Catalysis Today 147 (2009) 115–125

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic conversion of biomass-derived carbohydrates to fuels and chemicals by formation and upgrading of mono-functional hydrocarbon intermediates

Ryan M. West, Edward L. Kunkes, Dante A. Simonetti, James A. Dumesic *

University of Wisconsin-Madison, Department of Chemical and Biological Engineering, 1415 Engineering Drive, Madison, WI 53706, USA

ARTICLE INFO

Article history:
Available online 13 March 2009

Keywords:
Biomass
Carbohydrates
Fuels
Acid catalyst
Base catalyst
Supported metal catalyst

ABSTRACT

Aqueous solutions of sugars and polyols can be converted in a single catalytic process to produce a spontaneously separating organic phase consisting of hydrophobic mono-functional hydrocarbons. The process is shown to be stable for over 2 months time on stream at typical reaction conditions (e.g., 503 K and 18 bar total pressure). The composition and yield of this organic phase can be controlled by adjusting process variables, such as temperature, pressure and space velocity. This organic phase contains primarily mono-functional species such as ketones, alcohols, heterocycles, and organic acids. These oxygenated hydrocarbons can serve as an intermediate platform for the conversion of renewable biomass resources into chemicals and fuels. The organic phase can be separated into individual chemicals or can be upgraded to yield specific classes of chemicals. For example, heterocycles can be separated and used as solvents, additives or blending agents for transportation fuels, while aldol-condensation of the ketones and alcohols can produce long chains species for use as alkane fuels. Alternatively, this platform can be tuned to produce alcohols by reducing the ketone and acid groups. Dehydration of these alcohols produces olefins that have use in either the polymer industry, or as feeds for liquid fuels.

1. Introduction

Petroleum, a non-renewable resource in diminishing supply, currently provides the transportation sector with fuels that burn cleanly and that have high energy densities for efficient storage at ambient conditions. Petroleum derivatives are also utilized in the production of commodity and specialty chemicals [1]. With the cost of petroleum derived chemicals and fuels expected to increase in the coming years, investment into renewable chemicals might serve as a practical means of reducing costs [2]. Furthermore, energy production from fossil fuels generates CO_2, contributing to global warming. These issues associated with the continued use of petroleum by the chemical and fuels sectors would be ameliorated by producing clean burning liquid fuels and chemicals from renewable biomass resources. In this respect, the annual worldwide consumption of energy by the transportation sector is comparable to the amount of biomass that could be grown globally on a sustainable basis [3,4].

Cellulose and hemicellulose, the predominant components of ligno-cellulosic biomass, can be converted into sugars via acid or base hydrolysis. These sugars have a C:O stoichiometry of 1:1, giving them low volatility and high water solubility, properties that are undesirable for use either as transportation fuels or in catalytic chemical processes. The cost of producing fuels and chemicals from ligno-cellulosic biomass is currently not competitive with the cost of petroleum, due primarily to the high costs associated with the processing of biomass [5,6] in comparison with the cost of the biomass feedstock [2,7]. Accordingly, new processes for the conversion of biomass must involve a limited number of reaction steps to decrease the capital and operating expenses associated with multiple reaction steps and energy-intensive separation/purification processes between reaction steps [8].

The strategy considered in the present work is to convert sugars and polyols into mono-functional chemical intermediates in a single reactor over a PtRe/C catalyst by a combination of reforming and de-oxygenation reactions [9]. These reactions remove more than 80% of the initial oxygen content of the sugars and polyols, yielding a spontaneously separating organic phase. Furthermore, this work details several upgrading processes to convert the sugar/polyol-derived mono-functional compounds into fuel components and chemicals. Fig. 1 summarizes the classes of mono-functional organic compounds derived from the catalytic processing of either sorbitol or glucose over a PtRe/C catalyst at temperatures between 483 and 503 K. The wide variety of compounds and the diverse applications of these compounds suggest that the organic liquid stream produced from sugars over PtRe/C may serve as a versatile platform for the conversion of renewable biomass resources to

---

* Corresponding author.
E-mail address: dumesic@engr.wisc.edu (J.A. Dumesic).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.02.004

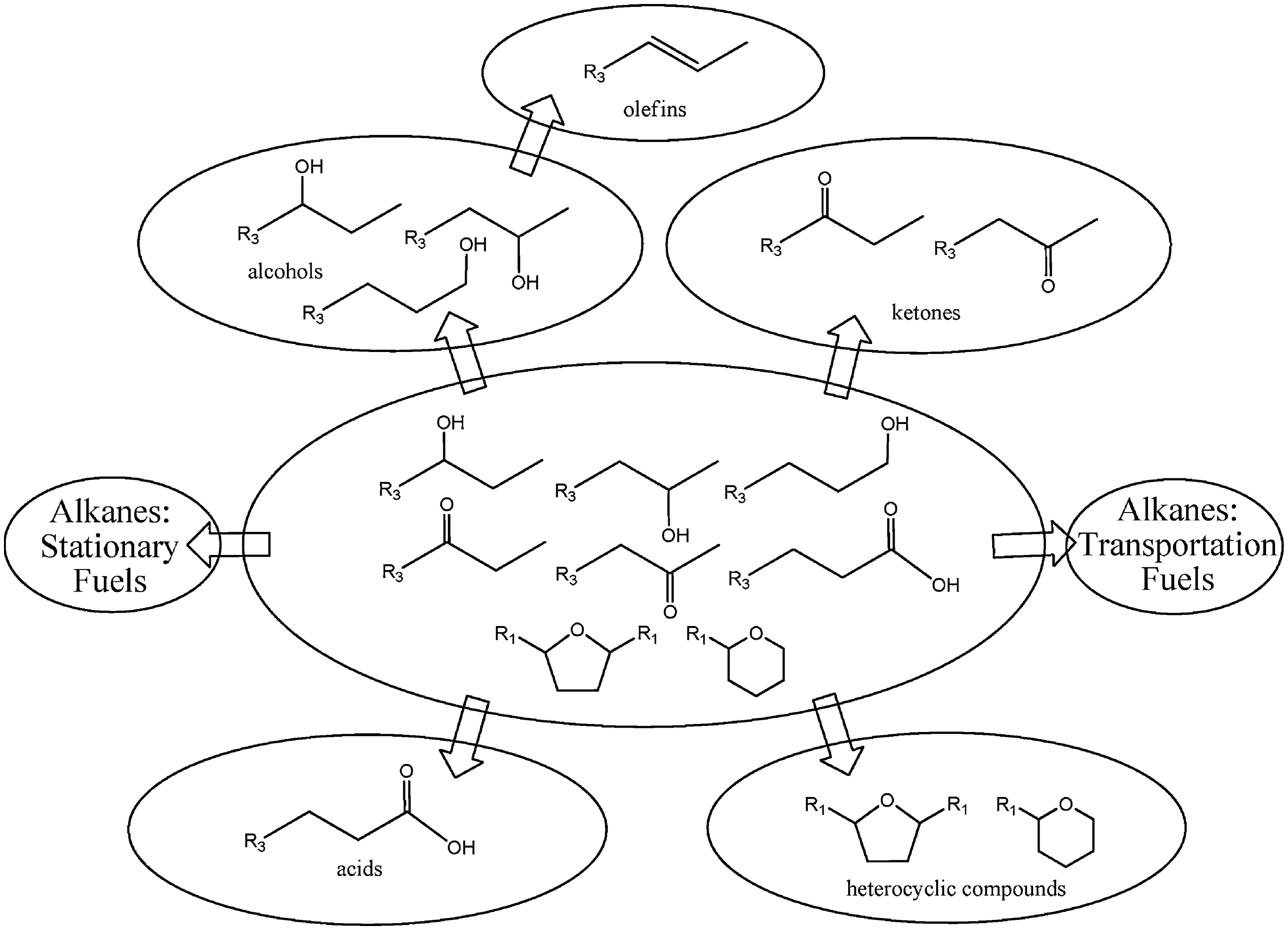

Fig. 1. Mono-functional organic compounds derived from sorbitol as a platform for the production of fuels and chemicals. R_3 represents CH_3, CH_3CH_2 or $CH_3CH_2CH_2$ groups and R_1 represents H or CH_3.

fuels and chemicals. This platform can be used to produce alkane fuels for high-volume stationary or transportation applications by controlling the extent of C–C bond coupling via various upgrading processes. These processes can be accomplished in a cascade approach using a limited number of catalytic reactors or beds (e.g., 2), without the need for complex separation/purification steps between reaction steps. Additionally, the composition of this platform can be tuned to favor the production of alcohols versus the production of ketones, depending on the requirements of the upgrading processes. The production of alcohols can be followed by the formation of olefins for the polymer industry. Furthermore, the carboxylic acids present in this liquid can be converted to alcohols, or they can be extracted for direct applications. Finally, the heterocyclic compounds present in this liquid can be extracted for use as solvents, as blending agents in transportation fuels, or as intermediates for further processing. It should be noted that all of the aforementioned compounds are currently produced from petroleum.

2. Experimental

2.1. Product analysis

The liquid effluents (organic and aqueous) were analyzed using gas-chromatograph (GC) analysis (Agilent 6890 with a flame ionization detector (FID) and HP-Innowax column, Shimadzu GC-2010 with an FID detector and Rtx-5 column, or Shimadzu GC-2010 with an mass spectrometer and DB-5ms column). Effluent gas streams were analyzed with gas chromatography: H_2 with a Carle GC (series 8700) using a thermal conductivity detector (TCD) and CO, CO_2 using either an HP 5890 GC with TCD and a Haysep DB 100/120 column (Alltech) or a Carle GC (Series 400 AGC) using a TCD detector and a Porapak Q packed column (Alltech). Gaseous alkanes were analyzed with a Varian GC (Saturn 3) using an FID detector and a GS-Q capillary column (J&W Scientific).

2.2. Catalytic activity studies

2.2.1. Catalytic conversion of sorbitol and glucose

The experimental conditions and catalyst preparation procedures are detailed elsewhere [9]. Briefly, a catalyst containing 5.1 wt.% Pt and 4.9 wt.% Re (atomic Pt:Re ratio of 1:1) on carbon was prepared by incipient wetness impregnation of carbon black (Norit-SX1G) with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ and $HReO_4$ (Strem Chemicals). The catalyst was mixed with fused SiO_2 granules, loaded in a stainless steel tube and held in place by quartz wool in a down flow reactor. The reactor was surrounded by aluminum blocks, heated by a well-insulated furnace with temperature monitored by type-K thermocouples (Omega) attached to the outside of the reactor. Mass-flow controllers (5850 Brooks Instruments) and an HPLC pump (Lab Alliance Series 1) were used to control the flowrates of H_2 and feed solutions. Catalyst reduction was performed in situ by ramping the temperature at a rate of 0.5 K min^{-1} to 723 K, holding for 2 h in flowing H_2 (200 cm^3(STP) min^{-1}) and then cooling to the desired reaction temperature under flowing H_2. After reaction conditions were attained, the H_2 flow was stopped, and feed flow was started. Liquid effluents (organic and aqueous) were collected at room temperature in a gas–liquid separator. Gas effluents passed through a back-pressure regulator (GO Regulator, Model BP-60) which controlled the system pressure.

2.2.2. Acid-catalyzed condensation

The 0.1-wt.% Pd/niobic acid catalyst was prepared by incipient wetness of niobic acid (HY-340 CBMM, Brazil) with $Pd(NO_3)_2$ (10 wt.% Aldrich). The resulting paste was dried at 393 K for 5 h and calcined in 20% oxygen in helium flowing at 250 cm^3(STP) min^{-1} by ramping over 3 h to and holding at 533 K. Catalytic tests were preformed in a similar reactor as described above with the feed introduced in an upflow direction.

2.2.3. Base-catalyzed condensation

The preparation of copper–magnesia–alumina catalyst with Cu:Mg:Al molar ratios of 1:10:7 was carried out as described by others [10]. The resulting $Cu/Mg_{10}Al_7O_x$ catalyst was mixed with an equal volume of fused SiO_2 granules, loaded in a down flowing reactor and reduced in flowing hydrogen (200 cm^3(STP) min^{-1}) for 3 h (0.5 K min^{-1} ramp) at reaction temperature.

2.2.4. Hydrogenation of ketones and acids to alcohols

A 5-wt.% Ru/C catalyst was prepared with an aqueous solution of $Ru(NO)(NO_3)_3$ by incipient wetness impregnation of Vulcan XC-72 (Cabot corp.). The catalyst was then dried in air for 12 h at 393 K. Hydrogenation reactions were performed at 433 K, under 55 bar H_2 for 12 h in a magnetically stirred, temperature controlled autoclave reactor (Model 4566, Parr Instruments).

2.2.5. Dehydration of secondary alcohols and oligomerization of alkenes

The dehydration of 2-pentanol and 2-hexanol (Aldrich) was carried out over niobic acid (HY-340 CBMM, Brazil) in an upflow reactor. Oligomerization of alkenes was performed using H-ZSM-5 (Si/Al = 14, Engelhard) in an upflow reactor.

3. Production of mono-functional hydrocarbons from sugars and polyols

3.1. Thermodynamics of alkanes and intermediate formation from sugars and polyols

In the temperature range of 450–600 K, and under anaerobic conditions, the most thermodynamically favored reaction pathway for the conversions of sugars or poyols is the complete dehydration/reduction to alkanes. As model compounds for the conversion of polyols and sugars into mono-functional chemicals and fuels, we consider glycerol as representative polyol, and glyceraldehyde or dihydroxyacetone (having a stoichiometry of $C_nO_nH_{2n}$) as representative sugars [11].

Without an external source of H_2, alkanes can only be produced if a portion of the sugar is first reformed into H_2 and CO_2. With this hydrogen, the formation of propane can proceed by successive dehydration/hydrogenation steps leading to complete reduction of glycerol. The stoichiometries of these two reactions are given by reactions (1) and (2). By properly combining the two reactions, a single reaction, reaction (3), can be written for the conversion of glycerol to propane. The values of ΔG° given in these equations are calculated at a reaction temperature of 520 K [11].

$$C_3O_3H_8 + 3H_2O \rightarrow 3CO_2 + 7H_2,\quad \Delta G^\circ = -53\,\text{kcal/mol}\quad \Delta H^\circ = 35\,\text{kcal/mol} \tag{1}$$

$$C_3O_3H_8 + 3H_2 \rightarrow C_3H_8 + 3H_2O,\quad \Delta G^\circ = -72\,\text{kcal/mol}\quad \Delta H^\circ = -62\,\text{kcal/mol} \tag{2}$$

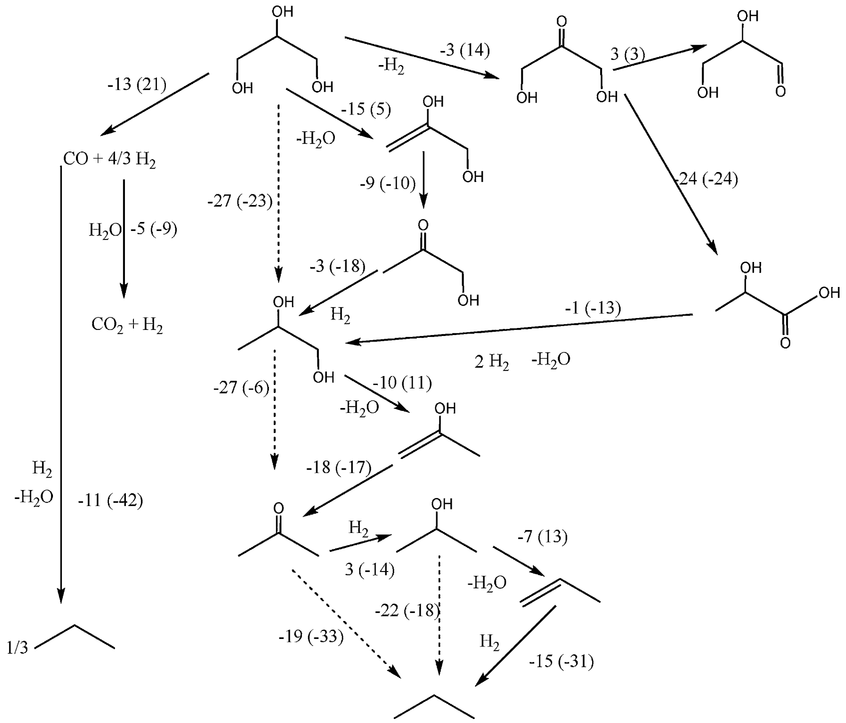

Fig. 2. Thermodynamics involved in the conversion of glycerol and intermediates to alkanes at 520 K. Values not in parentheses correspond to ΔG° (kcal/mol) and values within parentheses correspond to ΔH° (kcal/mol) [11].

$$C_3O_3H_8 \rightarrow \frac{7}{10}C_3H_8 + \frac{9}{10}CO_2 + \frac{6}{5}H_2O,$$
$$\Delta G^\circ = -67\,\text{kcal/mol}$$
$$\Delta H^\circ = -33\,\text{kcal/mol} \qquad (3)$$

Fig. 2 demonstrates a series of possible reactions and reaction intermediates for the conversion of glycerol to propane. The thermodynamic values at 520 K of ΔG° and ΔH° were obtained from either standard thermodynamic tables when available, or they were estimated using results from density functional theory calculations (using B3LYP/6-31G and Gaussian 03 software). The small value of ΔG° for the dehydrogenation of glycerol to dihydroxyacetone and glyceraldehyde suggests that all three species should be present under reaction conditions. The formation of carboxylic acids via the isomerization of dihydroxyacetone and glyceraldehyde is highly favorable ($\Delta G^\circ = -24$ kcal/mol), while the reduction of lactic acid to 1,2-propanediol acid is less favorable ($\Delta G^\circ = -1$ kcal/mol). Therefore, under low partial pressures of hydrogen, significant yields of carboxylic acids would be expected.

Glycerol can be converted to 1,2-propanediol via dehydration followed by hydrogenation or reductive C–O cleavage (hydrogenolysis). The removal of a hydroxyl group and subsequent reduction of the remaining molecule is thermodynamically favorable at 520 K ($\Delta G^\circ = -27$ kcal/mol). The reduction of a carbonyl group adjacent to a hydroxyl group (in this case acetol to propanediol) has a value of ΔG° equal to -3 kcal/mol. Propanediol is readily dehydrated at 520 K to form acetone ($\Delta G^\circ = -27$ kcal/mol). Unlike in the previous example, however, the hydrogenation of acetone to 2-propanol is not as thermodynamically favored ($\Delta G^\circ = 3$ kcal/mol). The dehydration of 2-propanol is favorable ($\Delta G^\circ = -7$ kcal/mol), as is the subsequent hydrogenation of propene to propane ($\Delta G^\circ = -15$ kcal/mol). Thus from a thermodynamic point of view, alkanes are the favored product in this series of reactions. To eliminate the complete dehydration and reduction of polyols, and thus to form intermediate mono-functionalized species, kinetic limitations must be present within the system.

The extent of saturation of C=C and C=O double bonds is critical in controlling reactivity. Dehydrogenation reactions of oxygenated compounds (HC–OH bonds) are thermodynamically more favorable than dehydrogenations of alkanes (HC–CH bonds). For example, the enthalpy changes (at 520 K) for the dehydrogenations of 2-propanol, 1-propanol, and propane to produce acetone, propanal, and propene are 14, 17, and 31 kcal/mol, respectively. These endothermic dehydrogenation reactions are favored at higher temperatures, and the temperatures above which

Table 1
Molar carbon distributions from typical operating conditions over PtRe/C (100% conversion of reagents).

	Total carbon distribution				Organic distribution			
	Sorbitol[a]			Glucose[b]	Sorbitol[a]			Glucose[b]
	Day 1	Days 3 and 4	Day 72	Days 1–20	Day 1	Days 3 and 4	Day 72	Days 1–20
CO_x	25.9%	29.1%	25.2%	28.1%	–	–	–	–
CO	0.02%	0.02%	0.03%	0.04%	–	–	–	–
CO_2	25.8%	29.1%	25.2%	28.1%	–	–	–	–
Alkanes	12.9%	11.0%	7.9%	12.6%	10.8%	6.0%	4.8%	4.0%
Methane	1.4%	1.4%	1.0%	1.0%	–	–	–	–
Ethane	1.8%	2.1%	1.5%	2.5%	–	–	–	–
Propane	2.4%	2.9%	1.9%	3.6%	–	–	–	–
Butane	1.5%	1.5%	1.0%	3.1%	0.9%	0.7%	0.4%	1.3%
Pentane	2.5%	1.7%	1.4%	2.1%	3.9%	2.6%	2.2%	2.5%
Hexane	3.3%	1.5%	1.2%	0.3%	5.9%	2.8%	2.2%	0.2%
Alcohols	9.7%	9.2%	10.6%	8.2%	18.0%	18.5%	21.3%	17.7%
2-Butanol	0.9%	0.3%	1.4%	1.1%	1.7%	0.6%	2.9%	2.3%
2-Pentanol	2.0%	2.0%	3.2%	1.4%	3.6%	4.1%	6.5%	3.0%
3-Pentanol	0.9%	0.5%	0.6%	0.4%	1.6%	1.0%	1.2%	0.8%
3-Hexanol	2.1%	2.2%	2.3%	1.8%	3.8%	4.5%	4.6%	3.9%
2-Hexanol	3.9%	4.1%	3.0%	3.6%	7.2%	8.2%	6.2%	7.8%
Heterocycles	13.5%	14.4%	13.9%	9.5%	25.0%	29.0%	28.1%	20.5%
Tetrahydrofuran (THF)	1.8%	1.7%	0.1%	1.0%	3.3%	3.4%	0.2%	2.1%
Methyl THF	3.6%	4.0%	4.5%	2.0%	6.7%	8.2%	9.1%	4.3%
Tetrahydropyran (THP)	0.5%	0.6%	0.9%	0.3%	0.9%	1.2%	1.9%	0.7%
Cis-dimethyl THF	3.0%	3.3%	2.7%	2.6%	5.5%	6.7%	5.5%	5.6%
Trans-dimethyl THF	1.7%	1.7%	1.7%	1.4%	3.1%	3.3%	3.4%	2.9%
Methyl THP	1.5%	1.4%	1.5%	1.5%	2.7%	2.8%	3.1%	3.2%
Hydroxy-Methyl THF	1.5%	1.6%	2.6%	0.8%	2.8%	3.3%	5.2%	1.7%
Ketones	18.4%	14.6%	14.8%	12.7%	34.1%	29.4%	30.0%	27.3%
2-Butanone	2.1%	0.9%	1.4%	1.3%	3.8%	1.8%	2.8%	2.8%
2-Pentanone	4.8%	3.9%	4.3%	3.2%	8.8%	7.8%	8.6%	6.9%
3-Pentanone	1.0%	0.9%	1.0%	0.8%	1.9%	1.8%	2.1%	1.7%
3-Hexanone	3.4%	3.1%	3.5%	2.4%	6.2%	6.2%	7.1%	5.3%
2-Hexanone	7.2%	5.8%	4.6%	4.9%	13.3%	11.7%	9.3%	10.6%
Acids	6.6%	8.4%	7.7%	14.1%	12.2%	17.1%	15.6%	30.5%
Butanoic acid	3.6%	3.9%	3.8%	5.4%	6.6%	8.0%	7.7%	11.7%
Pentanoic acid	1.8%	3.3%	2.7%	4.4%	3.4%	6.6%	5.5%	9.6%
Hexanoic acid	1.2%	1.2%	1.2%	4.3%	2.2%	2.5%	2.5%	9.2%
Gas	32.9%	37.1%	38.3%	38.9%	–	–	–	–
Organic	54.1%	49.5%	49.5%	46.4%	–	–	–	–
Aqueous	13.0%	13.4%	12.2%	14.7%	–	–	–	–

[a] 60 wt.% sorbitol, 503 K, 18 bar, WHSV = 0.6 h^{-1}.

[b] 40 wt.% glucose, 483 K, 18 bar, WHSV = 0.6 h^{-1}.

the values of ΔG° become negative are 478, 563, and 913 K, respectively. Thus, at typical reaction temperatures of 520 K and in the presence of hydrogen and metal catalysts to facilitate hydrogenation and dehydrogenation reactions, the concentrations of ketones should be high, the concentrations of aldehydes should be lower, and the concentrations of olefins should be very low. In effluents collected from typical reaction conditions and shown in Table 1, the concentration of ketones is high compared to the concentration of corresponding secondary alcohols, while the concentration of olefins is negligible compared to the concentration of paraffins. In this respect, the partial pressure of H_2 is an important variable for controlling the reaction chemistry.

Another important aspect of the reactivity of oxygenated compounds is that dehydration reactions to form ketones are more favorable compared to dehydration reactions leading to olefins. For example, the enthalpy change (at 520 K) for dehydration of isopropanol to propene is 13 kcal/mol, whereas the enthalpy change for dehydration of glycerol to acetol is −5 kcal/mol and propanediol to acetone is −6 kcal/mol. At a typical reaction temperature of 520 K, all three of these dehydration reactions are favorable, with values of ΔG° equal to −7, −24, and −27 kcal/mol, respectively.

In the absence of a catalyst that facilitates dehydration (e.g., a solid acid), the dehydration of alcohols can only proceed by hydrogenolysis. This limitation slows the conversion of alcohols to alkanes (via the thermodynamically favored hydrogenation of olefins). At low partial pressures of hydrogen, the dehydrogenation of alcohols to ketones would be favored. Therefore under the appropriate operating conditions, the expected relative concentrations of these three classes of compounds are alkanes $<$ alcohols $<$ ketones, as observed in the studies presented in this work.

Cyclic ethers such as tetrahydrofurans and pyrans are significant products of the conversion of longer chain (C_6) sugars/polyols over PtRe/C. Fig. 3 illustrates the two possible dehydration routes for a representative diol, 1,4-butanediol. As with Fig. 2, the thermodynamic values at 520 K of ΔG° and ΔH° were obtained from either standard thermodynamic tables when available, or were estimated from density functional theory calculations. The dehydration reactions of 1,4-butanediol to 3-butene-1-ol and to tetrahydrofuran (THF) are both favored thermodynamically. The value of ΔG° is equal to −8 kcal/mol for the production of THF versus −7 kcal/mol for 3-butene-1-ol, while ΔH is equal to 3 kcal/mol versus 13 kcal/mol, respectively. The dehydration of intermediate species with hydroxyl groups separated by four and five carbons should thus provide a route to cyclic ethers, thereby forming thermodynamically stable species whose ring is not as readily hydrogenated as an unsaturated C–C bond.

3.2. *Production of mono-functional hydrocarbons*

In a previous report, we demonstrated the production of mono-functional hydrocarbons from sugars and polyols [9]. Briefly, it was observed that the reaction temperature, total pressure, and space velocity could be adjusted to maximize the formation of mono-functional hydrocarbons from a 60-wt % sorbitol solution over a PtRe/C catalyst. For example, operating at higher pressures and temperatures (e.g., 523 K and 27 bar) is undesirable, since near-complete conversion to C_1–C_6 alkanes was observed. Alternately, operating at low pressures and temperatures (e.g., 483 K and 18 bar) yields a high fraction of water-soluble polyols containing two or more hydroxyl groups. Theoretical studies of ethanol decomposition on Pt(1 1 1) have demonstrated that cleavage of C–O bonds (leading to the formation of hydrocarbons) on Pt for an oxygenated hydrocarbon takes place through transition states that are more hydrogenated compared to transition states for cleavage of C–C bonds (leading to the formation of H_2 and CO_2) [12]. Therefore, higher hydrogen partial pressures are expected to lead to a greater abundance of hydrogenated intermediates, thereby increasing the rate of C–O versus C–C bond cleavage. At the appropriate reaction conditions, highly oxygenated reaction intermediates adsorb on the catalyst surface and undergo successive C–O scission until their binding energy becomes sufficiently low for desorption. Subsequent re-adsorption of these mono-functional species is inhibited by the presence on the surface of more strongly bound reactant species, thus preventing further reaction and complete conversion to alkanes.

3.3. *Chemical compositions*

The generic classes of compounds produced from the initial processing of sugars over PtRe/C are shown in Fig. 1 and described in the preceeding sections. The specific chemical compositions, broken down into individual components, are given in Table 1 as molar carbon percent. The compositions are given for the effluents of both a sorbitol and a glucose feed. In the first set of columns, the effluents are broken down to include the total distribution of all organic and gaseous components. For volatile species such as butane, pentane and hexane, this number is the sum of the gaseous and organic contributions. The total carbon distribution between gaseous, organic and aqueous phases is included at the bottom of these columns. In the second set of columns, the chemical compositions of the extracted organic phases are given.

A typical effluent composition derived from sorbitol is given in the first three columns of Table 1. For these samples, a 60-wt.% sorbitol solution was passed over 3 g of PtRe/C catalyst at a WHSV of 0.6 h^{-1} at 503 K and 18 bar total pressure. The first column corresponds to the initial drain of the reactor on day 1 of a run, the second column to days 3 and 4, and the third column to day 72. The values remain relatively constant for the duration of the run with slight variation. The most noticeable variation is the decrease in conversion to alkanes with time on stream. Initially, 12.9% of the inlet carbon is converted to alkanes. This value decreases to 11.0% by the third and fourth day and to 7.9% by day 72. All other concentrations remain relatively constant for the duration of the run. The largest single component in the organic phase is 2-hexanone. The next most abundant species are methyl-THF, 2-pentanone, 2-hexanol, 2-pentanol, butanoic acid and 3-hexanone.

The lower water solubility of glucose as compared to sorbitol, and its tendency to form coke deposits on the catalyst necessitated the use of a 40-wt % glucose feed and operation at lower temperatures. The glucose-derived effluent was obtained at 483 K, 18 bar pressure and a WHSV of 0.6 h^{-1} over the course of 20 days. The concentration of acid increased substantially as compared to the sorbitol-derived organic phase, such that butanoic acid represents the species in highest concentration followed by 2-hexanone, pentanoic and hexanoic acids. This increase is accompanied by a decrease in the yields of heterocycles and ketones.

4. Utilization of mono-functional hydrocarbon platform

4.1. *Thermodynamics of ketone and aldehyde condensation*

The dehydrogenation of alcohols to carbonyl compounds and the dehydration of alcohols to olefins are both thermodynamically favorable at temperatures near 520 K, while hydrogenation reactions of olefins to alkanes are also very favorable. Thus, one strategy to achieve C–C coupling between ketones in the presence of hydrogen at 520 K is to employ a bi-functional catalyst containing basic (or acid) sites and metal sites, where the basic

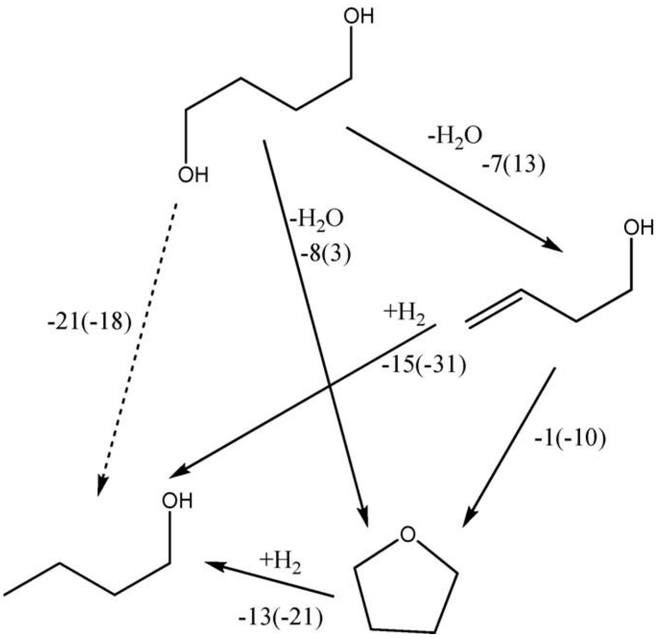

Fig. 3. Dehydration and hydrogenation thermodynamics of 1,4-butanediol to n-butanol at 520 K. Values not in parentheses correspond to ΔG° (kcal/mol) and values within parentheses correspond to ΔH° (kcal/mol).

(or acid) sites facilitate aldol-condensation and the metal sites facilitate hydrogenation and dehydrogenation reactions. Because the hydrogenation of ketones to alcohols is not favorable at 520 K, the concentration of ketones in the reactor remains high even in the presence of H_2, allowing bi-molecular aldol-condensation reactions to take place over basic (or acidic) sites. Subsequent dehydration of the aldol adducts produces a molecule with an unsaturated C–C bond that is readily hydrogenated at these reaction conditions.

Using the three carbon examples in Fig. 2, the aldol-condensation of two acetone molecules to form the six carbon species, diacetonealcohol, is not favored at 520 K ($\Delta G^\circ = 12$ kcal/mol); however, the dehydration of this six carbon alcohol to form the conjugated species, mesityloxide, is thermodynamically favorable ($\Delta G^\circ = -6$ kcal/mol), such that the formation of mesityloxide from acetone is only slightly unfavorable ($\Delta G^\circ = 6$ kcal/mol) [11]. While only low concentrations of mesityloxide are possible due to thermodynamic limitations, hydrogenation of the C=C double bond to methyl isobutyl ketone is favorable at 520 K ($\Delta G^\circ = -11$ kcal/mol). Hydrogenation thus allows high conversion of smaller ketones into large saturated branched ketones.

The reduction/dehydration of a branched ketone to the corresponding alkane is thermodynamically favorable. Under hydrogen pressure, methyl isobutyl ketone can be hydrogenated to the corresponding alcohol ($\Delta G^\circ = 10$ kcal/mol). Dehydration of this alcohol at 520 K and subsequent hydrogenation of the corresponding olefin to produce 2-methylpentane are favorable reactions ($\Delta G^\circ = -15$ and -13 kcal/mol, respectively). Thus, alkanes with longer carbon chains than the initial polyol or sugar reactant can be formed by first forming ketones, then aldol-condensing these ketones, and finished by combining hydrogenation and dehydration steps [11].

4.2. Acid-catalyzed condensation

The acid-catalyzed condensation of ketones, specifically acetone on a low loading of Pd on niobic acid catalysts, has been studied and patented as a means of producing larger ketones such as methyl isobutyl ketone [13–15]. The condensation of ketones is accompanied by the loss of water to form a more stable conjugated species. As discussed above, this reaction can be driven to high conversions by hydrogenating the conjugated species to form ketone 1 shown in Fig. 4. Alternatively, the conjugated intermediate species can further condense with a second ketone [15] and extend the conjugation system through subsequent dehydration. The ketones under investigation in this study differ from acetone in that only one primary carbon containing alpha hydrogen atoms is present. The alpha hydrogen atoms on the secondary carbon atom are not as reactive as those on the primary carbon due to steric and inductive effects [16]. Additionally, less reactive centers limit the number of additional condensation products beyond the first that can be formed. The available reactive pathways and specific condensation products are shown in Fig. 4. As with the single condensation product, these species can be hydrogenated to form ketone 2. Alternatively, these species can undergo a self-condensation to form aromatic compounds. Ketones 1 and 2 can also undergo hydrogenation to the corresponding alcohol, followed by dehydration and hydrogenation to form the corresponding alkanes.

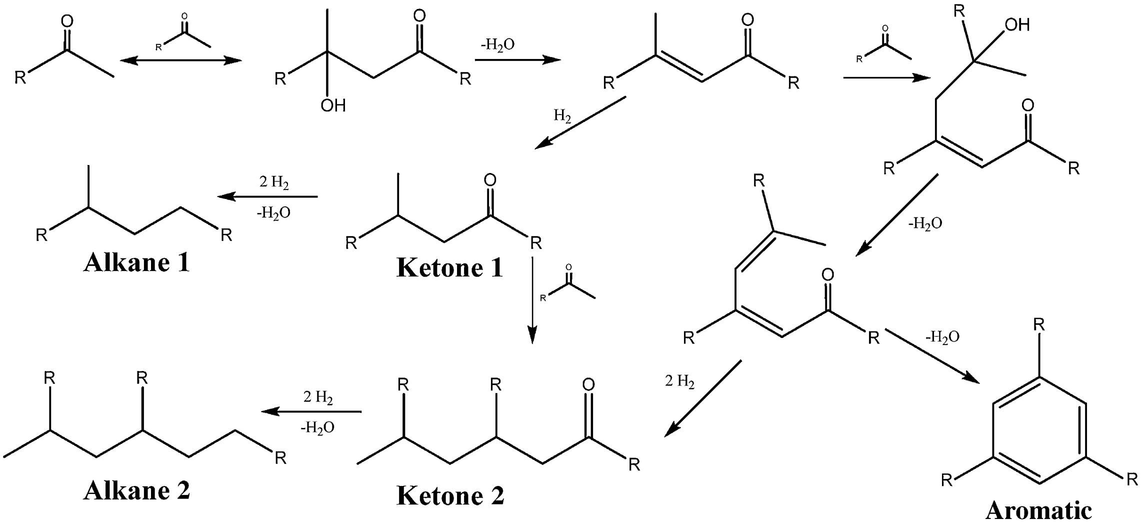

Fig. 4. Aldol-condensation and subsequent hydrogenation and aromatization products over a bi-functional catalyst. Condensation reactions occur on base/acid component while hydrogenations occur over metal component.

Table 2
Acid-catalyzed aldol-condensation of ketones and ketones/oxygenated-additive mixtures over a 0.1 wt.% Pd/niobic acid catalyst at 527 K and 55 bar.

Entry	Feed composition		Conditions		Conversion	Selectivity[b]				
	Feed ketone	Co species	H_2 flow[a]	WHSV (h^{-1})	Feed ketone	Propane/n-Butane	Alkane 1[b]	Ketone 1[b]	Alkane 2[b]/Aromatic[b]	Ketone 2[b]
1	Acetone	–	50	1.4	94.4%	3.5%	11.0%	27.3%	32.0%	26.1%
2	Acetone	–	0	1.4	63.9%	0.6%	2.7%	6.5%	69.5%	20.8%
3	2-Butanone	–	50	1.8	88.6%	1.6%	3.3%	70.8%	21.8%	2.5%
4	2-Butanone	–	25	0.8	93.5%	2.4%	4.5%	63.8%	24.7%	4.5%
5	2-Butanone	50 wt.% Hexane	25	0.3	98.0%	7.8%	5.3%	60.9%	21.0%	5.0%
6	2-Butanone	50 wt.% 2-Butanol	25	1.1	45.9%	[c]	3.4%	92.3%	4.3%	0.0%
7	2-Butanone	12.6 wt.% Water	25	1.9	62.2%	14.2%	4.2%	73.1%	8.3%	0.2%
8	2-Butanone	50 wt.% n-Butanol	25	0.7	13.8%	[c]	7.3%	35.4%	52.5%	4.9%
9	2-Butanone	10 wt.% n-Butanol	25	1.8	68.2%	8.7%	4.3%	67.7%	16.6%	2.7%
10	2-Butanone	10 wt.% Hexanoic Acid	25	0.9	65.1%	3.1%	3.7%	77.8%	14.7%	0.7%
11	2-Butanone	33.3 wt.% THP	25	1.2	66.4%	5.1%	5.2%	70.7%	14.0%	5.0%

[a] cm^3(STP) min^{-1}.
[b] See Fig. 4 for definitions, selectivity based on ketone conversion.
[c] Value not included due to dehydration and hydrogenation of co-species 2-butanol or n-butanol producing large concentrations of butane.

Organic acid tolerance is an advantage of solid acid catalyzed condensation over base catalyzed condensation. The effluents obtained from processing sugar and polyol feeds contain significant concentrations of organic acids (5–35%). For base catalyzed condensation, these organic acids must be neutralized prior to reacting to avoid deactivating the basic sites. Because these effluent stream contain large concentrations of ketones (among other species), an investigation was undertaken into the feasibility of condensing these ketones and the effect of other species on the performance of a solid acid catalyst.

The condensation of ketones larger than acetone was investigated using a 0.1-wt.% Pd/niobic acid catalyst. The four carbon ketone, 2-butanone, was chosen as a representative ketone for all methyl ketone species. All runs were performed at 527 K and 55 bar pressure and the results are given in Table 2 for the specified conditions. Acetone was first used to ensure proper reactivity. The feed was then switched to 2-butanone and operated at various conditions. Lastly, the influence of other representative chemical species found in the mono-functional hydrocarbons effluents was investigated. After testing a species, the feed was switched to pure 2-butanone to ensure that deactivation of the catalyst had not occurred. In Table 2, the selectivity of the Aromatic and Alkane 2 fractions are grouped together due to difficulty in separation of these components in the GC analysis. Weight hourly space velocity (WHSV) refers to the mass h^{-1} of reactant, in this case ketone, divided by the mass of catalyst.

In the condensation of acetone, a large drop in conversion and yield to the first condensation product can be seen when the hydrogen flow is stopped. The conversion drops from 94.4% with hydrogen to 63.9% without hydrogen. Without hydrogen to saturate the C=C double bonds, the selectivity shifts to the larger products such as aromatics that are more stable. Using 2-butanone at comparable conditions yielded similar results as acetone. 2-Butanone is slightly less reactive than acetone, 88.6% versus 94.4% conversion and yields a higher concentration of single condensation products 70.8% versus 27.3%, respectively. These differences can be attributed to the two sets of reactive methyl α-hydrogen atoms for acetone.

Decreasing the flow of 2-butanone (and the corresponding flow of hydrogen) slightly increased the conversion (Entry 4) while increasing the selectivity towards larger species. Diluting the feed with hexane (Entry 5) had a negligible effect on reactivity. The remaining co-fed chemicals all caused decreases in the rate of condensation, suggesting an influence beyond simple dilution. The four carbon alcohols 2-butanol and n-butanol can dehydrate to form either butenes or ethers under the conditions of this study with the butenes subsequently undergoing hydrogenation to form butane on Pd. These reactive molecules cause the greatest decrease in condensation of all molecules in this study. As shown in Entry 6, the conversion of 2-butanone drops to 45.9% from 93.5% at similar conditions when the feed is switched to 50% 2-butanol. At the same time, the selectivity shifts towards the single condensation products. The 2-butanol completely reacts to form butanes. When a 50% n-butanol feed is instead used (Entry 8), only 13.8% conversion of 2-butanone is observed. A 10% n-butanol feed also has a pronounced effect decreasing the conversion to 68.2% (Entry 9). In these cases, approximately 20% of the n-butanol was reacted to form butanes and to n-butyl ether.

The addition of water (the byproduct of both condensation and dehydration) was also investigated. A saturated solution of water in 2-butanone was prepared and determined to be 11.6 wt.% water. The presence of water decreased the reactivity of the catalyst, as shown in Entry 7; however, the effect of water alone cannot explain the drop in reactivity when alcohols are fed into the system. Two other non-reactive species found in the typical sugar-derived effluents were also investigated. Hexanoic acid (10%) and THP (33.3%) both decreased the conversion of butanone in a similar manner. It is interesting to note, however, that hexanoic acid at 10% concentration had a similar effect as 10% n-butanol.

The non-polar species, hexane had little to no effect on the condensation of 2-butanone, while all other polar species decreased the extent of acid condensation. This behavior suggests a possible binding of polar species on the catalyst to block reactivity. When the feed is switched back to 2-butanone, the reactivity returned to its initial value, suggesting that this binding is reversible.

To effectively couple 2-ketones under acidic conditions, the concentration of other oxygenated species must be kept to a minimum. From Table 1, the sugar-derived mono-functional hydrocarbon effluents typically contain around 30% ketones with 21–22% as 2-ketones. Approximately 60% of these effluents are other oxygenated species that could inhibit aldol-condensation. Aldol-condensation of a sorbitol-derived feed with Pd/niobic acid was unsuccessful at effectively condensing 2-ketones, as given in Table 4, column 1 (5.4% condensation products). The catalyst, however, was extremely effective in converting all of the alcohols into alkenes, which were subsequently hydrogenated to alkanes.

4.3. Base-catalyzed condensation

We have previously demonstrated that a bi-functional catalyst consisting of copper supported on a mixed magnesium/aluminum oxide is effective for catalyzing C–C coupling reactions of alcohols and ketones produced from the conversion of aqueous sorbitol

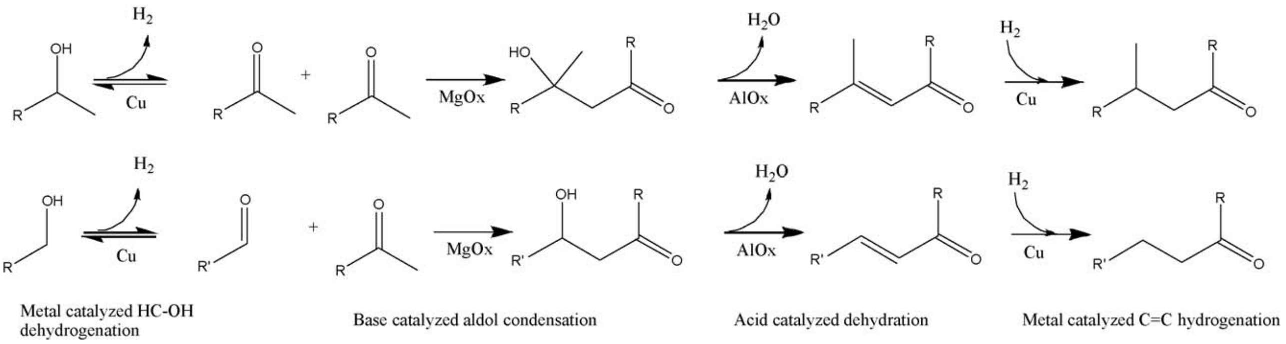

Fig. 5. Tandem dehydrogenation aldol-condensation schemes for primary and secondary alcohols over Cu/MgO_x.

solutions over a PtRe/C catalyst [9]. The overall coupling process of ketones with other species is shown in Fig. 5 and consists of Cu-catalyzed dehydrogenation of alcohol groups, followed by base-catalyzed (MgO_x) aldol-condensation, acid-catalyzed (AlO_x) dehydration and subsequent hydrogenation (Cu) of the α–β unsaturated aldol adduct. At 573 K and 5 bar H_2, copper catalyzes the dehydrogenation of secondary and primary alcohols into ketones and aldehydes, respectively, such that these reactions are equilibrated. At 573 K, the equilibrium constant for the dehydrogenation of secondary alcohols is an order of magnitude greater than the equilibrium constant for the dehydrogenation of primary alcohols into aldehydes. However, the lack of steric hindrance at the terminal carbonyl group of aldehydes allows for more facile aldol-condensation with methyl ketones as compared with the self-condensation of these ketones. Therefore, the consumption of aldehyde species in aldol-condensation reactions drives the dehydrogenation of primary alcohols.

Our previous work, as well as the work of other investigators [9,17] has demonstrated that small amounts of carboxylic acids deactivate the bi-functional catalyst by poisoning the MgO basic sites. However, base catalyzed ketone coupling has an advantage over acid catalyzed coupling, in that basic sites are less active towards the dehydration of primary and secondary alcohols as compared to acid sites. Therefore, alcohols (in equilibrium with carbonyl species) would not undergo dehydration to alkenes (which are hydrogenated into alkanes by metal functionality), and coupling reactions would proceed to a greater extent.

The aim of the work presented here is to determine the effect of other oxygenates such as primary alcohols, secondary alcohols, and cyclic ethers on the coupling of methyl ketones over Cu/$Mg_7Al_{10}O_x$. The effects of co-feeding other oxygenated species are summarized in Table 3. Methyl ketones such as 2-hexanone (Entry 1) and 2-butanone (Entry 2) react readily to form the saturated aldol adducts 7-methyl-5-undecanone and 5-methyl-3-heptanone, respectively. These adducts lack labile methyl α-hydrogen atoms, and do not undergo self-coupling, but can undergo coupling with methyl ketones to form branched C_{18} and C_{12} secondary products, respectively (Fig. 4). The higher selectivity towards secondary condensation products observed for the self-coupling of 2-butanone (16%) versus 2-hexanone (9%) can be attributed the higher steric hindrance of the carbonyl group in 7-methyl-5-undecanone as compared to 5-methyl-3-heptanone.

The addition of 10 mol% secondary alcohol (Entry 3) had a negligible effect on the conversion and selectivity of ketone coupling, since the secondary alcohol undergoes dehydrogenation yielding the corresponding ketone. The cyclic ether methyl tetrahydrofuran (MTHF) (Entry 4) is inert at these reaction conditions but tends to slightly diminish the reactivity of 2-butanone, as evidenced by the 7% decrease in 2-butanone conversion when compared to Entry 2. This decline in reactivity can be attributed to the competitive adsorption of MTHF, resulting in the blocking of catalytic sites.

The addition of small amounts of a primary alcohol (1-butanol) to 2-hexanone (Entry 5) produces a noticeable decline in overall ketone conversion (11%). Higher concentrations of primary alcohols (Entry 6) significantly suppress the self-coupling reactions of ketones. After 8 h on stream, only 3% of the 2-hexanone undergoes self-coupling. In Entries 5 and 6, 1-butanol reacts with the 2-hexanone to form linear 5-decanone with n-butanol conversions of 100% and 75%, respectively. It should be noted that once the 1-butanol containing feed is replaced with pure 2-hexanone, a product distribution similar to the one obtained in Entry 1 is observed, suggesting that the suppression

Table 3
Base-catalyzed vapor phase aldol-condensation of ketones and ketones/oxygenated-additive mixtures (WHSV = 1.0 h^{-1}) over Cu/$Mg_{10}Al_7O_x$ at 573 K and 5 bar with 20 cm^3(STP) min^{-1} H_2 co-feed.

Entry	Feed composition		Conversion[a]		Primary product(s)		Secondary product(s)	
	Ketone (balance)	Additive	Ketone[a]	Additive	Species	Selectivity[b]	Species	Selectivity
1	2-Hexanone	–	86%	–	7-Methyl-5-undecanone (C_{12})	91%	C_{18} ketones	9%
2	2- Butanone	–	89%	–	5-Methyl-3-heptanone	84%	C_{12} ketone	16%
3	2-Hexanone	10 mol% 2-Hexanol	90%	–	7-Methyl-5-undecanone (C_{12})	89%	C_{18} ketones	11%
4	2-Butanone	10 mol% Methyl THF	82%	0%	5-Methyl-3-heptanone (C_8)	87%	C_{12} ketones	13%
5	2-Hexanone	1 mol% n-Butanol	75%	100%	7-Methyl-5-undecanone (C_{12})/ 5-decanone (C_{10})	90% (C_{12})/3% (C_{10})	C_{18} ketones	7%
6[c]	2-Hexanone	10 mol% n-Butanol	9%	75%	7-Methyl-5-undecanone (C_{12})/ 5-Decanone (C_{10})	30% (C_{12})/70% (C_{10})	C_{18} ketones	0%
7[d]	Product of experiment 5		67%	100%	7-Methyl-5-undecanone (C_{12}) 5-Decanone (C_{10})	76% (C_{12})/16% (C_{10})	C_{18}/C_{16} ketones	4%(C_{18})/ 4%/(C_{16})

[a] Ketone conversion value also includes conversion of equilibrated secondary alcohol.
[b] Carbon selectivity.
[c] Reversible deactivation observed—conversion reported at 8 h on stream.
[d] Conversions and selectivities are calculated based on 10% n-butanol feed in Entry 5.

of 2-hexanone self-coupling reactions is reversible. In Entry 7, the product of Entry 6 is recycled through the catalyst bed, and a 67% conversion of 2-hexanone is observed, indicating that once the primary alcohol has completely reacted, the suppression of 2-hexanone self-coupling reactions is eliminated. The results of Entries 5–7 suggest that primary alcohols competitively inhibit the self-coupling of ketones.

Microcalorimetric studies have shown that primary alcohols and aldehydes bind stronger to metal and basic sites as compared to secondary alcohols and ketones [18,19]. Therefore, it is likely that the catalytic sites required for coupling of ketones are preferentially occupied by primary alcohols or aldehydes under reaction conditions, leading to inhibition of ketone coupling. An effective strategy for the conversion of both ketones as well primary alcohols would involve increasing the overall reaction residence time and allowing the primary alcohols to react to completion, thus permitting ketones to react without inhibition in the downstream sections of the catalyst bed.

4.4. Hydrogenation of ketones and acids to alcohols

The hydrogenation of acetone, as noted in Fig. 2, is slightly unfavorable ($\Delta G^\circ = 3$ kcal/mol) at 523 K and is an exothermic reaction ($\Delta H^\circ = -14$ kcal/mol). The dehydration of the resulting alcohol is favorable ($\Delta G^\circ = -7$ kcal/mol) at 523 K, but is endothermic ($\Delta H^\circ = 13$ kcal/mol). One strategy to hydrogenate chemical species to alcohols without dehydrating them to alkenes is to react the mixture at lower temperatures with excess hydrogen over a supported metal that will hydrogenate both acids and ketones. In the absence of a dehydration catalyst (e.g., a solid acid), and at lower temperatures, the dehydration of alcohols is not favored and the subsequent hydrogenation to alkanes (propylene to propane for example with $\Delta G^\circ = -15$ kcal/mol), will not occur.

Using a 5-wt.% Ru/C catalyst in a magnetically stirred, temperature controlled autoclave reactor at 433 K, under 55 bar H_2 for 12 h, a typical sorbitol-derived feed can be hydrogenated into mostly alcohols [9], as shown in Table 4, column 2. Compared to the feeds depicted in Table 1, it can be seen that most of the ketones, acids and some of the heterocycles have been converted into the corresponding alcohols. This hydrogenated organic phase contains 73% alcohols on a molar carbon basis with approximately 8% remaining as alkanes and 15% as heterocycles. It is important to note that a small fraction of ketones (0.1%) did not convert to alcohols. In the methods of quantification used in this study, acids are more difficult to detect in low concentrations than are ketones. Therefore the possibility exists that some acids remained unconverted as well, but their concentration is below the minimum level of detection. The remaining 3.7% of the molar carbon is attributed to other species, mostly ethers, but also larger alkanes (decane and dimethyl hexane) and larger alcohols (dimethyl pentanol) that form from dehydration of alcohols and various C–C bond forming reactions.

4.5. Dehydration of alcohols

In the absence of hydrogen and metal catalysts, alcohols can be dehydrated over solid acid catalysts to form alkenes without hydrogenation to alkanes. As previously noted, dehydration is favorable ($\Delta G^\circ = -7$ kcal/mol) and endothermic ($\Delta H = 13$ kcal/mol) at 523 K. An effective dehydration catalyst for this conversion must possess both acid sites as well as a resistance to water degradation, criteria met by niobic acid and niobium phosphate [20]. During studies involving aldol-condensation of ketones using a Pd/niobic acid catalyst, it was noted that niobic acid is effective for dehydration of the alcohols, as shown in Table 4, column 1. The ability of niobic acid to dehydrate pure feeds of the two most abundant alcohols from Table 4, column 2, into alkenes was thus investigated.

Table 4
Effluent compositions from catalytic processing of typical mono-functional streams derived from sorbitol (see Table 1 over PtRe/C at 503 K and 18 bar pressure).

	Dehydration[a]	Hydrogenation[b]
CO_2	0.1%	0.0%
Alkanes	45.9%	8.0%
Methane	0.0%	0.0%
Ethane	0.0%	0.0%
Propane	1.0%	0.0%
Butane	4.5%	0.1%
Pentane	18.4%	0.4%
Hexane	21.9%	7.5%
Alcohols	0.0%	73.0%
n-Propanol	0.0%	0.3%
2-Propanol	0.0%	3.3%
2-Butanol	0.0%	6.3%
n-Butanol	0.0%	0.2%
2-Pentanol	0.0%	22.7%
3-Pentanol	0.0%	2.3%
3-Hexanol	0.0%	16.5%
2-Hexanol	0.0%	21.7%
Heterocycles	17.8%	14.9%
Tetrahydrofuran (THF)	0.4%	1.1%
Methyl THF	3.7%	2.9%
Tetrahydropyran (THP)	4.5%	1.0%
Cis-dimethyl THF	2.4%	4.4%
Trans-dimethyl THF	1.7%	2.0%
Methyl THP	2.3%	1.4%
Hydroxy-methyl THF	2.8%	2.0%
Ketones	23.6%	0.1%
2-Butanone	2.5%	0.0%
2-Pentanone	5.7%	0.0%
3-Pentanone	2.4%	0.0%
3-Hexanone	4.9%	0.0%
2-Hexanone	8.2%	0.0%
Acids	7.3%	0.0%
Butanoic acid	2.9%	0.0%
Pentanoic acid	2.9%	0.0%
Hexanoic acid	1.4%	0.0%
Other products	5.4%[c]	3.7%[d]

[a] Upflow reactor, 0.1 wt.% Pd/niobic acid, WHSV = 0.48 h^{-1}, 527 K and 55 bar.
[b] Batch reactor, 15 g feed, 0.3 g 5 wt.% Ru/C, 12 h, 433 K and 55 bar H_2.
[c] Condensation products.
[d] Ethers, larger alkanes and larger alcohols, see text.

At 528 K over niobic acid at 18 bar, the conversion of 2-hexanol via dehydration spans from 98.7% at a WHSV of 1.4 h^{-1} to 99.4% at a WHSV of 0.5 h^{-1}. Similarly, 2-pentanol at a WHSV of 0.5 h^{-1} is converted at 98.7% while a higher velocity, 1.6 h^{-1} yields 98.5%. The major products of these dehydrations include the cis and trans forms of both 2-hexene and 2-pentene with a lower concentration of 1-hexene and 1-pentene. For 2-hexanol, at a WHSV of 0.5 h^{-1}, 3.6% of the hexenes dimerize into C_{12} species, while at 1.4 h^{-1}, only 0.5% of the hexenes dimerize. Similarly, for 2-pentanol at 0.5 h^{-1}, 0.5% of the pentenes dimerize to C_{10} species while at 1.6 h^{-1} only 0.1% of the pentenes react.

Decreasing the temperature to 503 K decreased the conversion, as shown in Fig. 6, for the dehydration of 2-pentanol over niobic acid at various values of WHSV. As the WHSV is decreased, the yields of pentenes and di-2-pentyl ether increase such that the total rate of dehydration remains relatively constant at 70–55 μmol min^{-1} g cat. The effluents from 503 K (including unreacted 2-pentanol, pentenes and ethers) were reprocessed at 528 K over niobic acid to yield similar products as for 2-pentanol conversion noted in the preceding paragraph (99.1% total conversion of 2-pentanol, with 0.2% of the pentenes dimerizing

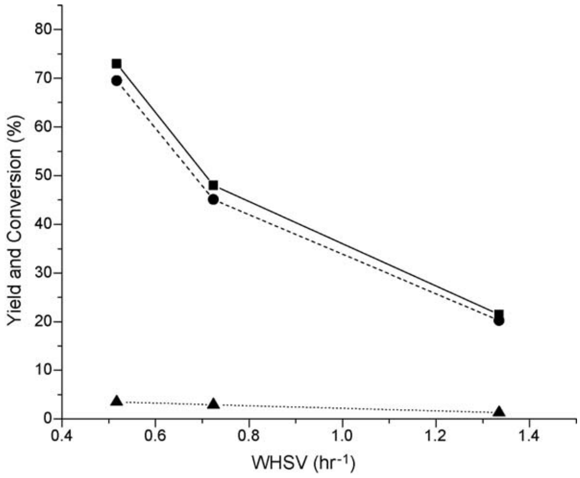

Fig. 6. Conversion of 2-pentanol and yield of dehydration products: conversion of 2-pentanol (■); yield of pentenes (●); yield of di-2-pentyl ether (▲).

to C_{10}). Di-2-pentyl ether was not observed in the reprocessed effluent, suggesting that dehydration to form two molecules of pentene took place.

By proper choice of conditions, the alcohols in mixtures of mono-functional hydrocarbons can be selectively dehydrated to the corresponding alkenes over niobic acid. As shown in Table 4, column 2, this dehydration occurs without interference from other oxygenated species such as ketones, acids and heterocycles. At the same time, nioic acid is very effective in dehydrating pure alcohol streams as demonstrated for 2-pentanol and 2-hexanol.

In general, the mono-functional effluents can effectively be converted into alkanes, alcohols and heterocycles as shown in Table 4, column 1. The alcohols could be dehydrated to form a mixture of alkenes and heterocyclic compounds. The alkenes and heterocycles could be separated by simple distillation due to the difference in the alkene and heterocyclic boiling points. The only difficulty in this separation would come in separating the largest alkenes, hexenes, with normal boiling points of 336–341 K from the smallest heterocycle THF, with a normal boiling point of 339 K. The concentration of THF in the mixture is low, 1.1%, and might be acceptable depending upon the application. The alkenes could then be used for polymer or other applications. The heterocycles could be used directly as additives or could be reacted to form additional alcohols through ring opening processes. It is noted however, that the specific concentration of any individual component (for example, cis 2-pentene) is small compared to the concentration of similarly grouped components (all pentenes). Applications using these separated products would likely need flexibility in composition as separating the individual components could be difficult and yield small individual fractions.

4.6. Oligomerization of alkenes

One possible use of alcohols is dehydration into alkenes followed by oligomerization into larger alkenes for use as liquid fuels. Alkylation reactions to form larger olefins, such as the coupling between two propylene molecules to form a C_6 alkene, are favorable at 520 K ($\Delta G^\circ = -2$ kcal/mol). Since this reaction is exothermic ($\Delta H^\circ = -23$ kcal/mol), and involves a reduction in the number of molecules (2 olefins to 1 olefin), the equilibrium conversion to larger olefins can be increased by operating at lower temperatures and higher pressures.

Studies of 1-hexene and 1-pentene oligomerization over solid acid catalysts, typically zeolites such as H-ZSM-5 and USY, have demonstrated that the reactive pathway to heavier components first involves isomerization, followed by a series of both oligomerization and cracking reactions to produce a distribution of products, as shown in Fig. 7 [21–25]. The isomerization of the terminal alkenes produces a mixture of linear 2-alkenes and branched alkenes. The alkenes produced via dehydration of alcohols are a mixture of terminal and 2-alkenes isomers that react more quickly than pure terminal alkenes. The linear 2-alkenes are rapidly equilibrated with the branched alkenes, while the terminal alkenes require slightly higher temperatures to react [22].

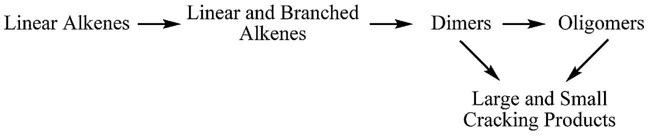

Fig. 7. Reaction pathways for alkene oligomerization and subsequent cracking.

Mixtures of linear alkenes created via the dehydration of alcohols and containing both terminal and 2-alkenes are oligomerized over H-ZSM-5 at temperatures from 523 to 563 K, as shown in Table 5. The reactive pathway shown in Fig. 7 describes the trends from previous studies. In particular, at high conversion, increasing the WHSV for both pentene and hexane feeds increases the yield of dimers, as expected in a series of reactions (Entries 1–4, 6 and 7). When the vapor phase is saturated with pure alkenes, decreasing the total system pressure only slightly decreases the initial rate of dimerization (Entries 1–4). The rate of dimerization and subsequent cracking is strongly influenced when an inert such as helium is introduced in the system (Entries 5 and 8). This reduction in rate is attributed to the drop in the partial pressure of alkenes. Increasing the temperature under diluted conditions (Entries 8–10), increases the rates of all reactions in this series.

The feasibility was investigated of converting alcohols directly into dimers in a two-bed system within one reactor consisting of niobic acid to first dehydrate the alcohols and HZSM-5 to oligomerize the alkenes. Based on previously noted studies, sufficient niobic acid was loaded to ensure that all the alcohols were converted to alkenes. The two beds were operated at the same temperature and the results are listed in Table 5. The WHSV is defined for these runs as the mass of alkenes (calculated from the total conversion of alcohols) per gram of H-ZSM-5 h^{-1}. This definition allows direct comparison with other results in Table 5. For 2-hexanol at 523 K, decreasing the WHSV increases the yield to dimers and larger products (Entries 11–14). At 563 K, decreasing the WHSV through the same range of temperatures decreases the yield of dimers while the larger products pass through a maximum at intermediate values (Entries 15–17). At 563 K, when 3-pentanol is used instead of 2-hexanol (Entries 18 and 19), the yield of dimer and large products increases. As similar trend was not observed when a mixture of pentenes (Entries 6 and 7 created from the dehydration of 2-pentanol) is compared with a mixture of hexenes (Entries 3 and 4 created from the dehydration of 2-hexanol). The difference in reactivity can be attributed to the type of alkene produced. Dehydration of 3-pentanol will only yield the more reactive 2-pentenes, while dehydration of 2-pentanol will yield both 2-pentenes and the less reactive 1-pentene.

The primary difference in using a two-bed system feeding alcohol and a one-bed system feeding alkenes is the reduction in alkene partial pressure due to presence of water. The results of co-feeding helium as a diluent at a set of conditions (Entries 5, 8, and 10) are similar to those when alcohol is the feed and the alkenes are thus diluted with water (Entries 12, 13, 17, and 19).

The alkene feeds outlined in this paper could contain heterocycles such as THF. Consequently, the influence of THF in this series of reactions was also investigated. THF did not react

Table 5
Oligomerization of alkenes at various reaction conditions.

Entry	Reacting conditions						Alkene effluent composition (Carbon mol%)[a]				
	Feed	Co feed (mol%)	Catalyst	Temperature (K)	Pressure (bar)	WHSV (h^{-1})[b]	Feed isomers	Dimers	Oligomers and large cracking	Small cracking	Sum of larger species
1	Hexenes	–	H-ZSM-5	523	52	0.36	10.9%	27.9%	55.1%	6.1%	83.1%
2	Hexenes	–	H-ZSM-5	523	52	1.03	12.2%	50.2%	35.6%	2.0%	85.8%
3	Hexenes	–	H-ZSM-5	523	18	0.30	13.6%	37.6%	46.3%	2.1%	83.9%
4	Hexenes	–	H-ZSM-5	523	18	1.04	13.6%	46.0%	37.4%	2.8%	83.4%
5	Hexenes	He (75%)	H-ZSM-5	523	18	0.53	71.4%	20.3%	6.7%	1.6%	27.0%
6	Pentenes	–	H-ZSM-5	523	18	1.03	13.1%	42.6%	43.3%	0.9%	84.4%
7	Pentenes	–	H-ZSM-5	523	18	0.31	6.9%	30.0%	60.2%	2.3%	86.4%
8	Pentenes	He (50%)	H-ZSM-5	523	18	0.92	73.6%	20.0%	6.1%	0.3%	26.1%
9	Pentenes	He (50%)	H-ZSM-5	543	18	1.01	67.4%	22.9%	9.1%	0.4%	32.0%
10	Pentenes	He (50%)	H-ZSM-5	563	18	1.00	53.6%	26.4%	18.8%	1.0%	45.2%
11	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	523	18	0.20	40.7%	26.3%	26.9%	6.1%	53.2%
12	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	523	18	0.48	41.4%	24.9%	29.0%	4.6%	53.9%
13	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	523	18	0.99	54.4%	14.9%	19.2%	11.2%	34.2%
14	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	523	18	1.32	79.2%	13.0%	5.6%	2.1%	18.7%
15	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	563	18	0.21	24.0%	15.5%	43.0%	17.4%	58.5%
16	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	563	18	0.50	28.4%	17.6%	44.7%	9.2%	62.4%
17	2-Hexanol	–	Niobic acid/H-ZSM-5[c]	563	18	1.00	26.7%	19.4%	43.4%	10.4%	62.8%
18	3-Pentanol	–	Niobic acid/H-ZSM-5[c]	563	18	0.24	12.4%	20.4%	61.1%	6.0%	81.5%
19	3-Pentanol	–	Niobic acid/H-ZSM-5[c]	563	18	0.95	19.2%	23.1%	53.4%	4.1%	76.5%
20	3-Pentanol	THF(57%)	Niobic acid/H-ZSM-5[c]	563	18	0.10	92.8%	1.0%	3.5%	2.6%	4.5%
21	3-Pentanol	THF(57%)	Niobic acid/H-ZSM-5[c]	563	52	0.10	79.6%	3.5%	13.0%	3.7%	16.5%
22	Pentenes	THF(59%)	H-ZSM-5	563	18	0.74	65.2%	9.7%	23.1%	1.9%	32.7%
23	Pentenes	THF(59%)	H-ZSM-5	563	18	0.27	59.3%	18.8%	21.0%	0.9%	39.8%
24	Pentenes	THF(59%)	H-ZSM-5	563	18	0.10	43.6%	25.9%	29.1%	1.3%	55.0%

[a] Includes alkenes and alkanes; for runs involving THF, THF was not reacted and does not contribute to this chart.

[b] WHSV is always defined here as the mass of alkenes (or calculated mass of alkenes in the case of alcohol feeds) per mass of H-ZSM-5 h^{-1}.

[c] Equal mass of each catalyst was loaded, although WHSV is only defined for H-ZSM-5.

under the conditions of these experiments. As with water, THF reduces the partial pressure of reactive species and consequently decreases the yields to larger products. The combination of water and THF (Entry 20) showed the lowest yield to larger species at low WHSV. At these low concentrations, increasing the system pressure to 52 bar increases the partial pressure of alkenes which in turn increases the rate (Entry 21). When THF is used as a diluent instead of helium, the results are similar for mixtures containing both terminal and 2-alkenes (Entries 10 and 22).

5. Conclusions

Mono-functional chemical intermediates can be produced from sugars and polyols in a single reactor over PtRe/C. These chemical intermediates including ketones, acids, alcohols and heterocycles can serve as an intermediate platform for the conversion of renewable biomass resources to fuels and chemicals. The individual components can be separated directly, reacted to more readily separable species, or can be reacted to form specific classes of chemicals. For example this platform can be selectively tuned to produce high concentrations of alcohols by reducing the ketone and acid groups. The alcohols can be dehydrated to form olefins for the polymer industry, or can be oligomerized to larger alkenes for use as liquid fuels. The ketones and alcohols can additionally undergo aldol-condensation to produce long chains species for use as alkane fuels. The heterocyclic compounds can be used as blending agents for transportation fuels, as solvents or additives for various chemical processes, or can be used as intermediates for further processing.

Acknowledgements

This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences and the National Science Foundation Chemical and Transport Systems Division of the Directorate for Engineering. We thank M. Mavrikakis for valuable discussions throughout this project, and we thank E.I. Gürbüz for help with flow reactor experiments.

References

[1] Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, New York, 2001.
[2] D.L. Klass, Biomass for Renewable Energy, Fuels and Chemicals, Academic Press, San Diego, 1998.
[3] G.J. Panuccio, B.J. Dreyer, L.D. Schmidt, AIChE J. 53 (2007) 187.
[4] M. Parikka, Biomass Bioenergy 27 (2004) 613.
[5] J.J. Bozell, ACS Symp. Ser. (2006) 1.
[6] B. Kamm, Angew Chem. Int. Ed. Engl. 46 (2007) 5056 (International ed. in English).
[7] Biomass as Feedstock for a Bioenergy and Bioproducts Industry, The Technical Feasibility of a Billion-Ton Annual Supply, Oak Ridge National Laboratory, 2005.
[8] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr., J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, Science (Washington, DC, U.S.) 311 (2006) 484.
[9] E.L. Kunkes, D.A. Simonetti, R.M. West, J.C. Serrano-Ruiz, C.A. Gärtner, J.A. Dumesic, Science 322 (2008) 417.
[10] J.I. Di Cosimo, G. Torres, C.R. Apesteguia, J. Catal. 208 (2002) 114.
[11] D.A. Simonetti, J.A. Dumesic, Catal. Rev., in press.
[12] R. Alcala, M. Mavrikakis, J.A. Dumesic, J. Catal. 218 (2003) 178.
[13] Y. Higashio, T. Nakayama, Catal. Today 28 (1996) 127.
[14] T. Maki, T. Yokoyama, Y. Sumino, Manufacture of methyl isobutyl ketone, Mitsubishi Chemical Industries Co., Ltd., Japan, 1988, , p. 3, Application: JP, JP.
[15] M. Paulis, M. Martin, D.B. Soria, A. Diaz, J.A. Odriozola, M. Montes, Appl. Catal. A 180 (1999) 411.
[16] G. Solomons, C. Fryhle, Organic Chemistry, 7th Edition, John Wiley and Sons, New York, 1999.
[17] J.I. DiCosimo, V.K. Díez, C.R. Apesteguía, Appl. Catal. A 137 (1996) 149.
[18] M.A. Natal-Santiago, J.M. Hill, J.A. Dumesic, J. Mol. Catal. A 140 (1999) 199.
[19] M.A. Natal-Santiago, M.A. Sanchez-Castillo, R.D. Cortright, J.A. Dumesic, J. Catal. 193 (2000) 16.
[20] R.M. West, D. Braden, J., J.A. Dumesic, J. Catal. 262 (2009) 134.
[21] J.M. Escola, R. Van Grieken, J. Moreno, R. Rodriguez, Ind. Eng. Chem. Res. 45 (2006) 7409.
[22] T. Maurer, B. Kraushaar-Czarnetzki, J. Catal. 187 (1999) 202.
[23] J.P.G. Pater, P.A. Jacobs, J.A. Martens, J. Catal. 179 (1998) 477.
[24] J.P.G. Pater, P.A. Jacobs, J.A. Martens, J. Catal. 184 (1999) 262.
[25] R. Van Grieken, J.M. Escola, J. Moreno, R. Rodriguez, Appl. Catal. A 305 (2006) 176.