

Direct Production of 5-Hydroxymethylfurfural via Catalytic Conversion of Simple and Complex Sugars over Phosphated TiO₂

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A water–THF biphasic system containing *N*-methyl-2-pyrrolidone (NMP) was found to enable the efficient synthesis of 5-hydroxymethylfurfural (HMF) from a variety of sugars (simple to complex) using phosphated TiO_2 as a catalyst. Fructose and glucose were selectively converted to HMF resulting in 98% and 90% yield, respectively, at 175 °C. Cellobiose and sucrose also gave rise to high HMF yields of 94% and 98%, respectively, at 180 °C. Other sugar variants such as starch (potato and rice) and cellulose were also investigated. The yields of HMF from starch (80–85%) were high, whereas cellulose resulted in a modest yield of 33%. Direct transformation of cellulose to

Introduction

5-Hydroxymethylfurfural (HMF) is a vital platform chemical that could revolutionize the biorefinery industry. It is a key component in the production of high-value chemicals, polymers, and fuels.^[1] For example, HMF can be readily oxidized to 2,5-furandicarboxylic acid (FDCA),^[2] a potential replacement for petroleum-based terephthalic acid, relevant to the plastic industry for the production of polyethylene terephthalate (PET).^[3] Rehydration of HMF gives levulinic acid from which γ -valerolactone can be produced, a useful chemical that serves as a solvent and fuel additive.^[4] Another important derivative of HMF is 2,5-dimethylfuran (DMF), a potential biofuel.^[5] DMF has an energy density comparable to gasoline (31.5 vs. 35 MJL⁻¹) and approximately 40% higher than ethanol (23 MJL⁻¹),^[6] making it suitable as a replacement for ethanol in gasoline–ethanol blends. 2-Methylfuran, which is an intermediate of HMF hydrogenoly-

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HMF in significant yield (86%) was assisted by mechanocatalytic depolymerization—ball milling of acid-impregnated cellulose. This effectively reduced cellulose crystallinity and particle size, forming soluble cello-oligomers; this is responsible for the enhanced substrate–catalytic sites contact and subsequent rate of HMF formation. During catalyst recyclability, P–TiO₂ was observed to be reusable for four cycles without any loss in activity. We also investigated the conversion of the cello-oligomers to HMF in a continuous flow reactor. Good HMF yield (53%) was achieved using a water–methyl isobutyl ketone + NMP biphasic system.

sis, also possesses excellent fuel qualities.^[5] Therefore, criticalto-efficient production of bio-fuels and chemicals as well as a replacement of petroleum-derived counterparts requires a cost-effective process for selective production of HMF from biorenewable feedstock.^[7]

HMF can be obtained by catalytic dehydration of simple sugars such as fructose and glucose or directly from cellulose (a complex sugar) as shown in Scheme 1. In spite of excellent production of HMF achievable from fructose and glucose,^[8] in practice it is more economical and sustainable to use a biomass-derived sugar that is readily available and accessible. Cellulose is readily obtained from industry, forestry, or agricultural residues.^[9] Unlike starch, which is consumed by humans, cellulose is inedible; thus, it has the added advantage of not impacting negatively on agricultural food production. Hence, a one-pot chemical transformation of cellulose to HMF is a potential strategy to effectively utilize this enormous biomass reserve to supply the next generation of chemicals and fuels. Nonetheless, chemical conversion of cellulose faces a major challenge, that is, its robust structure.^[10] Cellulose has a high crystallinity and chemical stability and is insoluble in water, which leads to poor reactivity. A possible solution to overcome this issue is to solubilize cellulose prior to reaction.

Although cellulose is known to be insoluble in most conventional solvents, recent advances in the dissolution of cellulose in the presence of ionic liquids^[11] or subcritical/supercritical fluids^[12] have been proposed. These techniques depolymerize cellulose into soluble oligosaccharides, thus allowing subsequent production of useful chemical compounds in high yields. Despite the success and viability of these strategies,





Scheme 1. Catalytic reaction pathway for conversion of sugar to HMF.

high costs associated with recycling of ionic liquids^[13] or high energy input required to generate sub- or super-critical fluids^[14] pose a number of challenges for process economics and sustainability. Alternatively, cellulose can be solubilized through mechanocatalytic depolymerization.^[15] This technique involves a contact between cellulose and an acid catalyst, followed by a mechanically assisted solid-state depolymerization. This approach of cellulose dissolution is scalable, amenable to multi-feedstock, involves less waste, and can be easily integrated into existing biorefineries.^[15a] Since the pioneering work of Hick et al.,^[15a] mechanocatalytic depolymerization of cellulose using acid catalysts has become of great interest for the complete dissolution of cellulose.^[15b,c]

Due to the realization of the depolymerization of cellulose into soluble oligomers, it would be highly desirable to develop an efficient heterogeneous catalytic route for HMF production under continuous flow conditions. A plethora of homogeneous and heterogeneous catalytic systems have been described in the literature for the conversion of solubilized cellulose to HMF in a batch process.^[16] For example, cellulose dissolution with 1butyl-3-methyl-imidazolium chloride ([BMIM]Cl) was demonstrated to facilitate the conversion of cellulose to sugars and further to HMF in high yields (62%) catalyzed by a paired CrCl₃/LiCl catalyst system.^[16c] Shi et al.^[16d] described the formation of 53% HMF by direct degradation of cellulose in a biphasic system using concentrated NaHSO₄ and ZnSO₄ as a co-catalyst. Nandiwale et al.^[16e] reported the catalytic conversion of cellulose using bimodal micro-/mesoporous H-ZSM-5 zeolite, in which HMF was formed in 46% yield and 67% cellulose conversion. Mascal and Nikitin^[16f, 17] reported another route of cellulose deconstruction in an aqueous HCI-LiCI solution, yielding mainly 5-chloromethylfurfural, which could subsequently be converted to high HMF in high yield (72%) by performing a simple hydrolytic reaction.^[16f] To the best of our knowledge,

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the only existing report of HMF production from cellulose utilizing a flow reactor is by McNeff et al.^[18] In their approach, a fixed-bed porous-metal-oxidebased catalytic process was utilized. Dissolution of cellulose was achieved by introducing a preheated water-organic mixture into a solubilization chamber containing cellulose. The cascade process of a preheatersolubilization chamber-catalytic reactor allowed the continuous depolymerization of cellulose, which resulted in 87% conversion of cellulose to produce HMF in 35% yield.

Herein, we report the catalytic production of HMF from sugars applying phosphated TiO_2 catalyst under batch as well as continuous flow conditions. The

main aim is to selectively transform cellulose to HMF. However, because of the complexity of working with cellulose, a parametrical activity study for the catalytic conversion of glucose to HMF using pure and modified TiO₂ with phosphorus, tungsten, molybdenum, and vanadium oxides was performed. In addition, the effect of phase modifiers on the aqueous phase of the biphasic water–organic medium was examined. The versatility of the batch process was checked by testing other sugar variants such as fructose, cellobiose, sucrose, starch, and cellulose. Dissolution rate and reactivity of cellulose was enhanced through a mechanocatalytic treatment using the procedure described by Shrotri et al.^[15c] Lastly, the viability of converting the water-soluble cello-oligomers to HMF in a biphasic continuous reactor was explored.

Results and Discussion

A neutral amine sol-gel method was used to prepare TiO₂ nanoparticles. A previous report of the material synthesis showed that the TiO₂ nanoparticles were of anatase phase with a mesoscopic structure.^[19] The material possessed Lewis acidity and was found active for the dehydration of glucose to HMF. In addition, the catalytic performance of TiO₂ was promoted by phosphate treatment due to enhanced surface acidity. Indeed, increasing the surface area and the accessibility of the active sites on TiO₂ was also reported by others to improve the catalytic performance of TiO₂ to efficiently catalyze the dehydration of sugars into HMF.^[20] In this study, we investigate the effect of tungstate, molybdate, and vanadate on the properties of TiO₂, especially on the surface acidity in comparison to that of phosphate. For this purpose, hydrated titanium hydroxide initially prepared through the neutral amine sol-gel method was impregnated with ammonium salts of phosphorus, tungsten, molybdenum, and vanadium.



Catalyst characterization

Powder X-ray diffractometry (XRD) was used to examine the crystalline structure of the as-synthesized materials. Figure 1 presents the XRD patterns of TiO_2 nanoparticles before and after modification.



Figure 1. XRD measurement of (a) $TiO_{2'}$ (b) V-TiO₂, (c) P-TiO₂, (d) W-TiO₂, and (e) Mo-TiO₂. (*) Vanadium oxide and (\bullet) rutile.

We observed a distinct peak reflection at 2θ value of 29.5° , which could be matched with the (101) plane of the JCPDS file no. 21-1272. This indicates the formation of the anatase TiO_2 polymorph in all samples. It is also of interest that no evidence of the crystalline phases of the phosphorus, tungsten, and molybdenum oxides were observed in Figure 1 c-e. This suggests that these oxides could be present in an amorphous phase or as crystals with very small sizes that are not detectable by XRD. Contrarily, weak reflections of crystalline vanadium oxide and the onset of rutile TiO₂ formation were identified in Figure 1 b, which can be correlated with JCPDS file numbers 01-089-0612 and 21-1276, respectively. The anatase-to-rutile transformation was described to proceed via the surface reaction of vanadium oxide with titanium sites governed by a grain growth mechanism.^[21] This fact is supported by the estimated crystal size determined by applying Scherrer equation to the (101) plane. It is noted that the average crystal size of TiO_2 increased approximately twofold from 27.3 to 53 nm on addition of vanadium ions, indicating crystal growth (Table 1). On the other hand, according to the XRD line broadening analysis of other modified TiO₂ samples, the crystal size of TiO₂ was reduced and estimated to be between 6 and 10 nm.

The result of the N₂ adsorption–desorption isotherm of the TiO₂ samples is also presented in Table 1. The isotherm of pure TiO₂ shown in Figure S1 a in the Supporting Information exhibits a sharp increase in the adsorbed N₂ volume at a relative pressure of 0.65, which is characteristic for capillary condensation of a material with uniform mesopore structures. The isotherms of the modified TiO₂ samples (Figure S1 b–d) are similar to the parent material, and the onset of the condensation step shifts to lower values (*P*/*P*₀ \approx 0.6), with the exception of V-TiO₂

Table 1.	Physical	and	acid	properties	of	pure	and	modified	TiO ₂	nanopar-
ticles.										

Entry	Sample	$S_{BET}^{[a]}$ [m ² g ⁻¹]	Pore volume ^[b] [cm ³ g ⁻¹]	Crystal size ^[c] [nm]	Acidity ^[d] PyL	[µmol g ⁻¹] PyB
1	TiO ₂	54.7	0.22	27.3	3.68	-
2	P-TiO ₂	151.0	0.43	6.12	0.72	3.81
3	W-TiO ₂	112.5	0.32	9.54	1.73	5.35
4	Mo-TiO ₂	115.2	0.33	9.36	-	18.2
5	V-TiO ₂	9.34	0.02	53.0	0.20	0.97
[a] BE	T surface	area. [k) Determined	by Barrett–Jo	yner–Haler	nda (BJH)

measurement at $P/P_0 = 0.99$. [c] Measured by XRD using Debye–Scherrer equation for the (101) plane. [d] Determined using the Lambert–Beer Law.

(Figure S1 e). The isotherm of V-TiO₂ resembles a typical material with low surface area. The reason for this can be ascribed to the phase transition from anatase to rutile,^[22] which causes a drastic reduction in the surface area and corresponding crystal growth.

TEM micrographs of the samples are shown in Figure 2. The morphological features of TiO_2 are influenced by the presence of other oxides. We clearly observed that the particle size of TiO_2 (Figure 2 a) is far larger than that of P-TiO₂, W-TiO₂, and Mo-TiO₂ (Figure 2 b–d), which can be used to explain the low specific surface area of TiO_2 in comparison with these three samples. The phosphate, tungstate, and molybdate ions in TiO_2 are believed to stabilize the TiO_2 structure and prevent sintering during thermal treatment, which could have led to grain growth.^[19,23] Contrarily, a remarkable increase in crystal size is observed with V-TiO₂, suggesting crystal growth (Fig-



Figure 2. TEM micrographs of (a) TiO_{2r} (b) P-TiO₂, (c) W-TiO₂, (d) Mo-TiO₂, and (e) V-TiO₂.



ure 2 e). Together with the XRD results, a mechanism of crystal growth can be deduced to occur by lattice strain relaxation, which involves reconfiguration of the TiO₂ crystal geometry and reduction of the induced strain arising from lattice distortion caused by the presence of vanadium ions.^[24] This behavior is facilitated by thermal treatment that increases mobility and segregation of vanadium oxide as well as transformation of the TiO₂ structure to the thermodynamically more stable rutile phase.^[24]

Pyridine adsorption experiments on the pure and modified TiO_2 nanoparticles were conducted to probe the presence of Lewis or Brønsted surface acid sites. As shown in Figure 3a, the pyridine infrared (py-IR) spectrum of TiO_2 is dominated by absorption bands in the regions of 1400–1450 cm⁻¹ and 1570–1620 cm⁻¹, typical of pyridine molecules coordinated with Lewis acid sites. Therefore, TiO_2 is defined here as a pure Lewis acid catalyst.



Figure 3. FTIR spectra of pyridine adsorbed on (a) TiO_2, (b) P-TiO_2, (c) W-TiO_2, (d) Mo-TiO_2, and e) V-TiO_2.

The surface interaction of TiO₂ with the oxides of phosphorus, tungsten, molybdenum, and vanadium leads to considerable modification of the nature of its surface acid sites. The detection of a band in the region of 1500–1560 $\rm cm^{-1}$ on $\rm TiO_2$ after modification with these oxides (Figure 3 b-e) allows us to identify the presence of Brønsted acid sites. The variation of the intensity of this band indicates a change in concentration of the available Brønsted acid sites. The estimated concentrations of Brønsted (PyB) and Lewis (PyL) acid sites are presented in Table 1. The result shows that the Brønsted acidity decreases in the order: $Mo-TiO_2 > W-TiO_2 > P-TiO_2 > V-TiO_2$. More so, Mo-TiO₂ appears to be a pure Brønsted acid catalyst because of the disappearance of all the bands associated with Lewis acid sites. Similarly, Damyanova et al.^[25] observed that pyridine adsorbed on TiO₂-supported 12-molybdophosphate existed predominantly in the protonated form (Brønsted acidity) when the sample was pretreated at 250 °C; however, Lewis acidity appeared on the sample pretreated at 350 °C due to the presence of isolated Mo⁶⁺ cations of molybdenum oxide phase(s). Hence, a plausible reason for the acidity change of TiO₂ from Lewis to Brønsted in Mo-TiO₂ may be as a result of the strong interaction between the surface of titanium hydroxide and molybdenum oxide. In the case of the other modified TiO_2 samples, the presence of weak band at 1450 cm⁻¹ implies that a relatively small amount of Lewis acid sites are still retained.

Catalyst evaluation

Simple sugars to HMF

Previously, we reported that P-TiO₂ exhibits a better catalytic performance than TiO₂ in the transformation of glucose to HMF in a water–butanol reaction medium.^[19] Herein, glucose dehydration is carried out in a water–THF biphase system, and the catalytic performances of TiO₂ and P-TiO₂ are compared. Preliminary experiments using 2 wt% glucose concentration as the reaction feed were conducted and the results are presented in Table 2. The outcome of the experiment confirmed the

Table 2. Catalytic conversion of glucose to HMF using TiO ₂ and modified TiO ₂ nanoparticles. ^[a]						
Entry	Sample	Glucose conc. [wt %]	Glucose conv. [%]	HMF yield [%]		
1	TiO ₂	2	90.4	72.8		
2	P-TiO ₂	2	93.6	83.4		
3	P-TiO ₂	5	96.5	62.8		
4	V-TiO ₂	5	99.9	35.5		
5	W-TiO ₂	5	98.5	27.5		
6	Mo-TiO ₂	5	99.9	17.0		
[a] Reaction conditions: glucose/cat. 4:1 w/w ratio, 100 mL solvent (water/THF = 1:4 v/v), 4 g NaCl, 105 min reaction time, 175 °C reaction temperature, 20 bar Ar gas.						

improved activity of P-TiO₂ over TiO₂. A conversion of 90.4% and 72.8% HMF yield was achieved with TiO₂ (Table 2, entry 1). However, the HMF yield increased to 83.4% at 93.6% conversion when P-TiO₂ was used as catalyst (entry 2). Other identifiable products were fructose, levoglucosan, levulinic acid, formic acid, and acetic acid; their corresponding yields are listed in Table S1.

However, from an industrial point of view, it is of interest to work at a relatively high glucose concentration to achieve a more economical and sustainable process. When conducting the reaction with 5 wt% glucose concentration on P-TiO₂ under similar reaction conditions, the HMF yield dropped to 62.8% (entry 3). This phenomenon can be explained as follows: at high concentration, glucose forms oligosaccharides that contain reactive hydroxy groups, which give rise to higher rates of cross-polymerizations with reactive intermediates and HMF.^[26] This hypothesis is supported by a color change of the catalyst from yellowish-white to dark brown at the end of the reaction (Figure S2). The color change can be ascribed to the deposition and coverage of the catalyst surface with humin compounds. Therefore, it is essential to develop a catalyst system that is resistant to humins or a reaction medium that hinders the formation of humins to achieve effective conversion of high glucose concentration feedstocks into HMF with



good selectivity and high conversion. Hence, TiO₂ was modified by the introduction of molybdenum, vanadium, and tungsten oxides in a similar procedure as that for phosphorus oxide.^[19] This attempt was unsuccessful as lesser yields of HMF were achieved (entries 4-6). The catalytic performance of these materials can be understood with respect to their surface acidity. On the basis of the py-IR results, Mo-TiO₂ is characterized mainly by Brønsted acidity and very low HMF yield could be achieved. This is because the isomerization of glucose to fructose, crucial to HMF formation, is catalyzed by Lewis acidity. On the other hand, W-TiO₂ and V-TiO₂ have both Brønsted and Lewis acid functionalities just as P-TiO₂. The band intensities of W-TiO₂ suggest the presence of a higher concentration of acid sites than P-TiO₂. The reduced HMF yield on W-TiO₂ may then be ascribed to the presence of excess acid sites, which could be responsible for favoring unwanted reactions. There is a general consensus that interaction of bulk vanadium oxide with the surface of TiO₂ forms a thin monolayer of vanadium oxide.[27] We reason that the segregated vanadium oxide led to partial monolayer coverage of the TiO₂ surface. As a result, the Brønsted acidity of the vanadium oxide comes into contact with the glucose substrate and only a few Lewis acid sites are available to play a relevant role during the isomerization of glucose to fructose. However, V-TiO₂ results in a higher HMF yield in comparison to W-TiO₂ (35.5% vs. 27.5%), which can be ascribed to the acid site concentration. W-TiO₂ has a higher concentration of acid sites (especially Brønsted sites), which can easily promote rapid degradation of HMF.

The other approach was to modify the reaction medium to minimize HMF degradation. Undesired side reactions can be suppressed through the addition of phase modifiers.^[28] In this study, organic solvents such as acetone, acetonitrile (AN), *N*-methyl-2-pyrrolidone (NMP), and toluene were examined. Figure 4a shows that selectivity to HMF was significantly improved by the addition of NMP. For example, addition of 10 mL of NMP to the water–THF medium enabled about 80% HMF yield. According to a report from Román-Leshkov et al.,^[28] NMP acts as an aqueous phase modifier that can suppress humin formation in water and simultaneously enhance parti-



Figure 4. (a) Influence of organic co-solvents on the selective conversion of glucose to HMF; 10 mL organic co-solvent, 70 mL THF. (b) Volume ratio effect of THF/NMP on glucose-to-HMF reaction. Reaction conditions: 4:1 glucose/cat. *w/w* ratio, 1.25 g P-TiO₂ catalyst, 100 mL solvent (water/organic = 1:4 *v/v*), 4 g NaCl, 105 min reaction time, 175 °C reaction temperature, 20 bar Ar gas. ($_{\odot}$) Glucose conversion and ($_{\odot}$) HMF yield.

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tioning of HMF into the organic layer. Horvat et al.^[29] explained the mechanism of HMF transformation in aqueous medium. The authors stated that addition of water to the 2,3-carbon positions on HMF is responsible for the undesired polymerization reactions to humin, whereas water added to 4,5-carbon positions gave way to levulinic acid formation via decarboxylation to produce formic acid. Therefore, we can say that the beneficial role of NMP on HMF formation is related to its ability to minimize ring opening of these carbon atoms. The less intense color change of the catalyst after reaction also supports the fact that NMP helps to reduce humin formation and deposition on the catalyst (Figure S3) in comparison to the reaction without NMP.

Furthermore, we attempted to favor the formation of HMF by increasing the volume of NMP added to the water-THF reaction medium. We observed that HMF yield increased to a maximum value of 90.5% at 60:20 THF/NMP volume ratio (Figure 4b). Further increase in NMP volume caused a drastic reduction in HMF yield. This is because a single phase reaction system formed at the end of the reaction. Since there is a lack of partitioning, the already formed HMF undergoes further reaction. Thus, the optimal reaction medium for subsequent experimental design is 20:60:20 water/THF/NMP volume ratio.

Using these reaction conditions, glucose was replaced with fructose as the feed in the production of HMF. The results are presented in Table 3 and show that conversion of fructose into HMF proceeds significantly faster than with glucose, achieving 98.6% HMF yield within 30 min of reaction time (Table 3, entry 2). This suggests that the mechanism for the transformation of glucose to HMF occurs via the rate-determining step (formation of the intermediate fructose). Other simple sugars also investigated for the production of HMF are cellobiose and sucrose. Cellobiose and sucrose are dimers consisting of glucose-glucose and glucose-fructose monomers, respectively. It is expected that the presence of additional functional groups in each of these dimers will increase the multistep reactions, beginning with hydrolytic reaction to produce their constituent monomer units, followed by isomerization and dehydration reaction steps. Therefore, we carried out the reaction with

the dimers at a higher temperature to facilitate the hydrolysis step. Identical results of HMF formation were obtained for both cellobiose and sucrose (entries 3 and 4). However, the higher HMF yield obtained from sucrose in comparison with cellobiose (98.2% vs. 94.2%) is attributed to the presence of fructose in the dimer structure, which can undergo dehydration faster than glucose.

Complex sugars to HMF

Considering the successful production of HMF in high selectivity from simple sugars, we investigated a much more practical and sustainable production of HMF from complex sugars. Thus, we explored the reactivity of starch and cellulose towards HMF formation. The conversion of starch into HMF proceeds significantly faster and with higher selectivity than cellu-



Entry	Substrate	<i>Т</i> [°С]	Conversion [%]	HMF yield [%]
1	fructose ^[b]	175	99.9	98.6
2	alucose	175	98.2	90.5
3	cellobiose	180	99.7	94.2
4	sucrose	180	99.8	98.2
5	starch-rice	180	99.7	80.7
6	starch-potato	180	99.8	84.6
7	cellulose	180	56.7	33.0
8	pretreated cellulose	180	99.9	86.2

lose (Table 3, entries 5-7). Starch from rice and potato gave rise to good yields of HMF (80-85%), whereas a modest HMF yield (33%) was obtained from cellulose. The reason for the disparity in the reactivity of starch and cellulose can be attributed to the structural difference of the two polymers. Starch is a polymer of glucose units linked together through α -1,4 or α -1,6 linkages whereas cellulose is a polymer of glucose units linked together in an unbranched β -1,4 fashion, which are densely packed because of strong inter-chain hydrogen bonds.^[9b] Due to the presence of strong glycosidic bonding between the sugar moieties of cellulose, it is more crystalline and less soluble than starch. On this basis, reactivity is low due to poor interaction between cellulose and the catalyst, which are both present in solid state. However, cellulose is more ideal as a starting material for HMF production, as it is the most abundant naturally occurring feedstock. Conversion of cellulose to HMF in significant yields can be achieved through a mechanocatalytic depolymerization of cellulose, which should reduce cellulose crystallinity and simultaneously facilitate the cleavage of β -1,4-glycosidic bond linkages.^[15a-e] By acid impregnation of cellulose, formation of soluble cello-oligomers during ball milling is facilitated. Entry 8 of Table 3 shows that conversion rate of cellulose was significantly promoted after the pretreatment process, producing 86.2% yield of HMF. Our research group has previously shown through X-ray diffraction and scanning electron microscopy analyses that the structure of the pretreated cellulose is amorphous and has a reduced particle size.^[15c] Furthermore, liquid state nuclear magnetic resonance results suggest the formation of oligomers comprising mainly C1-C6 carbons. All these factors are responsible for the enhanced solubility and reactivity of the pretreated cellulose. In this way, a good HMF yield can be effectively produced from cellulose.

Catalyst recyclability

To minimize cost and environmental impact of catalytic industrial processes, it is desirable that the catalyst is stable and can be easily recycled once the reaction ends. Recycling efficiency of P-TiO₂ catalyst was investigated using the conversion of glucose to HMF as a representative reaction. The reaction was performed in a water/(THF + NMP) medium at 175 °C for 105 min. After each reaction, the catalyst was recovered by filtration and the spent catalyst was washed with acetone and kept under vacuum at 80 °C overnight for drying. The recovered catalyst was reused without any post treatment. This procedure was followed for four subsequent cycles, and the results are shown in Figure 5. The activity of the catalyst resulted in > 90% yield of HMF and remained fairly constant even after its repeated use for four times. As reported previously, catalyst regeneration was performed because of deactivation resulting from catalyst surface coverage by deposited humins, albeit structural stability of the catalyst was maintained.^[19] With NMP serving as an aqueous phase modifier, unwanted reaction to



Figure 5. Catalyst recyclability test. Reaction conditions: glucose/cat. 4:1 *w*/ *w*, 100 mL solvent (water/THF + NMP = 1:4 *v*/*v*), 4 g NaCl, 105 min reaction time, 175 °C reaction temperature, 20 bar Ar gas. ($_{\odot}$) Glucose conversion and (**=**) HMF yield.

humins was greatly inhibited. This was further supported through a quantitative analysis of deposited humins on the catalyst. The spent catalysts after the reaction, with and without NMP in the reaction system, were recovered, washed with deionized water, filtered, and kept under vacuum at 80 °C overnight for drying. The carbon content of a known amount of samples was analyzed using a CHNS-O elemental analyzer. The carbon content of the fresh catalyst sample was also analyzed for reference. The result shows that <0.4% carbon was present on the fresh sample. For the reaction system with NMP, 4.1% carbon was found on the spent catalyst, which increased to 21.2% on the spent catalyst from the reaction system without NMP. The measured carbon content can be related to the amount of humins deposited on the catalyst surface, which is relatively high in the reaction system without NMP. Thus, we can deduce that the inhibitory effect of NMP on humin deposition on the catalyst surface seems to explain the observed stability of the catalyst activity.

HMF production under continuous flow conditions

To further improve the attractiveness of HMF production and simulate an industrial scenario, we investigated the catalytic performance of phosphated TiO_2 for the conversion of cellu-



lose in a biphasic continuous flow reactor. The reactor system consisted of a U-shaped stainless steel tubular reactor, two HPLC pumps (Alltech 426), heating oil bath, back pressure regulator, and a reservoir to collect the reaction product. A schematic diagram of the reactor setup is shown in Figure 6.

The biphasic system consists of a sugar solution (aqueous solution of the soluble cello-oligomers obtained from treated cellulose) and an organic solvent mixture [methyl isobutyl ketone (MIBK)/NMP 3:1 v/v]. The choice of MIBK in replacing THF as the organic extracting solvent is based on its very low



Figure 6. Schematic diagram of the flow reactor setup for the conversion of cello-oligomers to HMF.

miscibility with water even at high reaction temperature.^[18] The two feed streams were delivered by the HPLC pumps, and then connected by a 'T' connection to form a single premixed stream prior to entering the flow reactor. A back pressure regulator was connected to the reactor outlet to control the pressure of the reaction system. Under a steady flow rate at 60 bar (back pressure), the preloaded reactor with P-TiO₂ catalyst (400 mg) was immersed in the heating oil bath, which was maintained at the reaction temperature. A short induction period was noticed, which may be attributable to back mixing of liquid in the pressure regulator. A factor used to measure the efficiency of the reactor is liquid hourly space velocity (LHSV). Herein, it is defined as the ratio of the volumetric flow rate of the feed solution (in mLh^{-1}) to the heated reactor volume (in mL).

The role of LHSV on the catalytic transformation of the cellooligomers was investigated. The different LHSVs were obtained by changing the total flow rates of the feed streams between 0.2 and 0.4 mLmin⁻¹, which corresponds to a LHSV of 12.6– 25.2 h⁻¹. The flow rate of the two feed streams was kept at a ratio 1:1. As shown in Figure 7a, an initial experiment at 220 °C showed that a maximum HMF yield of 53% could be reached at a total flow rate of 0.3 mLmin⁻¹, corresponding to a LHSV of 18.6 h⁻¹. At higher LHSVs, the yield of HMF started to decline, which is attributable to shorter residence time within the reactor and, hence, reduced contact time of the sugar substrate with the catalyst.

The effect of reaction temperature was also investigated, and the experiments were carried out between 210-230 °C at a fixed LHSV of 18.9 h⁻¹. In Figure 7 b, we observed that the temperature has a significant effect on the HMF yield. When the temperature rose from 210 to 220 °C, the HMF yield increased significantly from about 40% to 53% within 60 min



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Figure 7. Effect of the reaction parameters (a) LHSV, (b) reaction temperature, (c) catalyst loading amount on the production of HMF in a flow reactor using P-TiO₂ as catalyst. Reaction conditions: 5 g cello-oligomer in 100 mL water, 3:1 MIBK/NMP *v*/*v* ratio , 1:1 water/MIBK + NMP *v*/*v* ratio, and 60 bar back pressure.

time on stream. This suggests that a higher temperature accelerates glycosidic bond cleavage of the cello-oligomers, and thus reactivity is enhanced. However, a further increase of the reaction temperature to 230 °C was detrimental for HMF yield as shown in Figure 7 b. This may be due to an unwanted reaction producing humins. Another factor that may enhance reaction performance is catalyst loading. Under a fixed LHSV of 18.9 h^{-1} and reaction temperature of 220 $^\circ\text{C},$ we studied the effect of catalyst loading amount between 350 and 450 mg. Based on the results illustrated in Figure 7 c, we observed HMF yield to increase with an increase in catalyst loading from 350 to 400 mg. The enhanced productivity can be ascribed to more active sites being accessible by the reactant. With further increase in catalyst loading, the yield of HMF declined. We can deduce that catalyst loading of 400 mg provides the required acid sites for the multi-step reactions in the conversion of the cello-oligomers to HMF. Above 400 mg, excessive acid sites can promote degradation of HMF, resulting in the decline of HMF yield. In spite of a considerable activity decay as the reaction progressed beyond 40 min time on stream, which may be due to glucose fractions of the cello-oligomers turning into char or humins, we were able to demonstrate the feasibility of the continuous production of HMF from cellulose in a relatively good yield. Further optimization of reactor configuration and process conditions may effectively enhance the application of this biphasic continuous reactor for the production of HMF.



Conclusions

We described a batch and continuous process of catalytic conversion of sugars to HMF in a biphasic system. The effectiveness of the catalytic process to selective formation of HMF was enhanced by adding N-methyl-2-pyrrolidone (NMP) to the reaction medium. This effect was the consequence of the suppression of undesired polymerization of HMF to humins. Phosphated TiO₂ was found to be an efficient and versatile solid acid catalyst in the selective conversion of a variety of sugars towards HMF formation. The reaction system with water-THF + NMP medium and P-TiO₂ as catalyst operated as a batch reaction process afforded fructose and glucose conversion efficiencies up to 98% and 90% HMF yields. Furthermore, cellobiose and sucrose conversions achieved 94% and 98% HMF yields, respectively. The minor difference in their reactivity was ascribed to differences in the dehydration rate of the monomeric units of the dimers. Sucrose contains fructose, which is more reactive than glucose. Similarly, a higher HMF yield (80-85%) could be obtained from starch (rice, potato) than from cellulose (33%), which was mainly attributed to the hydrolysis rate as glucose units of cellulose are strongly linked by β-1,4-glycosidic bonds. Mechanocatalytic depolymerization of cellulose was used as an efficient pretreatment process for the production of soluble cello-oligomers that can be easily hydrolyzed to glucose units, subsequently achieving 86% HMF yield. A catalyst recyclability study showed that the P-TiO₂ catalyst could be easily recovered and that reproducible and stable activity was achieved.

A flow reactor system was also used to demonstrate the capability of a continuous production of HMF. Utilizing the soluble oligomers obtained from pretreated cellulose in a water– MIBK+NMP biphasic system and P-TiO₂ as catalyst, a reasonably good yield of HMF (53%) was obtained. Thus, the pretreatment of cellulose to give soluble oligomers appears to be advantageous and applicable for the continuous production of HMF using a flow reactor. Hence, this approach is amenable to direct transformation of real biomass for production of HMF in scalable quantities.

Experimental Section

Materials and catalyst preparation

The following chemicals were used: glucose (\geq 99.5%, Sigma–Aldrich), fructose (99%, Sigma–Aldrich), cellobiose (\geq 98%, Sigma–Aldrich), cellulose (Sigmacell Type 20, 20 µm), starch-rice (Sigma–Aldrich), starch-potato (Sigma–Aldrich), 5-hydroxymethyfurfural (\geq 99%, Sigma–Aldrich), titanium(IV) butoxide (97%, Sigma–Aldrich), *n*-butanol (\geq 99.4%, Sigma–Aldrich), ammonium phosphate monobasic (\geq 98%, Sigma–Aldrich), ammonium molybdate tetra-hydrate (81–83% MoO₃ basis, Sigma–Aldrich), ammonium metavanadate (\geq 99%, Sigma–Aldrich), aqueous ammonia solution (28 wt%, Sigma–Aldrich), tetrahydrofuran (99.9%, Merck), methyl isobutyl ketone (99.5%, Sigma–Aldrich), *N*-methyl-2-pyrrolidone (99.5%, Sigma–Aldrich), acetonitrile (99.9%, Merck), toluene (99.9%, Merck), and acetone (99.9%, Merck). Ultra pure water (18 M Ω cm⁻¹)

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from Elga ultra pure apparatus was used for catalyst synthesis and reaction.

TiO₂ and modified TiO₂ nanoparticles were prepared according to our previously developed method.^[19] Typically, titanium hydroxide hydrate was prepared by the neutral amine sol-gel technique using titanium(IV) butoxide as the TiO₂ precursor. Excess solvent was evaporated and the sample was dried at 80°C overnight. Phosphating was accomplished by treating the titanium hydroxide hydrate with ammonium phosphate monobasic. Titanium hydroxide was slurred in a minimum amount of aqueous ammonium phosphate solution. The mixture was stirred for 4 h before the removal of excess water by evaporation and dried at 80°C overnight. TiO₂ containing 15 wt% phosphate was employed in this study. Addition of molybdate, vanadate, and tungstate to TiO₂ was carried out in a similar procedure outlined above using ammonium molybdate, ammonium metavanadate, and ammonium metatungstate, respectively. Samples were then calcined at 600 °C for 4 h. Catalyst samples were designated as x-TiO₂, where x represents P, Mo, V, and W heteroatoms.

Catalyst characterization

Structural analysis of the samples were characterized by X-ray diffraction (XRD) using a Rigaku Miniflex diffractometer with a filtered monochromatic CoK_a radiation. The diffraction patterns were collected in the range of $10^{\circ} \le 2\theta \le 90^{\circ}$ with a step size of 0.02. Specific surface area was determined by carrying out N₂ adsorption at -196 °C using a Micromeritics TriStar II 3020 surface area and porosity analyzer. Prior to analysis, the samples were outgassed at 200 °C for at least 8 h under vacuum to remove the surface adsorbed species. The surface area was calculated by using the Brunauer-Emmett-Teller (BET) method. Total pore volume was estimated using the volume of $N_{\rm 2}$ gas adsorbed at a relative pressure (P/ P_{0}) of 0.99. The morphology of the synthesized particles was investigated by transmission electron microscopy (TEM, JEOL JSM 2100), operated at an acceleration voltage of 200 kV. Pyridine infrared spectroscopy analysis was used to identify the nature of surface acid sites. Prior to pyridine adsorption, the catalysts were activated at 200 °C under vacuum for 1 h and then cooled to 150 °C. Pyridine was then added to the system to saturate the exposed catalyst surface (50 mg, 25 mm thickness). Chemisorption of pyridine was maintained at 150 °C for 30 min. Gaseous and physisorbed pyridine were then evacuated under a N_2 flow at 150 °C for another 30 min. FTIR spectra of the samples were recorded at room temperature using a Nicolet 6700 (Smart Orbit Accessory). The concentration of Brønsted and Lewis acid sites were estimated using the Lambert-Beer Law in the form $C = A/(\epsilon \rho)$, where C is the concentration of the vibrating species (μ molg⁻¹), A is the intensity of the band (cm^{-1}) , ε is the integration extinction coefficient $(cm \mu mol^{-1})$, and ρ is the sample thickness (g cm⁻²).^[30] Values of 1.67 cm μ mol⁻¹ and 2.22 cm μ mol⁻¹ were used as the integrated molar extinction coefficients for pyridine bands at 1545 (PyB) and 1455 cm⁻¹ (PyL), respectively.[31] A CHNS-O elemental analyzer (FLASH EA 1112 series, Thermo Electron Corporation) was used to analyze the carbon content of fresh and spent catalyst samples. 2-3 mg of each sample was placed in a tin container, which was combusted in a furnace at 900 °C. The gaseous products were separated chromatographically and analyzed using a thermal conductivity detector (TCD).

Mechanocatalytic depolymerization of cellulose

Water-soluble, cellulose-based oligomers were produced by using methods described elsewhere. $^{[15c]}$ In a typical method, $\rm H_2SO_4$



(2.5 mmol) was diluted to a volume of 40 mL. Sigmacell microcrystalline cellulose (10 g) was then added to this solution, and the solution was stirred for a few minutes. The resulting slurry was dried using a rotary evaporator, followed by drying overnight in air at 50 °C. The acidified cellulose powder thus obtained was then milled in a planetary ball mill using 5 mm stainless steel balls, with a cellulose-to-ball weight ratio of 1:10. The mill was operated at 300 rpm, with a 20 min pause after every 15 min of continuous milling. The pause allowed dissipation of heat generated during milling, which prevented overheating of reactants. The milling time reported refers only to the active milling time.

Catalytic reactions

Batch transformation reaction of sugars to HMF was carried out in a two-phase reaction system consisting of water/THF (1:4 v/v). In a typical experimental run, substrate (5 g), catalyst (1.25 g), and solvent (100 mL) were charged into a 300 mL reactor vessel provided by Parr Instrument Company. NaCl (4 g) was added to the reaction medium to maintain a biphasic reaction medium as well as improve the efficiency of HMF extraction by the organic layer. The reactor was purged with Ar (99.9%) and then pressurized to 20 bar. The temperature and stirring were controlled by a 4843 Controller provided by Parr. Temperature in the reactor was monitored by a thermocouple in the solution, and a constant stirring rate of 500 rpm was used for the reaction. After the reaction was complete, the product mix was collected, centrifuged, and the supernatant was collected for analysis. Catalytic runs were repeated with an experimental error of $\pm 2\%$.

Continuous flow reactions were performed on a custom-built fixed-bed reactor system. Two Alltech HPLC pumps were used for feeding the sugar solution and the organic solvent into the fixedbed reactor. A U-shaped fixed-bed reactor was designed by using 1/4 in (1 in = 2.54 cm) OD SS316 Swagelok tubing and tube fittings. The powdered P-TiO₂ was used as is without any pelletisation. The catalyst was loaded into the reactor, and a small amount of quartz wool was inserted from both sides of the reactor to hold the catalyst in place. A 7 µm Swagelok inline filter was connected to the reactor exit, which was followed by a Swagelok back pressure regulator. A steady flow was established through the system until the desired pressure was achieved. The reactor was then dipped slowly into a stirred oil bath set at the reaction temperature, and the reaction time was noted as 0 min. Reaction conditions were typically 5 g cello-oligomer dissolved in 100 mL water, 3:1 MIBK/NMP v/v ratio, 1:1 water/MIBK+NMP v/v ratio, and 60 bar back pressure while the flow rate, reaction temperature, and catalyst dosage were varied between 0.2-0.4 mLmin⁻¹, 210-230 °C, and 350-450 mg, respectively.

Liquid products were analyzed using a Shimadzu Prominence HPLC equipped with both refractive index (RID-10) and UV/Vis (SPD-M2OA) detectors using a Bio-Rad Aminex HPX-87H as the analytical column. The column was operated at 50 °C using 5 mm H₂SO₄ as the mobile phase at a flow rate of 0.6 mL min⁻¹ for the analysis of both the aqueous and organic phases. The concentrations of glucose, fructose, HMF, and other identifiable products were quantified by means of HPLC analysis through the external standard method and calibration curves of commercially available standard substrates. Sugar conversion (Conv.) and product yield were calculated according to Equations (1) and (2):

Conv. [mol%] =
$$\left(1 - \frac{nC_6}{nC_6^0}\right) \times 100\%$$
 (1)

Product yield [mol%] =
$$\left(\frac{n_i}{nC_6^0}\right) \times 100\%$$
 (2)

where nC_6 and nC_6^0 denote number of moles of C_6 sugars in the product and feed, respectively, and n_i is the number of moles of identified products (HMF, levulinic acid, levoglucosan, etc.).

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- [1] a) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* 2007, 46, 7164–7183; *Angew. Chem.* 2007, 119, 7298–7318; b) J. J. Bozell, G. R. Petersen, *Green Chem.* 2010, 12, 539–554.
- [2] O. Casanova, S. Iborra, A. Corma, ChemSusChem 2009, 2, 1138-1144.
- [3] a) C. Moreau, M. Belgacem, A. Gandini, *Top. Catal.* 2004, 27, 11–30;
 b) A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa, M. Gomes, *J. Polym. Sci. Part A* 2009, 47, 295–298.
- [4] a) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Green Chem.* 2013, *15*, 584–595; b) I. T. Horváth, H. Mehdi, V. Fabos, L. Boda, L. T. Mika, *Green Chem.* 2008, *10*, 238–242; c) Á. Bereczky, K. Lukács, M. Farkas, S. Dóbé, *Nat. Resour.* 2014, *5*, 177–191.
- [5] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* 2007, 447, 982–985.
- [6] J. B. Binder, R. T. Raines, J. Am. Chem. Soc. 2009, 131, 1979-1985.
- [7] X. Tong, Y. Ma, Y. Li, Appl. Catal. A 2010, 385, 1-13.
- [8] a) G. Yong, Y. Zhang, J. Y. Ying, Angew. Chem. Int. Ed. 2008, 47, 9345–9348; Angew. Chem. 2008, 120, 9485–9488; b) R. Huang, W. Qi, R. Su, Z. He, Chem. Commun. 2010, 46, 1115–1117; c) J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, Green Chem. 2007, 9, 342–350; d) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 2007, 316, 1597–1600; e) Y. Román-Leshkov, J. Dumesic, Top. Catal. 2009, 52, 297–303; f) J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, Green Chem. 2011, 13, 2678–2681; g) Z. Zhang, Q. Wang, H. Xie, W. Liu, Z. Zhao, ChemSusChem 2011, 4, 131–138; h) X. Qi, M. Watanabe, T. M. Aida, J. R. L. Smith, Green Chem. 2008, 10, 799–805.
- [9] a) M. Stöcker, Angew. Chem. Int. Ed. 2008, 47, 9200–9211; Angew. Chem.
 2008, 120, 9340–9351; b) P. L. Dhepe, A. Fukuoka, ChemSusChem 2008, 1, 969–975.
- [10] a) Y. Nishiyama, P. Langan, H. Chanzy, J. Am. Chem. Soc. 2002, 124, 9074–9082; b) Y. Nishiyama, J. Sugiyama, H. Chanzy, P. Langan, J. Am. Chem. Soc. 2003, 125, 14300–14306; c) D. Klemm, B. Heublein, H.-P. Fink, A. Bohn, Angew. Chem. Int. Ed. 2005, 44, 3358–3393; Angew. Chem. 2005, 117, 3422–3458.
- [11] a) Y. Su, H. M. Brown, G. Li, X.-d. Zhou, J. E. Amonette, J. L. Fulton, D. M. Camaioni, Z. C. Zhang, *Appl. Catal. A* **2011**, *391*, 436–442; b) Y. Zhang, H. Du, X. Qian, E. Y. X. Chen, *Energy Fuels* **2010**, *24*, 2410–2417; c) E. Ohno, H. Miyafuji, *J. Wood Sci.* **2014**, *60*, 428–437; d) M. P. Foley, L. M. Haverhals, D. K. Klein, W. B. McIlvain, W. M. Reichert, D. W. O'Sullivan, H. C. De Long, P. C. Trulove, *Am. J. Biomass Bioenergy* **2014**, *3*, 68–82; e) R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975; f) Y. Cao, J. Wu, J. Zhang, H. Li, Y. Zhang, J. He, *Chem. Eng. J.* **2009**, *147*, 13–21; g) O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, T. Heinze, *Biomacromolecules* **2007**, *8*, 2629–2647.



- [12] a) Z. Fang, J. A. Koziński, Proc. Combust. Inst. 2000, 28, 2717–2725;
 b) L. K. Tolonen, M. Juvonen, K. Niemelä, A. Mikkelson, M. Tenkanen, H. Sixta, Carbohydr. Res. 2015, 401, 16–23; c) S. Kumar, R. B. Gupta, Ind. Eng. Chem. Res. 2008, 47, 9321–9329; d) M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri, K. Arai, Ind. Eng. Chem. Res. 2000, 39, 2883–2890; e) Y. Ishikawa, S. Saka, Cellulose 2001, 8, 189–195; f) A. Koriakin, H. Van Nguyen, D. W. Kim, C.-H. Lee, J. Supercrit. Fluids 2014, 95, 175–186; g) F. S. Asghari, H. Yoshida, Carbohydr. Res. 2010, 345, 124–131.
- [13] D. Klein-Marcuschamer, B. A. Simmons, H. W. Blanch, Biofuels Bioprod. Biorefin. 2011, 5, 562–569.
- [14] K. T. Tan, K. T. Lee, Renewable Sustainable Energy Rev. 2011, 15, 2452–2456.
- [15] a) S. M. Hick, C. Griebel, D. T. Restrepo, J. H. Truitt, E. J. Buker, C. Bylda, R. G. Blair, *Green Chem.* **2010**, *12*, 468–474; b) N. Meine, R. Rinaldi, F. Schüth, *ChemSusChem* **2012**, *5*, 1449–1454; c) A. Shrotri, L. K. Lambert, A. Tanksale, J. Beltramini, *Green Chem.* **2013**, *15*, 2761–2768; d) R. Carrasquillo-Flores, M. Käldström, F. Schüth, J. A. Dumesic, R. Rinaldi, ACS Catal. **2013**, *3*, 993–997; e) J. Hilgert, N. Meine, R. Rinaldi, F. Schüth, *Energy Environ. Sci.* **2013**, *6*, 92–96; f) M. Käldström, N. Meine, C. Fares, F. Schüth, R. Rinaldi, *Green Chem.* **2014**, *16*, 3528–3538; g) P. Dornath, H. J. Cho, A. Paulsen, P. Dauenhauer, W. Fan, *Green Chem.* **2015**, *17*, 769–775.
- [16] a) W.-H. Peng, Y.-Y. Lee, C. Wu, K. C. W. Wu, J. Mater. Chem. 2012, 22, 23181–23185; b) Y. Su, H. M. Brown, X. Huang, X.-d. Zhou, J. E. Amonette, Z. C. Zhang, Appl. Catal. A 2009, 361, 117–122; c) P. Wang, H. Yu, S. Zhan, S. Wang, Bioresour. Technol. 2011, 102, 4179–4183; d) N. Shi, Q. Liu, Q. Zhang, T. Wang, L. Ma, Green Chem. 2013, 15, 1967–1974; e) K. Y. Nandiwale, N. D. Galande, P. Thakur, S. D. Sawant, V. P. Zambre, V. V. Bokade, ACS Sustainable Chem. Eng. 2014, 2, 1928–1932; f) M. Mascal, E. B. Nikitin, Green Chem. 2010, 12, 370–373.
- [17] a) M. Mascal, E. B. Nikitin, Angew. Chem. Int. Ed. 2008, 47, 7924–7926; Angew. Chem. 2008, 120, 8042–8044; b) M. Mascal, E. B. Nikitin, Chem-SusChem 2009, 2, 859–861.
- [18] C. V. McNeff, D. T. Nowlan, L. C. McNeff, B. Yan, R. L. Fedie, Appl. Catal. A 2010, 384, 65–69.
- [19] L. Atanda, S. Mukundan, A. Shrotri, Q. Ma, J. Beltramini, *ChemCatChem* 2015, 7, 781–790.

- [20] a) A. Chareonlimkun, V. Champreda, A. Shotipruk, N. Laosiripojana, *Fuel* 2010, *89*, 2873–2880; b) S. De, S. Dutta, A. K. Patra, A. Bhaumik, B. Saha, *J. Mater. Chem.* 2011, *21*, 17505–17510; c) S. De, S. Dutta, A. K. Patra, B. S. Rana, A. K. Sinha, B. Saha, A. Bhaumik, *Appl. Catal. A* 2012, *435–436*, 197–203; d) S. Dutta, S. De, A. K. Patra, M. Sasidharan, A. Bhaumik, B. Saha, *Appl. Catal. A* 2011, *409–410*, 133–139; e) A. Dutta, A. K. Patra, S. Dutta, B. Saha, A. Bhaumik, *J. Mater. Chem.* 2012, *22*, 14094–14100; f) C.-H. Kuo, A. S. Poyraz, L. Jin, Y. Meng, L. Pahalagedara, S.-Y. Chen, D. A. Kriz, C. Guild, A. Gudz, S. L. Suib, *Green Chem.* 2014, *16*, 785–791; g) K. Nakajima, R. Noma, M. Kitano, M. Hara, *J. Mol. Catal. A* 2014, *388–389*, 100–105.
- [21] M. A. Bañares, L. J. Alemany, M. C. Jiménez, M. A. Larrubia, F. Delgado, M. Lopéz Granados, A. Martínez-Arias, J. M. Blasco, J. L. G. Fierro, J. Solid State Chem. 1996, 124, 69–76.
- [22] E. C. Bucharsky, G. Schell, R. Oberacker, M. J. Hoffmann, J. Eur. Ceram. Soc. 2009, 29, 1955–1961.
- [23] A. K. Dalai, R. Sethuraman, S. P. R. Katikaneni, R. O. Idem, Ind. Eng. Chem. Res. 1998, 37, 3869–3878.
- [24] L. E. Depero, P. Bonzi, M. Musci, C. Casale, J. Solid State Chem. 1994, 111, 247-252.
- [25] S. Damyanova, M. L. Cubeiro, J. L. G. Fierro, J. Mol. Catal. A 1999, 142, 85-100.
- [26] B. F. M. Kuster, Starch/Staerke 1990, 42, 314-321.
- [27] G. Centi, Appl. Catal. A 1996, 147, 267-298.
- [28] Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, Science 2006, 312, 1933– 1937.
- [29] a) J. Horvat, B. Klaić, B. Metelko, V. Šunjić, *Tetrahedron Lett.* **1985**, *26*, 2111–2114; b) J. Horvat, B. Klaic, B. Metelko, V. Sunjic, *Croat. Chem. Acta* **1986**, *59*, 429–438.
- [30] A. A. Budneva, E. A. Paukshtis, A. A. Davydov, *React. Kinet. Catal. Lett.* 1987, 34, 63–67.
- [31] C. A. Emeis, J. Catal. 1993, 141, 347-354.

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