugar maple was obtained from The State University of New York College of Environmental Science and Forestry (SUNY-ESF). The cellulose (SimgaCell), chemicals, and all the commercial catalysts used were obtained from Sigma Aldrich (Sigma Aldrich, St. Louis, MO).) The TiO_2 nanorods were synthesized at the Center for Functional Nanomaterials (CFN) at BNL. The impregnation of Ni and Pt metals on both TiO_2 nanorods and TiO2 nanopowder was done at BNL's Chemistry Department. For impregnation, TiO_2 catalysts were calcined at 500 ^oC under dry air flow prior to dispersion in 100mL distilled water solutions of Ni $(NO_3)_2.6H_2O$ and $H_2Pt(CO)_6$ precursors. The resulting mixtures were stirred and aged overnight at room temperature. Drying of the impregnated samples was done at 100 ^oC and calcination at 500 ^oC for 8h with air flow. Initial characterizations of the catalysts were done by transmission electron microscopy (TEM). The HRTEM analysis was carried out on JEOL 2100F Transmission Electron Microscope.

Acknowledgement

The authors acknowledge funding support from Brookhaven National Laboratory Internal Funding, LDRD project #19086. Dr. Weiqiang Han (formerly of Center for Functional Nanomaterials at BNL) is acknowledged for the synthesis of the anatase TiO_2 nanorods. We would also like to thank Dr. Shankhamala Kundu for catalyst impregnation efforts.

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Table of contents entry

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