Selective Coupling of Bioderived Aliphatic Alcohols with Acetone Using Hydrotalcite Derived Mg–Al Porous Metal Oxide and Raney Nickel

Bálint Fridrich,† Marc C. A. Stuart,†‡ and Katalin Bartà*†§

†Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
‡Department of Electron Microscopy, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 7, 9747 AG Groningen, The Netherlands
§Supporting Information

ABSTRACT: Fermentation of sugars to the so-called ABE mixture delivers a three component mixture of shorter chain oxygenates: acetone, n-butanol and ethanol. In order to convert these into liquid transportation fuels that are analogous to the currently used fossil energy carriers, novel catalytic chain elongation methods involving C–C bond formation are desired. Herein we report on a simple, non-noble-metal-based method for the highly selective coupling of 1-butanol and acetone into high molecular weight (C7–C11) ketones, as well as ABE mixtures into (C5–C11) ketones using the solid base Mg–Al–PMO in combination with small amount of Raney nickel. Upon hydrogenation, these ketones are converted to fuel range alkanes with excellent carbon utilization (up to 89%) using Earth abundant metal containing catalysis.

KEYWORDS: Bioethanol, 1-Butanol, ABE mixture, Raney nickel, Porous metal oxides

INTRODUCTION

Lignocellulosic biomass is a globally available, carbon-neutral, renewable resource that does not compete with the food supply and that could, in principle, provide suitable and sustainable alternatives to the fossil-based chemicals currently made.1–3 It could also be used to produce liquid transportation fuels that are, in their chemical structure, analogous to the generally utilized petroleum derived sources and are therefore fully compatible with existing infrastructures.4 However, the conversion of noncellulosic feedstocks is the so-called ABE (acetone, butanol, ethanol) fermentation,13,14 which provides a three component mixture of shorter chain oxygenates: acetone, n-butanol and ethanol. In order to convert these into liquid transportation fuels that are, in their chemical structure, analogous to the generally utilized petroleum derived sources and are therefore fully compatible with existing infrastructures.4 However, the conversion of noncellulosic feedstocks is the so-called ABE mixture.13,14 The required dehydrogenation, aldol condensation and hydrogenation sequence was performed using the physical mixture of Pd@C and K₃PO₄ to yield chain elongated ketones. Next, the group introduced recyclable hydrotalcite-based catalyst doped with various metals.15 Later, a synergistic effect was found in a Pd/Cu doped hydrotalcite that allowed for high product selectivity at 200 °C in the gas phase.16 An in depth study of the hydrogenation and decarboxylation of butanals over various PdCu bimetallic catalysts comprising different supports was conducted.17 Further, it was observed that HTC doped with up to 2.5% Cu (prepared by impregnation), upon calcination, leads to excellent reaction rates.18 Other groups also found excellent results in this and related reactions, such as the palladium catalyzed chain elongation of diluted aqueous ABE mixture,21 or the related iPrOH, EtOH, BuOH mixture.22 The copper catalyzed alkylation of acetone with BuOH23 and the catalytic dehydration of ABE mixture over γ-alumina catalyst show the versatility of this chemical platform.24 For instance, Lee and co-workers have used Pd@C with CaO as a solid base for the conversion of ABE mixture in a batch reactor at 180 °C without any added solvent to obtain a mixture of ketones and their corresponding alcohols with 78% yield based on acetone.25 The mixture was further converted one-pot to the corresponding alkane mixture using 34.5 bar H₂ at 270 °C, with 74.7% overall yield based on acetone. Onyestýák and co-workers designed a flow reactor containing two separated beds for the consecutive
coupling and hydrodeoxygenation sequence to produce C5−C7 alkanes from ethanol-acetone mixture.26 Tan, Shen and co-workers have introduced a Ni-MgO-SiO2 catalyst with improved water resistance for the highly selective conversion of solvothermal ABE mixtures to C5−C15 ketones and alcohols at 240 °C.27

Herein we describe a simple catalyst system consisting of Mg−Al−PMO and Raney nickel, for the very efficient coupling of acetone and 1-butanol28 as well as the selective coupling of ABE mixture to long chain ketones at 200 °C and hydrodeoxygenation of these over non-noble-metal catalysts to the corresponding fuel range alkanes with excellent carbon balance.

**EXPERIMENTAL PROCEDURE**

**Catalyst Preparation.** The HTC (hydrotalcite) catalyst precursor was prepared by a coprecipitation method, according to literature procedures.29−31 A solution containing MgCl2-6H2O (0.15 mol, 30.05 g), AlCl3·6H2O (0.05 mol, 12.07 g) in deionized water (0.2 L) was slowly added to an aqueous solution (0.2 L) of Na2CO3 (0.05 mol, 5.3 g) at 60 °C under vigorous stirring. The pH was carefully maintained between 9 and 10 by adjusting with frequent additions of an aqueous solution of NaOH (1 M). The mixture was vigorously stirred for 72 h at 60 °C. After cooling to room temperature, the suspension was filtered, and the solid was washed with deionized water and resuspended into a solution of Na2CO3 (2 M), which was stirred for 24 h at 40 °C. After, the catalyst precursor was filtered and washed with deionized water until the washings were chloride-free (tested with AgNO3 solution). The solid was dried at 120 °C overnight, and the hydrotalcite precursor (HTC) was obtained as a white powder (14.7 g). The corresponding porous metal oxide (PMO) was obtained after calcining a portion of the HTC material at 460 °C for 24 h. Elemental analyses were performed on a PerkinElmer instrument (Optima 7000DV) after full solubilization of the PMO catalysts in diluted nitric acid.

The various doped hydrotalcites (Cu20PMO, Cu10Ni10PMO, Cu10Zn10PMO, Ni20PMO, Co20PMO) were prepared by replacing a portion of the Mg2+ ions with additional metal dopants, otherwise following the procedure above. In Cu20PMO, Ni20PMO and Co20PMO, 20 mol % of the Mg2+ were replaced by the corresponding two valent metal ions Cu2+, Ni2+ and Co2+ respectively. In the Cu10Ni10PMO and Cu10Zn10PMO, 10 mol % of Mg2+ was replaced by Cu ions whereas 10 mol % was replaced by Ni and Zn, respectively. To demonstrate the successful incorporation of the two-valent transition metal ions, the composition of PMO catalysts was investigated by ICP analysis, which typically resulted in an elemental composition closely matched the theoretical one (for a detailed description, see Supporting Information, Section 4.1). In order to independently confirm the formation of hydrotalcite structures, XRD spectra for all HTCs and for the corresponding PMOs were recorded (see Supporting Information, Section 4.2 for details). Indeed, this analysis confirmed the formation of the envisioned hydrotalcite structures in all samples.

**Representative Procedure of a Catalytic Coupling of Butanol with Acetone.** First, 15 mg of Raney nickel slurry was placed in a Swagelok stainless steel microreactor (10 mL) equipped with a Teflon coated magnetic stirring bar followed by a rapid addition of 1-butanol (5.46 mmol, 0.5 mL), acetone (2.7 mmol, 0.2 mL), and dodecane (0.22 mmol, 50 μL, internal standard). Next, 200 mg of Mg−Al−PMO and heptane (2×1 mL) was added. The reactor was sealed and placed in an aluminum block preheated at the desired temperature. After the indicated reaction time, the microreactor was cooled down with an ice−water bath and subsequently carefully opened. The liquid sample as well as the catalysts were quantitatively transferred to a 15 mL centrifuge tube. Additional MeOH (2×1 mL) was used to wash the reactor and recover all catalyst residues. After centrifugation, the solution was transferred into a glass vial, washed four times with 2 mL MeOH and analyzed by GC-FID (Hewlett-Packard 6890 series equipped with a HP-5 capillary column) in order to determine the 1-butanol and acetone conversion and selectivity of the products. Compounds were also identified by GC−MS and the injection of pure reference standards for the comparison of retention times in the GC column.

For ABE mixture, acetone (2.9 mmol, 0.21 mL), butanol (4.6 mmol, 0.42 mL), and ethanol (1.2 mmol, 70 μL) were used as substrate; otherwise, the procedure was identical. The ratio of A:B:E is kept at 2.3:3.7:1 molar ratio as expected from the mixture accessible directly from ABE fermentation.

**Catalytic Hydrodeoxygenation of Long Chain Ketones to Alkanes.** The mixture of chain elongated ketones obtained following the previous procedure, (or model compounds) in hexane (∼10 mL) were loaded into a 15 mL autoclave equipped with a magnetic stirring bar and 100 mg Ni@Al2O3−SiO2 catalyst. The reactant was additionally purged with H2 three times then pressurized to 40 bar, the autoclave was placed in a metal block preheated at 220 °C and the reaction proceeded for 12 h. After, the reactor was cooled down by compressed air and ice−water bath, respectively. The content of the reactor was transferred to a 15 mL centrifuge tube and the reactor was washed with additional amounts (5× 0.5 mL) of cold hexane. The catalyst was separated by centrifugation, a sample from the liquid phase was injected to GC−MS and parallel to GC-FID and the carbon yield was calculated based on carbon number relatively to the intensity of the internal standard. More details on product analysis are given in the Supporting Information, Section 1.2 and 1.5.

**RESULTS AND DISCUSSION**

Inspired by the above-described prior art and following our interest in the use of hydrotalcite derived doped porous metal oxides for the conversion of renewables involving hydro−

generation or hydrogen transfer processes,29,33 as well as diverse C–C bond formation reactions including the Guerbet coupling...
of ethanol to butanol and the coupling of challenging alcohol mixtures with cyclopentanone, we set to design a simple, entirely noble-metal-free catalyst system for the transformation of ABE mixture to long chain ketones and subsequently to fuel-range alkanes. We have first focused our attention on finding an appropriate catalyst for the coupling of 1-butanol and acetone, two main components of the ABE mixture. As shown in Scheme 1, the transformation of acetone and 1-butanol to long chain ketones requires efficient dehydrogenation of the primary alcohol, followed by a cross aldol condensation with acetone and subsequent hydrogenation of the double bond in the corresponding aldol condensation product. A number of side reactions, previously also identified by Toste and others, exist in this system, making the selective formation of 6-undecanone challenging.

First, we have selected a number of hydrotalcite derived solid bases, high surface area porous metal oxides (PMO) comprising various dopants (Cu, Ni, Zn, Co), as starting point for our investigation (Figure 1, Table S1). We expected that the nature of the dopant will influence reactivity since in our earlier study on the Guerbet reaction we observed significant differences in the extent of dehydrogenation, aldol condensation as well as the Tishchenko pathway, depending on the PMO composition. Gratifyingly, there was considerable conversion of both acetone and 1-butanol with all PMO catalyst tested, and a significant amount of the one side coupling product 2-heptanone together with the corresponding alcohol 2-heptanol. Indeed, with diverse metal dopants, the extent of side reactions appeared different. As expected from earlier studies, Cu20PMO exhibited significant amounts of butyl-butyrate and a similar behavior was observed with Cu10Zn10PMO (Table S1, entries 1 and 2). A related behavior was observed by Goulas et al who reported a significant esterification side reaction with HTC supported Cu catalyst prepared by impregnation. Interestingly, the Cu10Ni10PMO containing the same amount of Cu dopant, but Ni instead of Zn resulted in much less butyl butyrate (7%) and higher amount (56%) of 2-heptanone as well as (13%) long chain ketone 6-undecanone (Table S1, entry 3). The PMO containing Ni or Co both resulted in very similar substrate conversion values, up to ~60% ketones and more significant amount of higher Mw products (Table S1, entries 4 and 5). Although among these catalysts the best results were achieved with the Cu10Ni10PMO and the conversion values and low selectivity to the double coupling products were not yet satisfactory.

A very high selectivity to (C7–C11) ketones was described by Goulas et al reporting the beneficial use of a CuPd bimetallic catalyst prepared by incipient wetness impregnation on a commercially available HTC catalyst. The group has identified decarbonylation as one of the major source of side reactions, catalyzed by the Pd contained in the catalysts. Because the Cu containing catalysts were giving significant Tishchenko activity, and none of the doped PMO tested gave sufficient conversion levels, we turned our attention to the use of simple Mg−Al−PMO obtained directly by calcination of a typical hydrotalcite that is known to efficiently catalyze aldol condensation processes. Furthermore, instead of Pd we have selected Raney nickel that is a highly efficient transfer hydrogenation catalyst, but is expected to have less decarbonylation activity. Very recently, Zhang and co-workers have shown that cyclopentanone can be converted to C10 and C15 oxygenates in the presence of Raney Ni and a PMO with a different Mg/Al ratio (2:1 compared to 3:1 in our case).

Combination of Raney Nickel and PMO for Increased Activity. Gratifyingly, when we have attempted the coupling reaction between acetone and 1-butanol in the presence of 15 mg Raney Ni and 200 mg Mg−Al−PMO, excellent results were obtained (Figure 2, Table S2, Entry 1). Almost full substrate conversion was seen alongside high selectivity (61.5%) of 6-undecanone.
higher molecular weight side products were detected, but no butylybuterate was formed. The superior activity of this catalyst can be explained by the fact that Raney Ni is a more efficient dehydrogenation and hydrogenation catalyst, compared to the various metal dopants in the PMO previously tested, present in their oxide form. When the Mg−Al−PMO was used alone, the color of the reaction mixture turned orange and the formation of higher MW products, originating from acetone self-condensation, was clearly observable even after reaction (for more, see the Supporting Information, Table S2).

In our hands, the freshly prepared, not activated Ni20PMO revealed homogeneously distributed nickel and a porous structure as evidenced by TEM and EDX analysis (Figure S13). Upon activation at 500 °C in H2 flow, formation of particles was visible by TEM analysis; however, their sizes were too small (1−4 nm) to discriminate them from the matrix by elemental mapping (Figure S14). Therefore, from the same batch of porous metal oxide precursor, we prepared a new batch of activated catalyst at 600 °C in H2 flow. Indeed, in this case the formation of larger, Ni-rich particles (7−11 nm) was observed (Figures S15 and S19).

The catalyst, which was activated at 600 °C, showed slightly better conversion and similarly good selectivity toward the chain elongated products (Table S2, entry 5).

Next, both Ni-PMO (activated at 500 and 600 °C, respectively) were analyzed by TEM and EDX after reaction (Figure S18 vs S19).

The flexible incorporation of Ni into the PMO structure synthetically, will open possibilities for potential future fine-tuning of catalyst composition and preparation methods, because the amount of Ni in the PMO during coprecipitation method can be carefully adjusted.

**Effect of Various Reaction Parameters.** Next, we conducted a series of experiments by gradually increasing the substrate amounts by maintaining the total volume of 2.8 mL of the reaction mixture (Figure 3, Table S3). Experiments were conducted between 4.1 and 32.8 mmol total substrate loading. Interestingly, though the acetone conversion did not significantly change, the 1-butanol conversion and 6-undecanone selectivity gradually decreased with an increasing amount of substrate loading. Gratifyingly, the neat conditions and relatively high substrate loading also resulted in an excellent selectivity for C7−C11 ketones and alcohols (combined 86.3%), albeit with lower conversion values.

In the next experiments, the acetone to butanol ratio was varied as 1.9, 2.0, 2.1 (Figure S1 and Table S4). The 1:2 acetone to butanol ratio resulted in the highest amount of double
alkylated C11 ketones and alcohols (combined 73%). Next, the reaction was conducted at 180−220 °C reaction temperatures (Figure S2, Table S5) without significant variation in results. The reproducibility of the system was also verified by running 3 parallel experiments (Figure S3 and Table S6), resulting in a negligible variation, within 60.5−62% of 6-undecanone selectivity.

Mechanistic Considerations. Although the primary reaction pathways (Scheme 1) en route to 2-heptanone and 6-undecanone, involving 1-butanol dehydrogenation, aldol condensation with acetone (or 2-heptanone) and hydrogenation appear straightforward, this transformation is complicated by a number of side reactions. The full proposed reaction network is depicted on Scheme 2, which can be used to explain the product profiles that were obtained during catalyst screening, and even the differences between the catalysts tested.

We found that the Raney Ni/PMO catalyst system leads to excellent substrate conversions and good selectivity of the desired products, resulting in minimal side reactions such as the formation of butyl-butyrate or acetone-self-condensation and related products. The latter process was the major pathway when PMO was used without any metal catalyst that promotes alcohol dehydrogenation (Table S2). We were further interested in other specific side reactions, such as, for example the origin of the long branched ketones (Scheme 2). These should originate from the coupling of 2-ethyl-hexanol, the product of the Guerbet reaction of 1-butanol, with acetone. In order to clarify this, a separate experiment was conducted using acetone and 2-ethylhexanol (Figure S4, Table S9) confirming the formation of higher alkylation products. An interesting question is the presence of 2-heptanol and 6-undecanol in addition to the desired ketones, as also observed by Goulas et al.20 Though their presence is not problematic given the next reaction step being a hydrodeoxygenation to alkanes, their formation indicates that an extra equivalent of hydrogen is produced in the system. One source of this is the Tishchenko pathway, the dehydrogenation of the hemiacetal to form butyl-butyrate. Another possible source of the hydrogen may be the decarbonylation reaction, which results in only gaseous products: carbon-monoxide and propane from butanal. Gas phase analysis of a typical reaction, using GC-TCD was performed, confirming the presence of propane as well as CO in addition to hydrogen (for description, see the Supporting Information, Section 2.1.2).

Product Formation Profiles and Hydrodeoxygenation. To investigate the capacity of our system, we have conducted experiments from 1.25 to 10 h at 200 °C under optimized conditions (Figure 4, Table S7). To our delight, already after 1.25 h, the acetone and butanol conversion reached 79.4% and 63.1%, respectively and already a considerable amount of C11 products were formed. Interestingly already after 2.5 h, the reaction was almost complete with 93% of acetone conversion (calculated 4656 µmol·g cat⁻¹·h⁻¹) and a total 87% selectivity to chain elongated products was obtained, from which 71% were ketones (58% C7+ ketones) and 16% alcohols (9.6% C7+ alcohols). The combined selectivity to C11 alcohols and ketones combined was as high as 64.7%. Over 20 h, the amount of alcohols obtained from the ketone products slightly increased and the total C7+ oxygenates were slightly increased from 67% to 71%.

Next, we have performed the hydrodeoxygenation (HDO) of the obtained mixtures in order to obtain clean mixtures of alkanes. To this end, the commercially available Ni/SiO2−Al2O3 catalyst was selected at 220 °C with 40 bar H2 and 12 h reaction time. These reaction conditions have been found through optimization using 2-heptanone as a model compound. Upon HDO, the carbon yield of the product mixture was carefully examined, indeed showing very good results (Figure 5, Table 1, Figure S7). Already after 2.5 h, the amount of C11 alkanes was significant (212.2 mg) and excellent carbon yield were obtained (78.4%). All the carbon yields are calculated based on the carbon content of the initial AB and ABE mixture (Section S3.2.1). The slight loss of mass balance is attributed to two factors, first to the loss of carbon-containing gases via decarbonylation in the first
° BuOH (5.46 mmol, 0.5 mL), acetone and 15 mg Raney Ni catalysts, acetone (2.70 mmol, 0.2 mL), 1-butanol (2.1 mL, solvent), dodecane (0.22 mmol, 50 μL, internal standard), 220 °C. For all data in table format, see the Supporting Information, Table S12.

Next, catalytic HDO of this mixture was performed and the carbon yields of alkanes (Figure S8.) were calculated based on an internal standard. According to this, an excellent 84% total carbon yield was achieved (Table 2, Table S13). The carbon yield of C7+ alkanes was found to be slightly lower compared to the value seen with the AB mixture, because acetone mono or dialkylation with EtOH yields C5–C7 ketones, which do not contribute to the C7+ region after HDO.

**CONCLUSIONS**

Here we describe that the solid base Mg–Al–PMO in combination with small amount of Raney Ni provides high selectivity in the coupling of 1-butanol with acetone as well as ABE mixture to longer chain ketones. The extent of common side reactions such as ester formation and decarbonylation could be minimized. Notably, this catalyst system provides high selectivity to chain elongated ketones (73%) and alcohols (12%) as well as a total C7+ ketones (62%) and alcohols (9.1%) in the coupling of acetone and 1-butanol at 200 °C and it functions comparably well at 180 °C. The observation that a 20% Ni doped PMO, preactivated in H2 stream provides higher activity and selectivity toward C7+ oxygenates than simple Ni20PMO, suggests that novel catalyst systems could be easily prepared and examined with careful variation of the Ni, Mg, and Al ratios and the addition of other dopants can be investigated to further tailor catalyst performance. In Ni20PMO, the formation of Ni nanoparticles upon activation in H2 flow was confirmed by TEM analysis and EDX elemental mapping. Last, a simple hydrodeoxygenation protocol was established that enables the conversion of these mixtures into obtain fuel range alkanes with excellent carbon utilization (up to 89%).

The Ni/SiO2–Al2O3 catalyst was also used in our earlier work for the HDO of lignocellulose derived product mixtures at 250 °C. It displayed excellent robustness and recyclability without coking in the HDO of model compound 4-propylcyclohexanone for 20 consecutive cycles, converting 12.4 g (88.5 mmol) substrate with just 200 mg catalyst. Therefore, we postulate that this catalyst will be highly suitable for a continuous flow setup involving HDO of products originating from the coupling of ABE mixtures.

**Coupling of ABE Mixture and Hydrodeoxygenation.** Under the conditions found ideal for the AB mixture, we have explored the catalytic coupling of the ABE mixture at 200 °C (Figure 6, Table S8). The molar ratio of the substrates was kept (2.3:3.7:1), mimicking the real fermentation mixture. Gratifyingly, full 1-butanol and ethanol conversion and 87.3% acetone conversion was seen after 20 h (581 μmol·g cat⁻¹·h⁻¹) and an excellent 88.4% selectivity toward oxygenates was achieved. There oxygenates comprised ketones (77.4%, out of which 57.6% were C7+ ketones) and a smaller amount of alcohols (11% out of which 7.5% were C7+ alcohols). Moreover, the extent of side reactions was minimal, since only 9.6% of high molecular weight side products and 0.2% MIBUK were obtained.

Table 1. Weight and Carbon Yield of Alkanes Obtained from the HDO of Catalytic Coupling Mixtures from Acetone and 1-Butanol

| Reaction Time (h) | C3  | C4  | C5  | C7  | C8  | C9  | C10 | C11 | C12+ | Total Alkanes | Carbon Yield (%) |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|------|--------------|-----------------|
| 2.5               | 2.3 | 0.5 | 4.7 | 71.5| 0   | 2.2 | 6.2 | 212.2| 34.2 | 333.8        | 78.4            |
| 5                 | 11.9| 0   | 9.7 | 73.6| 2.7 | 0   | 7.7 | 223.9| 37.2 | 366.5        | 86.0            |
| 10                | 8.3 | 0   | 9.0 | 68.7| 0.4 | 2.6 | 7.1 | 231.1| 39.9 | 369.2        | 86.6            |
| 20                | 3.4 | 0.7 | 15.2| 60.0| 0.8 | 2.4 | 7.5 | 244.7| 44.1 | 378.7        | 88.9            |

ACS Sustainable Chem. Eng. 2018, 6, 8468–8475

American Chemical Society
Figure 6. Results of the catalytic coupling of ABE mixture. Left: GC-FID trace of the product mixture showing all main components. Right: Product selectivities. Reaction conditions: 100 mg cat: Ni@Al₂O₃−SiO₂, dodecane (0.22 mmol, 50 µL, internal standard), 220 °C. Values determined by FID, using internal standard. For all data in table format, see the Supporting Information, Table S8.

Table 2. Weight and Carbon Yield of Alkanes Obtained from the HDO of Catalytic Coupling Mixtures from Acetone, Ethanol, and 1-Butanol

| Reaction Time (h) | C3   | C4   | C5   | C7   | C8   | C9   | C10  | C11  | C12+ | Total Alkanes | Total C7+ |
|------------------|------|------|------|------|------|------|------|------|------|---------------|-----------|
| 20               | 3.4  | 0.6  | 22.9 | 68.5 | 3.4  | 62.7 | 6.3  | 152.7| 30.5 | 351.0         | 84.0      | 61.3       |

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b00733.

Additional details regarding the materials, experimental procedures, characterization of catalysts, analysis of products and calculations (PDF)

**AUTHOR INFORMATION**

* Corresponding Author
K. Barta. Email: k.barta@rug.nl.

**ORCID**

Marc C. A. Stuart: 0000-0003-0667-6338
Katalin Barta: 0000-0002-8046-4248

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

K.B. is grateful for financial support from the European Research Council, ERC Starting Grant 2015 (CatASus) 638076. This work is part of the research program Talent Scheme (Vidi) with project number 723.015.005 (K.B.), which is partly financed by the Netherlands Organisation for Scientific Research (NWO). B.F. is grateful for the financial support from the Hungarian Ministry of Human Capacities (NTP-NFTÓ-17-B-0593). The authors are grateful to Léon Rohrbach for helping with the analysis of the gas phase of the reaction and to Zhuohua Sun for helping with the XRD measurements.

**REFERENCES**

(1) Horváth, I. T. Introduction: Sustainable Chemistry. Chem. Rev. 2018, 118, 369–371.
(2) Cséfalvy, E.; Akien, G. R.; Qi, L.; Horváth, I. T. Definition and application of ethanol equivalent: sustainability performance metrics for biomass conversion to carbon-based fuels and chemicals. Catal. Today 2015, 239, 50–55.
(3) Horváth, I. T.; Mehl, H.; Fábos, V.; Boda, L.; Mika, L. T. γ-Valerolactone—a sustainable liquid for energy and carbon-based chemicals. Green Chem. 2008, 10, 238–242.

(5) Alonso, D. M.; Bond, J. Q.; Dumesci, J. A. Catalytic conversion of biomass to biofuels. Green Chem. 2010, 12, 1493–1513.

(26) Onystyak, G.; Novodarskis, G.; Welisch, Á. F.; Pihlät, A. Upgraded biofuel from alcohol-acetone feedstocks over a two-stage flow-through catalytic system. Catal. Sci. Technol. 2016, 6, 4516–4524.

(12) Jin, Y.; Cheng, J. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour. Technol. 2002, 86, 506–577.

(29) Barta, K.; Matson, T. D.; Pettig, M. L.; Scott, S. L.; Iretskii, A. V.; Ford, P. C. Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol. Green Chem. 2010, 12, 1640–1647.

(30) Barta, K.; Bottari, G.; Sun, Z. Supercritical methanol as solvent and carbon source in the catalytic conversion of 1,2-diaminobenzenes and 2-nitroanilines to benzimidazoles. Green Chem. 2015, 17, 5172–5181.

(31) Matson, T. D.; Barta, K.; Iretskii, A. V.; Ford, P. C. One-Pot Catalytic Conversion of Cellulose and of Woody Biomass Solids to Liquid Fuels. J. Am. Oil Chem. Soc. 2011, 88, 14090–14097.

(32) Kumarapati, A. J.; Bottari, G.; Enno, P. M.; Heeres, H. J.; Barta, K. Tunable and Selective Conversion of 5-HMF to 2,5-Furandimethanol and 2,5-Dimethylfuran over Copper-Doped Porous Metal Oxides. ChemSusChem 2014, 7, 2266–2275.

(33) Barta, K.; Ford, P. C. Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids. Acc. Chem. Res. 2014, 47, 1503–1512.

(34) Sun, Z.; Couto Vasconcelos, A.; Bottari, G.; Stuart, M. C. A.; Bonura, G.; Cannilla, C.; Frusteri, F.; Barta, K. Efficient Catalytic Conversion of Ethanol to 1-Butanol via the Gubert Reaction over Copper and Nickel-Doped Porous. ACS Sustainable Chem. Eng. 2017, 5, 1738–1746.

(35) Sun, Z.; Bottari, G.; Afanasenko, A.; Stuart, M. C. A.; Deuss, P. J.; Fridrich, B.; Barta, K. Complete lignocellulosic conversion with integrated catalyst recycling yielding valuable aromatics and fuels. Nature Catalysis 2018, 1, 82–92.

(36) Abate, S.; Barbera, K.; Giglio, E.; Deorsola, F.; Bensaid, S.; Perathoner, S.; Pirone, R.; Centi, G. Synthesis, Characterization, and Activity Pattern of Ni–Al Hydroxalate Catalysts in CO₂ Methanation. Ind. Eng. Chem. Res. 2016, 55, 8299–8308.

(37) Biao, L.; Wang, W.; Xia, R.; Li, Z. Ni-Based Catalyst Derived from Ni/Al Hydroxalate-like Compounds by the Urea Hydrolysis Method for CO₂ Methanation. RSC Adv. 2016, 6, 677–686.

(42) Li, G.; et al. Synthesis of diesel or jet fuel range cycloalkanes with 2-methylfuran and cyclopentane from lignocellulose. Energy Fuels 2014, 28, 5112–5118.